ADSORPTION OF CHLORIMURON – ETHYL AND METSULFURON – METHYL ON SELECTED SELANGOR AGRICULTURAL SOILS

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Abstract

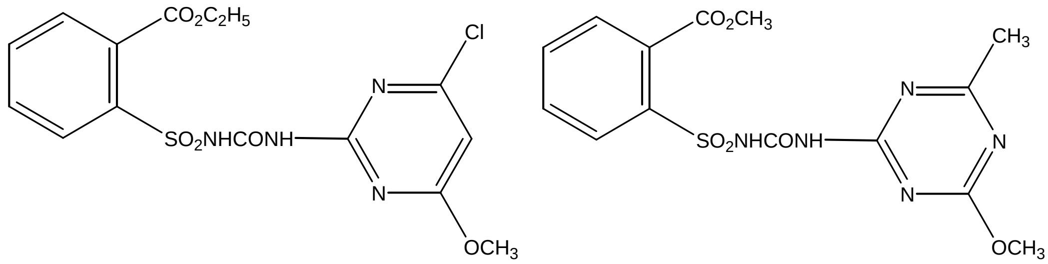
The adsorption of chlorimuron-ethyl and metsulfuron-methyl herbicide in four types of soil samples taken from an oil palm estate in Selangor has been investigated at two different depths (0-10cm and 20-30cm) using a batch technique. The adsorption behaviour of both herbicides was evaluated using Freundlich and linear adsorption isotherms. Results indicate that soils from KLG 3 and KLG 4 stations exhibited significant stronger adsorption affinity for both herbicides ($p<0.05$). The adsorption affinity of chlorimuron-ethyl is stronger than metsulfuron-methyl in all soils studied and the adsorption affinity decreased with soil depth. Comparison of the soil physicochemical properties revealed that the organic matter content of KLG 3 and KLG 4 soils are significantly different from other soils although their pH values were similar. In agreement with previously reported studies, organic matter content and pH exert a dominant role in controlling the adsorption of sulfonylurea herbicides in the four soils studied. Thus it could be concluded that the varying adsorption coefficient values observed in the present study could be attributed to the differences in soil properties.

Keywords*:* adsorption; chlorimuron-ethyl; metsulfuron-methyl; soils; sulfonylurea herbicides

Introduction

Sulfonylurea herbicides are widely used for pre-emergence control of grass weed in a large variety of crops including corn, soybeans, potatoes, tomatoes and several tropical crops. Their mechanism is related to the inhibition of acetolactate synthase (ALS), a key enzyme involved in the biosynthesis of branched-chain amino acids in plants, but absent in animals and humans. Chlorimuron-ethyl (ethyl 2-[[(4-chloro-6-methoxy-pyrimidin-2-yl)aminocarbonyl]-aminosulfonyl]benzoate) and metsulfuron-methyl (methyl 2-[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-aminocarbonyl]-aminosulphonyl]-benzoate) (Figure 1) are the two most commonly used sulfonylurea herbicides in Malaysia. These compounds are weak acids and the solubilities in water are greatly influenced by pH [1] as shown in Table 1. They are generally assumed to be environmentally safe because of their relatively short half-life in the environment, low application rates (7-30 g/ha) and low toxicity to mammals [2]; however there have been studies which showed to the contrary [3,4], giving rise to concerns over the leaching potential of these herbicides into the groundwater system as well as movement to the surface waters via run-offs.

Adsorption processes in soil play an important role in all physical processes affecting the residue behaviour of pesticides in the agroenvironment. The adsorption behavior, leaching behaviour and environmental fate of these herbicides have been well studied in temperate climates. The physicochemical properties of soils under tropical conditions may differ significantly from soil types commonly found in the temperate zone. There is still limited information on the fate and behaviour of these herbicides in the tropical environment, although there have been several reports in recent years on the sorption behaviour of these chemical in Malaysian soils [5-7]. The objective of this study was to investigate the adsorption behaviour of chlorimuron-ethyl and metsulfuron-methyl in Selangor agricultural soils in order to assess the potential risk of these herbicides to contaminate the environment.



Chlorimuron-ethyl   Metsulfuron-methyl

Figure 1: Structure of chlorimuron-ethyl and metsulfuron-methyl.

Table 1: The physical and chemical properties of chlorimuron-ethyl and metsulfuron-methyl.

