ADSORPTION OF METSULFURON–METHYL ON SOILS UNDER OIL PALM PLANTATION: A CASE STUDY

NORHAYATI MOHD TAHIR[1]* & NICHOLAS YEOW JEE SING[2]

Abstract. The adsorption of metsulfuron-methyl herbicide in four types of soil series taken from an oil palm estate has been investigated using a batch technique with the herbicide detected using a reversed phase C_{18} HPLC technique. Selected soil physicochemical properties were also analysed. The adsorption behaviour of the herbicide in the soils was evaluated using Freundlich and linear adsorption isotherms. Results indicated that soil from Bernam series exhibited strongest adsorption affinity for the herbicide followed by Jawa, Selangor and Tongkang soil series with distribution coefficient value of ca. 29.0, 19.2, 18.3 and 18.0, respectively. Comparison of the soils physicochemical properties revealed that whilst Tongkang and Selangor soil series have similar pH values, their organic matter content differed significantly from one another. Bernam soil on the other hand exhibited the lowest pH values compared to the other three soils but its organic matter content is similar to that of Selangor soil and is significantly higher than Tongkang and Jawa soil series. Thus it could be concluded that differences in soil properties contributed to the varying adsorption coefficient values observed in the present study. In agreement with previously reported studies, this observation supports the contention that soil properties play an important role in controlling the adsorption behaviour of metsulfuron-methyl herbicide in soils.

Keywords: Adsorption, metsulfuron-methyl, soils, sulfonyl urea herbicides, oil palm plantation

Abstrak. Satu kajian mengenai penjerapan herbisid metsulfuron-metil dalam empat jenis siri tanah telah dilakukan dengan menggunakan teknik kelompok. Tanah-tanah tersebut diambil di satu ladang kelapa sawit manakala kepekatan herbisid ditentukan dengan menggunakan kaedah HPLC fasa terbalik. Beberapa parameter fizik dan kimia tanah juga ditentukan. Penjerapan herbisid pada tanah dinilai berdasarkan isoterma Freundlich dan penjerapan linear. Keputusan menunjukkan tanah dari siri Bernam mempunyai keupayaan menjerap herbisid paling tinggi diikuti dengan siri tanah Jawa, Selangor dan Tongkang dengan nilai pekali penjarapan masing-masing sebanyak 29.0, 19.2, 18.3 dan 18.0. Perbandingan sifat-sifat fizik dan kimia tanah menunjukkan Tongkang dan Selangor mempunyai nilai pH yang hampir sama manakala kandungan organik yang jauh berbeza diantara satu sama lain. Siri tanah Bernam pula mempunyai nilai pH tanah yang paling rendah berbanding tanah-tanah lain manakala kandungan organiknya hampir sama dengan siri Selangor tetapi jauh lebih tinggi berbanding siri Tongkang dan Jawa. Justeru, perbezaan pekali penjerapan yang diperolehi dalam kajian ini boleh dikaitkan dengan perbezaan ciri-ciri fizik dan kimia tanah-tanah tersebut. Sepertimana yang dilapurkan oleh kajian terdahulu, pemerhatian ini jelas menunjukkan bahawa ciri-

[1&2]Environmental Research Group (ERG), Department of Chemical Sciences, Faculty of Science and Technology, Universiti Malaysia Terengganu (UMT), Mengabang Telipot, 21030 Kuala Terengganu, Malaysia

* *Corresponding author*: Tel: 609-6683258; Fax: 609-6694660; Email: hayati@umt.edu.my

ciri tanah memainkan peranan penting dalam mengawal sifat penjerapan herbisid metsulfuron-metil dalam tanah.