Herbicide	Melting point (^oC)	Molecular weight	Dissociation constant (pKa)	Vapor pressure (mmHg at 25^oC)	Partition coefficient (octanol-water, at 25^oC)		Water solubitily (ppm at 25^oC)	
					pH 5	pH 7	pH 5	pH 7
Metsulfuron-methyl	158	381	3.3	2.5×10^{-12}	1.0	0.01	1100	9500
Chlorimuron-ethyl	186	415	4.2	3.7×10^{-12}	320	2.3	11	1200

Materials and methods

Four soil samples (0-10cm and 20-30cm) were obtained from Ladang Bukit Raja Bahagian Barat near Pekan Meru in Klang, Selangor. Bulk soils were air-dried, ground and passed through a 2mm sieve. Sub-samples of freshly collected soils were dried at 110^oC to determine the initial soil moisture content. Soil pH was determined in a 1:2.5 soil/water suspension; soil organic matter (OM) by Walkley and Black's Titration Method; particle size distribution by using particle size analyzer.

The commercial formulation of chlorimuron-ethyl (trade name Classic®) which contains 10.5% of active ingredient and metsulfuron-methyl (trade name Ally®) which contains 20% of active ingredient were used in this study. All herbicide solutions were prepared in 0.02M calcium chloride and its concentration was determined by a reversed phase C_{18} HPLC using a mobile phase of acetonitrile in water containing orthophosphoric acid (60:40:0.25). Detection of herbicide was carried out at 242nm wavelength. Adsorption study was carried out using a batch equilibrium method. Triplicate samples of the air-dried soil (5g) were equilibrated with 10ml of herbicide solutions (initial concentration, C_i = 0-10 mg/L), shaken for 24h and then allowed to stand followed by centrifugation. The clear supernatants 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 chlorimuron-ethyl and metsulfuron-methyl in $CaCl_2$ without the soil subjected to similar equilibration process resulted in non-significant losses of the herbicide.

Results and discussion

The physicochemical properties of the soils are given in Table 2. The KLG 2 and KLG 3 soils were observed to have significantly richer ($p<0.05$) OM content compared to the KLG 1 and KLG 4 soil. Results showed that KLG 4 soil exhibited lower pH value compared to other soil, however statistical analysis suggests the differences is insignificant ($p>0.05$). Generally, the soils are sandy with moisture content ranged from 32.3 to 43.5%.

Table 2: Physicochemical properties of soil samples.

Station	Moisture content (%)	Organic carbon (%)	Organic matter (%)	pH	Sand (%)	Silt (%)	Clay (%)	Texture
KLG 1 (0-10cm)	40.8	2.51	4.33±0.15	3.97	99.8	0.17	0.02	Sandy
KLG 1 (20-30cm)	43.5	0.68	1.17±0.02	3.43	99.5	0.42	0.09	Sandy
KLG 2 (0-10cm)	36.1	4.37	7.53±0.10	3.29	96.5	3.00	0.54	Sandy
KLG 2 (20-30cm)	38.2	3.79	6.53±0.10	3.23	98.6	1.06	0.30	Sandy
KLG 3 (0-10cm)	29.6	5.37	9.26±0.10	3.29	95.8	3.16	1.02	Sandy
KLG 3 (20-30cm)	40.0	5.28	9.10±0.10	3.12	98.9	0.75	0.32	Sandy
KLG 4 (0-10cm)	33.3	2.78	4.79±0.03	2.29	98.9	0.70	0.39	Sandy
KLG 4 (20-30cm)	32.3	1.41	2.43±0.10	2.92	99.4	0.39	0.23	Sandy

The adsorption isotherms for chlorimuron-ethyl and metsulfuron-methyl in the soil samples (0-10cm and 20-30cm) are shown in Figure 2-5. 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 $C_s = K_dC_e$. The adsorption isotherms of both chlorimuron-ethyl and metsulfuron-methyl in all the soils fitted the Freundlich adsorption equation, $C_s = K_fC_e^{1/n}$ with r^2 values > 0.91. In addition, the K_d values of all soils normalized with respect to percentage of organic carbon (%OC) present in the soil, $K_{oc} = K_d/\%OC \times 100$), were also calculated. The values obtained for the constants mentioned above are given in Table 3 and Table 4.