Kata Kekunci: Penjerapan; metsulfuron-metil; tanah; herbisid sulfonyl urea; ladang kelapa sawit

1.0   INTRODUCTION

Metsulfuron-methyl (Figure 1) is a post emergence sulfonylurea herbicide with high herbicidal activity even at low application rate and is widely used worldwide including Malaysia for effective control of a wide range of weeds in cereal, pasture and plantation crops. Sulfonylurea herbicides inhibit acetolactate synthase, a key enzyme in the biosynthesis of branched amino acids in plants. They are generally assumed to be environmentally safe because of their relatively short half-life in the environment, low application rates and low toxicity to mammals; however there have been studies which showed to the contrary [1-5], giving rise to concerns over the possible environmental contamination of this herbicide, particularly its leaching potential to the ground water system. The leaching potential of any pesticide, in general, can be assessed by the degree of their adsorption at the soil-water interface. This adsorption process is, in turn, influenced by the physical and chemical properties of soil, chemical nature of the herbicide and also the climatic factors [6]. Although the adsorption behaviour of sulfonylurea herbicides has been well studied in temperate soils [7-8 and literature cited therein], only limited similar studies have been carried out in tropical soils [9-11]. Since tropical soils may differ significantly in terms of their physico-chemical properties compared to those commonly found in temperate climate, there is still a need to obtain information on the influence of soil properties on the sorption behaviour of these herbicides in tropical soils. The objective of this study was to investigate the adsorption behaviour of metsulfuron-methyl in four types of soil series commonly found in palm oil plantation in order to provide data to assess the potential risk of this herbicide to contaminate the environment.
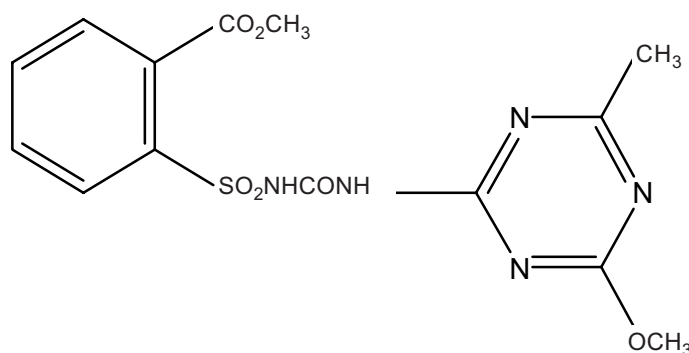

Figure 1   Structure of metsulfuron-methyl

2.0 MATERIALS AND METHOD

Surface soil samples (0 – 10 cm) from the Selangor, Tongkang, Jawa and Bernam series were taken from an oil palm estate in Sungai Buloh, Selangor Darul Ehsan. Bulk soils were air-dried, ground and passed through a 2 mm sieve. Sub-samples of freshly collected soils were dried at 110°C until there is no significant change in weight (approx. 24h) to determine initial soil moisture content. Soil organic matter (OM) content was determined using the Walkley and Black method [12] whilst soil pH was determined using a glass electrode in a 1 : 2.5 soil to 0.02 M calcium chloride suspension.

The commercial formulation of metsulfuron-methyl herbicide (trade name Ally®) containing 20% active ingredient was used in this study. All herbicide solutions were prepared in 0.02 M $CaCl_2$ and its concentrations determined by a reversed phase C_{18} HPLC using a mobile phase of acetonitrile in water containing orthophophoric acid (60 : 40 : 0.25). Detection of the hebicide was carried out at 242 nm wavelength. Adsorption kinetic study was carried out with 5 g of soils and 10 mL of herbicide solution (2, 6 and 10 mg L^{-1}) to determine equilibration time. Samples were collected at different time intervals (0 – 26 hours), centrifuged and supernatant analysed by HPLC. Adsorption study was then carried out using a batch equilibrium method [7]. Triplicate samples of the air-dried soil (5 g) were equilibrated with 10 ml herbicide solutions (initial concentration, C_i = 0 – 10 mg L^{-1}), shaken for 24h and then allowed to stand followed by centrifugation. The clear supernatants thus obtained were analysed for their herbicide content using HPLC technique described above. The amount of herbicide adsorbed by the soil was estimated as the differences between that initially present in solution (C_i) and that remaining after equilibration with soil (C_e). Solutions of metsulfuron-methyl in $CaCl_2$ without the soil subjected to similar equilibration process resulted in non-significant losses of the herbicide. All experiments were done at room temperature (28 – 30°C).

3.0 RESULTS AND DISCUSSION

Table 1 presents the physicochemical properties of the soils used in this study. Results obtained showed that Selangor exhibited relatively higher surface soil moisture content compared to Jawa, Bernam and Tongkang soils; statistical analysis (ANOVA) however

Table 1   Selected physicochemical properties of the soil samples

Soil Properties	Tongkang	Selangor	Bernam	Jawa
Moisture Content (%)	23.2	28.5	22.6	26.1
pH (0.02 M $CaCl_2$)	3.45	3.46	3.05	3.24
Organic Matter (%)	4.40	15.2	15.8	8.50
Organic Carbon (%)	2.55	8.80	9.17	4.93

suggests that this differences is insignificant (p>0.05). The Selangor and Bernam soils were observed to have similar OM content but significantly richer (p<0.05) in OM content compared to the Jawa and Tongkang soil, respectively. Interestingly, soil pH of the Tongkang soil was comparable to that of Selangor soil but both were found to be significantly higher (p<0.05) than that of the Jawa and Bernam soil series.

Figure 2 shows the results of the metsulfuron-methyl adsorption kinetic experiments; which clearly indicated that the adsorption of metsulfuron-methyl onto the soil reaches
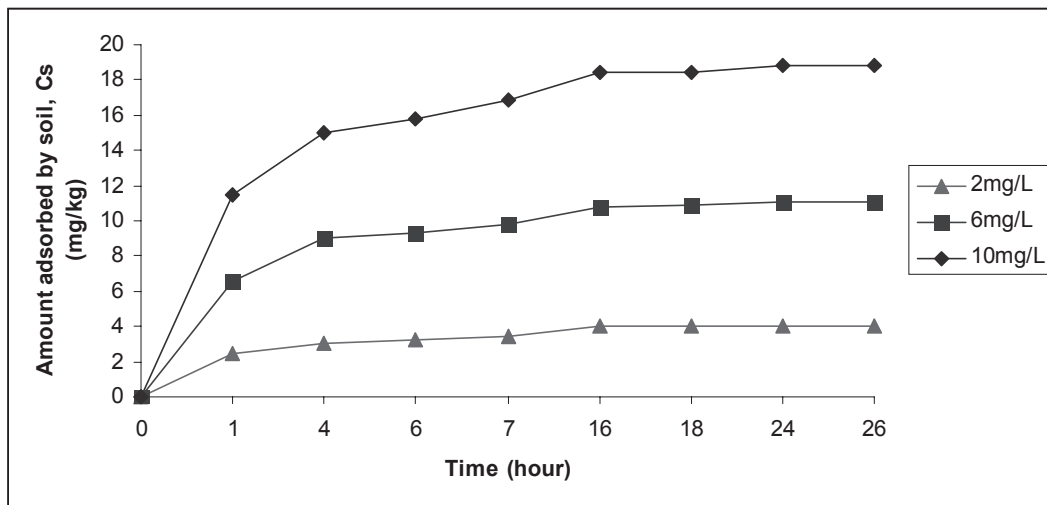

Figure 2   Kinetics of metsulfuron-methyl adsorption on soils at different concentrations

equilibrium in 16-18 hrs, similar to the results reported by Ismail and Chong [13].