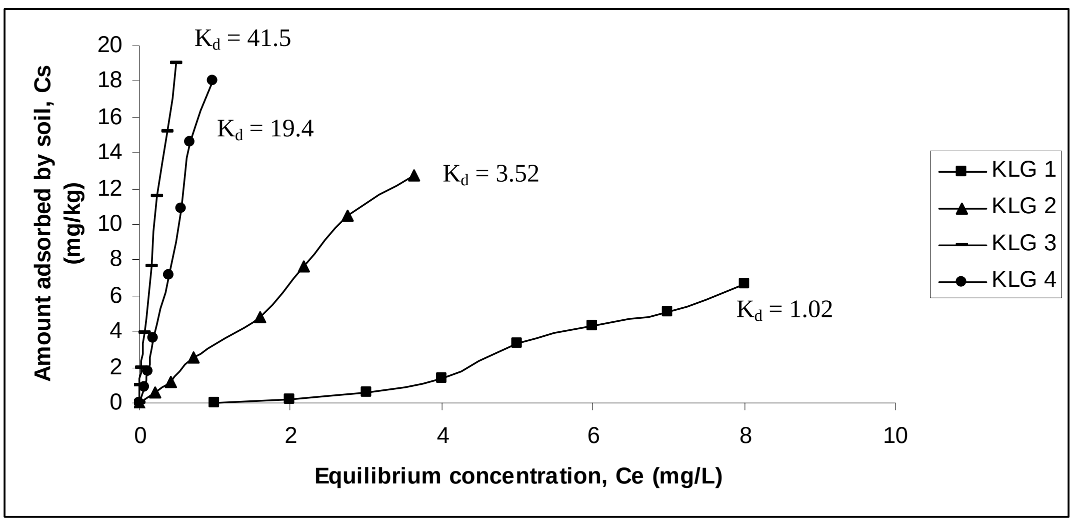


Figure 2: Adsorption isotherm of chlorimuron-ethyl in soil samples (0-10cm).

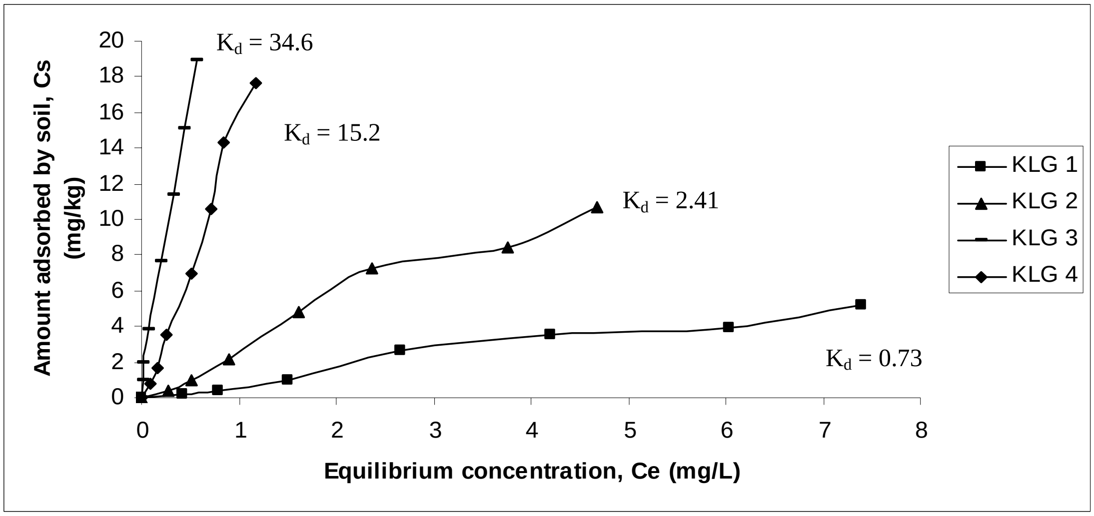


Figure 3: Adsorption isotherm of chlorimuron-ethyl in soil samples (20-30cm).

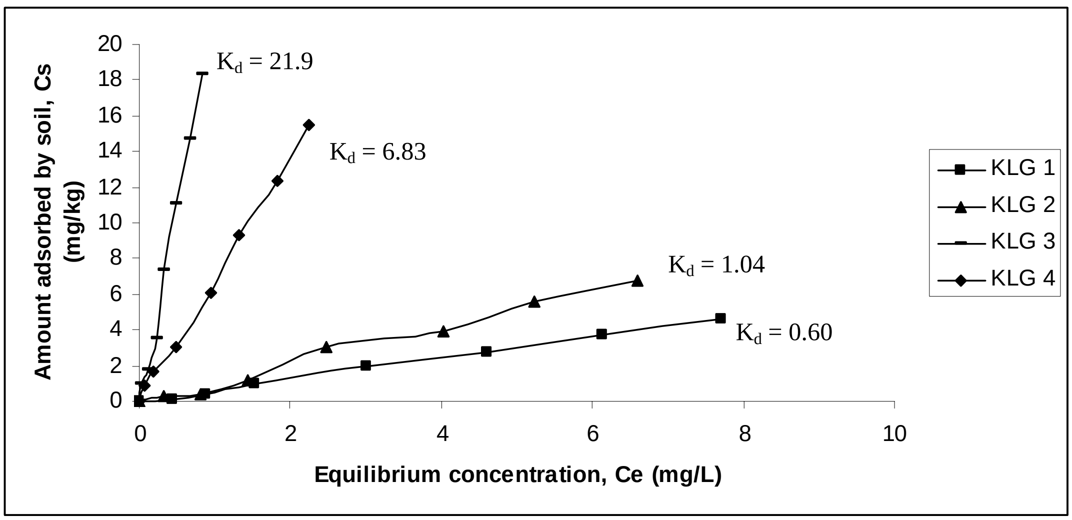


Figure 4: Adsorption isotherm of metsulfuron-methyl in soil samples (0-10cm).

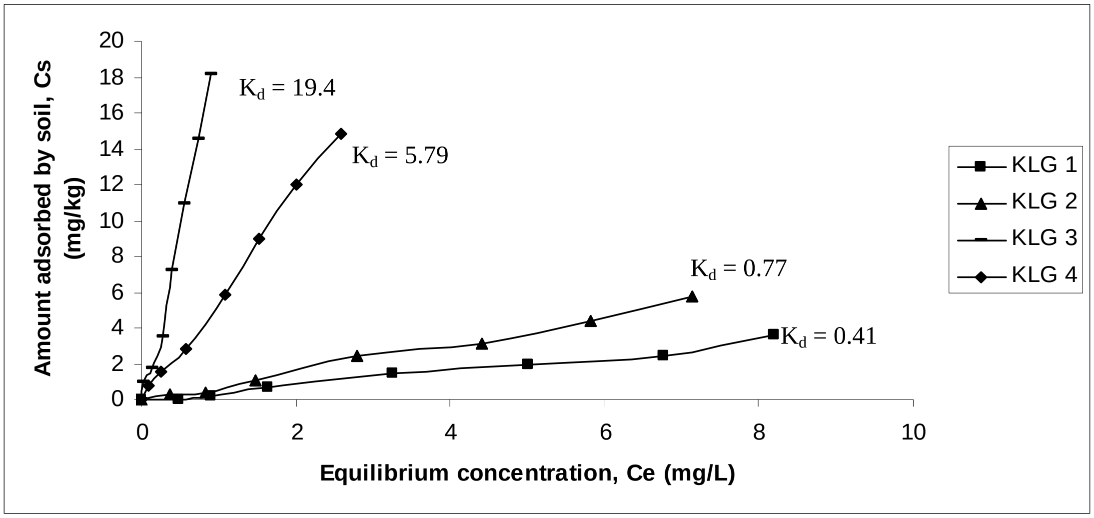


Figure 5: Adsorption isotherm of metsulfuron-methyl in soil samples (20-30cm).

Table 3: Distribution coefficient (K_d) and Freundlich constants (K_f and n) for adsorption of chlorimuron-ethyl on various soil samples.

	K_{oc}	K_d	r^2	K_f	n	r^2
KLG 1 (0-10cm)	40.6	1.02	0.97	0.86	0.86	0.97
KLG 1 (20-30cm)	107	0.73	0.96	0.57	0.84	0.97
KLG 2 (0-10cm)	80.6	3.52	0.99	3.24	0.92	1.00
KLG 2 (20-30cm)	63.5	2.41	0.96	2.20	0.88	0.98
KLG 3 (0-10cm)	773	41.5	0.97	30.6	1.39	1.00
KLG 3 (20-30cm)	656	34.6	0.99	26.1	1.42	1.00
KLG 4 (0-10cm)	699	19.4	0.99	21.0	0.87	0.99
KLG 4 (20-30cm)	1081	15.2	0.99	16.2	0.81	0.99

Table 4: Distribution coefficient (K_d) and Freundlich constants (K_f and n) for adsorption of metsulfuron-methyl on various soil samples.