The adsorption isotherms for metsulfuron-methyl in the soil samples are shown in Figure 3. In contrast to earlier results with other soil and herbicide systems [9-11], generally all the adsorption isotherms corresponded to the H-type curve according to classification of Giles *et al.,* [14]. This behaviour indicates a very high herbicide-soil affinity such that complete adsorption of the herbicide occurred at low herbicide concentration; the adsorption then further increased with increasing solution concentration with no constant value being reached in the concentration range used in this study. The adsorption coefficient (K_d), which represents the partitioning of the herbicide between liquid (C_e) and solid phases (C_s) in equilibrium was calculated using Equation 1. The empirical Freundlich adsorption isotherm (Equation 2), which allows the evaluation of experimental constants K_f and *n*, was also calculated using the linearised form of the equation (Equation 3). The Freundlich isotherm takes into account the non-linearity of sorption at increasing concentration and the values of K_f will equal K_d when *n* equals 1. In addition, the distribution coefficient values of all soils normalized with respect to percentage of organic carbon (%OC) present in the soil, K_{oc}, [15] were also calculated (Equation 4); typically a very narrow range of K_{oc}
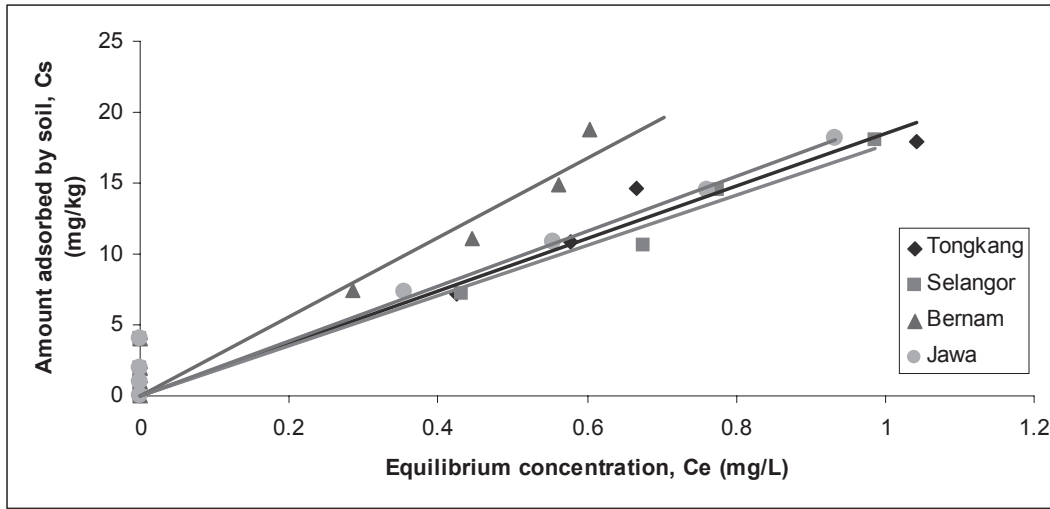
Figure 3 Adsorption isotherm of metsulfuron-methyl in soil samples

among soils with varying levels of organic carbon is indicative of the latter being the major factor in controlling adsorption process whereas a wider range would suggest that possibly other soil properties influenced the herbicide adsorption.

$$C_s = K_d \, C_e \qquad (1)$$

$$C_s = K_f \, C_e^{1/n} \qquad (2)$$

$$\text{Log } C_s = \text{Log } K_f + 1/n \text{ Log } C_e \qquad (3)$$

$$K_{oc} = K_d \, / \, \%\text{OC} \qquad (4)$$

The values of the K_d, Freundlich contants, K_f and n, and K_{oc} thus obtained are given in Table 2 and the effect of soils properties could clearly be seen from, these data. All the adsorption isotherms showed a reasonably good fit with the Freundlich isotherms ($r^2 > 0.92$) and the K_f values calculated for the soils were quite close to the K_d values with n values approximated to unity indicating that the adsorption behaviour

Table 2 Freundlich constants (K_f and n), distribution coefficient (K_d) and organic carbon normalized distribution coefficient (K_{oc})