	K_{oc}	K_d	R^2	K_f	n	r^2
KLG 1 (0-10cm)	24.1	0.60	1.00	0.43	0.81	0.98
KLG 1 (20-30cm)	60.1	0.41	0.98	0.18	0.65	0.94
KLG 2 (0-10cm)	23.7	1.04	0.99	0.85	0.90	0.96
KLG 2 (20-30cm)	20.4	0.77	0.99	0.64	0.90	0.98
KLG 3 (0-10cm)	408	21.9	0.99	17.7	1.19	0.91
KLG 3 (20-30cm)	368	19.4	0.99	16.0	1.14	0.91
KLG 4 (0-10cm)	246	6.83	1.00	6.97	1.14	0.99
KLG 4 (20-30cm)	410	5.79	1.00	5.85	1.12	0.98

The values of K_f and K_d (Table 2 and 3), considered as a first approximation in characterizing adsorption capacity were used in the present work to compare the adsorption of both pesticides in different soil samples. In general KLG 3 and KLG 4 exhibited a much stronger adsorption affinity for both herbicides compared to KLG 1 and KLG 2, as shown by significant difference among the K_d and K_f values obtained ($p<0.05$). The K_d and K_f values obtained indicated that the order of adsorption is KLG 3 > KLG 4 > KLG 2 > KLG 1 for both herbicides at both depths. Results showed that chlorimuron-ethyl exhibited stronger adsorption affinity than metsulfuron-methyl in all soil samples, and the adsorption affinity seems to decrease with soil depth. KLG 3 soil with the highest OM content was found to exhibit the highest adsorption capacity whilst KLG 1 soil, which had the lowest OM content, exhibit the lowest adsorption capacity. Simple correlation coefficients between K_d and the OM content was carried out to determine the degree of influence of OM on the adsorption of sulfonylurea herbicides. The correlation coefficient was found to be 0.62 for chlorimuron-ethyl and 0.67 for metsulfuron-methyl, indicating a fairly strong positive correlation between percent of OM and adsorption.

A wide range of values obtained for the K_{oc} among soils suggested that soil organic matter alone could not account for the observed variations in K_d found in the present study. Previous studies have shown that the adsorption of sulfonylurea herbicides is dependent on soil pH. As weak acids with pKa value of 3.3 and 4.2, metsulfuron-methyl and chlorimuron-ethyl will dissociate above their pKa value and tend to be present in the ionic form in neutral and alkaline soil solution. Results in this study shows that soil with the highest pH (KLG 1) exhibited the lowest adsorption capacity. For KLG 4 with the lowest pH value, higher Kd value has been obtained compared to KLG 1 which exhibited comparable OM content but much higher soil pH to KLG 4. A correlation analysis between K_{oc} with pH gives a negative correlation (-0.61 for chlorimuron-ethyl and -0.47 for metsulfuron-methyl). The correlation is stronger for chlorimuron-ethyl since the soil pH (range from 2.29 to 3.97) is lower than its pKa whereas for metsulfuron-methyl only KLG 4 soil pH above its pKa value of 3.3. Thus pH seems to play an important role in controlling the herbicide adsorption. The relatively lower correlation values than previous studies [5,6] might be indicative of other additional factor in controlling the adsorption behaviour of sulfonylurea herbicides in the soils studied.

Mobility of pesticide in soils with low organic matter contents is often related to the active components of the inorganic fraction, which is predominantly the clay-sized fraction, extractable Fe and Al [8,9]. Results obtained in this study indicated that clay content also plays an important role in controlling the adsorption behaviour of the herbicides studied, in which the correlation analysis of clay content of chlorimuron-ethyl and metsulfuron-methyl with K_d gives r value of 0.69 and 0.67, respectively. However since the soil pH is below the pKa of chlorimuron-ethyl and metsulfuron-methyl except for KLG 1, the herbicides tend to be present in the molecule form rather than ionic form in soil solution. Thus, the molecular form of sulfonylurea herbicides is expected to adsorb strongly to organic matter in the soil studied and the effect of clay content are negligible although it appears to be positively correlated with both of these soil components. In addition, a moderate positive correlation between soil moisture content and K_d (0.56 for chlorimuron-ethyl and 0.57 for metsulfuron-methyl) also suggested the influence of soil moisture content on adsorption of sulfonylurea herbicide.

Conclusions

Results obtained from the present study indicated that soil properties such as organic matter content and pH play an important role in controlling the adsorption behaviour of chlorimuron-ethyl and metsulfuron-methyl in selected Selangor agricultural soils. Consistent with previous report, it was observed that soils with higher organic matter content and lower pH value exhibited higher adsorption affinity towards the herbicides. Chlorimuron-ethyl exhibited stronger adsorption affinity compared to metsulfuron-methyl in all soil studied, and the adsorption affinity decreased with soil depth.

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