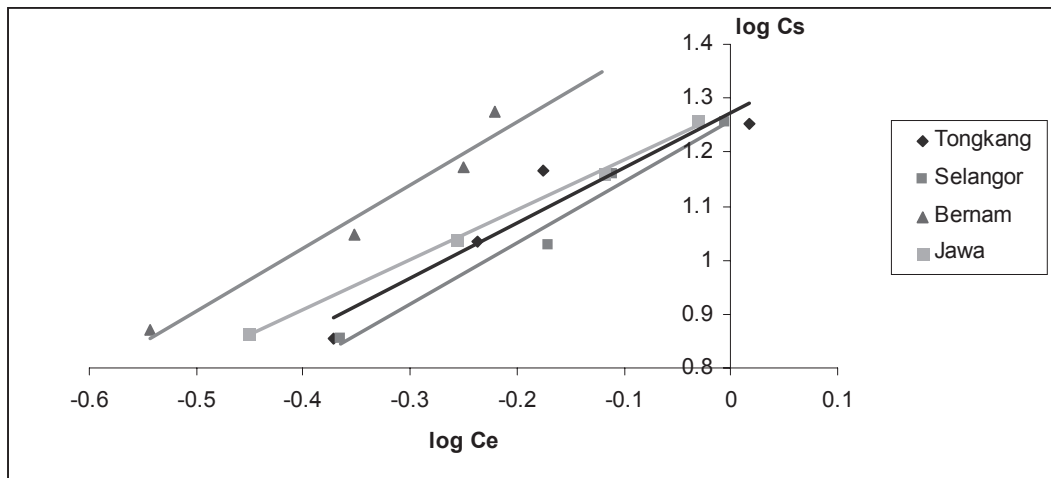| Soil	K_{oc}	Distribution Coefficient		Freundlich Constants		
		K_d	R^2	K_f	n	r^2
Tongkang	7.06	18.0	0.91	18.8	0.96	0.91
Selangor	2.07	18.3	0.92	18.1	0.88	0.97
Bernam	3.16	29.0	0.92	31.6	0.84	0.96
Jawa	3.89	19.2	0.93	19.0	1.09	1.00

Figure 4   Freundlich adsorption isotherm of metsulfuron-methyl in soil samples

is effectively linear for the soil-herbicide systems under investigation (Figure 4). The adsorption capacity of the soils towards metsulfuron-methyl was evaluated by comparing the values of K_d and K_f obtained. Bernam soil with highest OM and lowest pH exhibited the highest value of K_d followed by Jawa, Selangor and Tongkang soil, respectively. A similar trend was observed for the Freundlich adsorption coefficient (K_f) except that Tongkang soil, instead of Selangor, exhibited the lowest adsorption capacity towards the herbicide. Interestingly, Selangor and Tongkang soils have similar soil pH (3.46 and 3.45, respectively) but the Selangor soil has almost four times more organic matter content than Tongkang soil. Another interesting feature to note is that although Selangor soil contained comparable OM content to Bernam soil (Table 1), the adsorption capacity of Bernam soil significantly exceeds that of Selangor soil series. OM has been reported to be one of the major factors that influence the extent of pesticide adsorption on soils where adsorption increases with increasing OM matter content of the soil [7-11, 16]. With the exception of Selangor soil series, the extent of pesticide adsorption on soil based on organic matter followed similar trend for Bernam, Jawa and Tongkang series. However an anomaly was observed for Selangor soil; this is probably an indication that OM content alone could not account for the observed trend in this study. A simple correlation test between soil OM and K_d and K_f, respectively was carried out to assess the extent of which OM influence the adsorption of metsulfuron-methyl; the coefficient was found to be 0.59 and 0.54, respectively. These values were relatively smaller than previously reported [8, 11] indicative of lesser role played by organic matter in controlling adsorption affinity in these soils. In addition, a lower correlation values is probably indicative of other additional factor(s) imparting their role in controlling the adsorption behaviour of metsulfuron-methyl in the soils studied. A wide range of values obtained for the distribution coefficient values

normalized with respect to percentage of organic carbon (%OC) present in the soil, K_{oc}, also support the contention that OM alone could not account for the observed variation in K_d and K_f values between these soils.

Previous studies have shown that the adsorption of sulfonylurea herbicides is also pH dependent [7-11]. This is not surprising since metsulfuron-methyl is a weak acid with a pK_a value of ca. 3.3 and thus its speciation is pH dependent; this herbicide will dissociate above its pK_a value and tend to be present in the ionic form in neutral and alkaline soil solution. Figure 5 shows the influence of soil pH on the adsorption of metsulfuron-methyl. This figure clearly shows that soil with the lowest pH (Bernam) exhibited the highest adsorption capacity whilst soil with highest pH exhibited the lowest capacity to adsorb the herbicide. A correlation analysis between K_d and K_f with pH gives a strong negative correlation (–0.90 and –0.87, respectively) which indicated a strong inverse relationship between soil pH and adsorption capacity. This result is consistent with Abdullah *et al.,* [11] and Walker *et al.,* [8] who also observed a negative relationship (r^2 = –0.821 and –0.795, respectively) between adsorption of metsulfuron-methyl and the pH of the soils they studied. Other researchers have found a similar negative relationship between other sulfonyl urea herbicides and soil pH [7-9, 16-19]. The results obtained by Abdullah *et al.,* [11] and Walker *et al.,* [8] gives similar correlation values between organic matter and pH versus adsorption, indicating the importance of both parameters in controlling adsorption of metsulfuron-methyl in the soils studied. However relatively lower correlation coefficient value between organic matter and K_d compared to correlation between pH and K_d had been obtained in this present study, clearly indicating that pH is the dominant factor in controlling adsorption affinity of metsulfuron-methyl in the four soil systems.
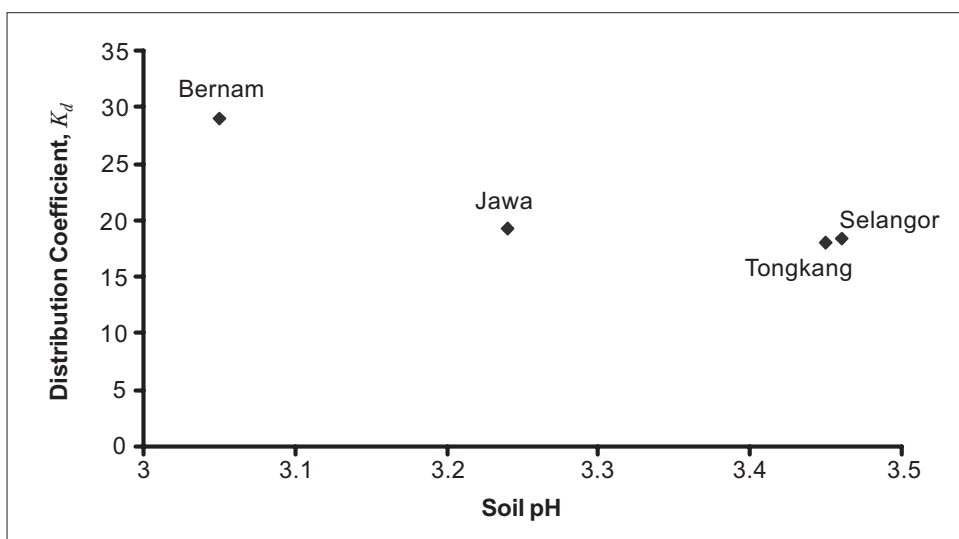

Figure 5   Influence of soil pH on adsorption of metsulfuron-methyl

4.0 CONCLUSION

Results obtained in the present clearly indicated the influences of soil organic matter content and soil pH on the adsorption of metsulfuron-methyl in Bernam, Selangor, Jawa and Tongkang soils series which are commonly found in oil palm plantations in Malaysia. Consistent with previously reported work, it was observed that soils with high organic matter content exhibited a high adsorption affinity for the herbicide whilst a high soil pH resulted in a low adsorption affinity for the herbicide. However, of the two parameters, it would seem that soil pH exert a more dominant role in controlling the adsorption of metsulfuron-methyl in the four soils studied.

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