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Adsorption and Desorption of Glufosinate Ammonium in Soils Cultivated with Oil Palm in Malaysia

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ABSTRACT

In Malaysia, glufosinate ammonium (GLUF) is a commonly used herbicide in oil palm plantations to control broad-leaved weeds and grasses. Adsorption and desorption of (GLUF) were studied using the batch equilibrium technique in four mineral soils, Inceptisols (Selangor), Oxisols (Munchong) and Ultisols (Serdang and Rengam) series and peat (Histosols) collected under oil palm cultivation from 0-15 cm and 15-30 cm depths. Adsorption coefficients of the herbicide were correlated with soil properties i.e. organic matter content, clay content, cation exchange capacity (CEC) and pH. The concentrations of GLUF used were (0, 0.25, 0.5, 1, 1.5, 3, 5 and 10 μg/mL). The adsorption and desorption isotherms were fitted using linear and Freundlich equations. Adsorption of GLUF was in the following order: Selangor > Rengam> Munchong> peat > Serdang. The results indicate that the adsorption of GLUF is positively correlated only with clay content. The high sorption of the Selangor soil could be explained by the high clay content in Selangor series soil compared to the other soil series. However, the order of GLUF desorption was in the following order: Serdang> peat> Munchong> Rengam> Selangor. Results indicate that adsorption of GLUF was mainly on the clay fraction of the soil and the binding strength of adsorbed GLUF was high as indicated by the order of GLUF desorption from the soils.

Keywords: Batch equilibrium test, linear equation, Freundlich equation, Glufosinate ammonium, sorption isotherm

INTRODUCTION

In Malaysia, glufosinate ammonium (GLUF), which is an organophosphate broad-spectrum contact herbicide, is widely used in the oil palm plantations for the control of a wide range of broad-leaved weeds and grasses, to make it easier for the collection of palm oil fruitlets and to ensure the safety of workers against snakes. Glufosinate ammonium is now registered for use in 50 countries and has been marketed through several trade names including Basta, Rely, Finale

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and Challenge. This herbicide was introduced to the Malaysian market in 1980s (Ismail and Ahmad 1994). Basta is one of the most commonly used GLUF in Malaysia. Duke and Lydon (1987) reported that GLUF was developed with two attributes common to many other new agricultural chemicals: (1) it is formulated in water rather than solvents and (2) it was originally developed from a natural microbial product. Glufosinate ammonium is a natural compound isolated from two species of streptomycetes (Tachibana *et al*. 1986; Krieg *et al.* 1990). This causes photosynthesis to stop and the herbicides reaction results in death of the plant cells. This herbicide is also being incorporated into the field cropping systems with the use of transgenic, glufosinate tolerant, crops. The introduction of genetically modified crops, resistant to GLUF has lead to a significant increase in the use of this herbicide. (Jewell and Buffin, 2001).

Knowledge of a pesticide's structure and some of its physico-chemical properties often permits an estimation of its behaviour and adsorption mechanism. Its properties, such as acidity or basicity (denoted by pKa or pKb), water solubility and molecular size, affect the adsorption-desorption by soil colloids (Bailey and White 1970). Glufosinate ammonium, which has a molecular structure of $C_5H_{15}N_2O_4P$, has a very high water solubility of 1370 g/L (Behrendt *et al.* 1990). Its half-life has been determined in numerous laboratory studies and it varies from 3 to 42 days in some studies and up to 70 days in others (Behrendt *et al*. 1990; Faber *et al*. 1997; Tomlin 2000; Devos *et al.* 2008). The shortest half life tends to be in soils with a high clay and organic matter content (Ismail and Ahmad 1994). The nature of the functional groups is one of the structural factors determining the chemical characteristic of a pesticide molecule thus influencing its adsorption on soil colloids and the adsorption mechanism. Both amino and carbonyl groups that exist in GLUF chemical structure may participate in hydrogen bonding. Hydrogen bonding appears to be the most important mechanism for adsorption of polar non-ionic organic molecules such as GLUF on clay minerals (Khan 1980).

Following its application, a large proportion of GLUF will settle on the soil. Adsorption is one of the most important factors that affect the fates of pesticides in the soil and consequently determine their distribution in the soil and water system (Giles *et al*. 1960). Glufosinate ammonium has been shown to be strongly adsorbed by soil high in clay content and low in soil with low clay content (Behrendt *et al*. 1990, Jewell and Buffin 2001; Autio *et al*. 2004).

While much is known about the physiological activity, efficacy, and mode of action of GLUF, little data or information is available concerning their adsorption and desorption in soils cultivated under oil palm in Malaysia (Ismail and Ahmad 1994) where life cycle assessment of oil palm is important. Nowadays, environmental safety is an important aspect to be considered in the oil palm industry to ensure minimum environmental impact of agronomic practices and for the product to be labeled as environmentally friendly, especially in exporting palm oil to other countries with high environmental safety standards. Therefore, the objectives of this study are to determine the adsorption and desorption of GLUF in different soil types on which oil palms are grown and the correlations between the properties of these soils (clay content, organic matter, pH, CEC) with adsorption and desorption of GLUF.

MATERIALS AND METHODS

Chemicals Used in the Study

Glufosinate ammonium was obtained from Riedel-de Haen (Seelze, Germany). The chemical structure and basic properties of GLUF are shown in Fig. 1 and Table 1, respectively. Acetonitrile, acetone and diethyl ether, all of HPLC grade, were purchased from Scharlau Science (Barcelona, Spain). Analytical-reagent grade potassium dihydrogenphosphate, disodium tetraborate decahydrate, and hydrochloric acid (37%), potassium hydroxide and 9-Fluorenylmethyl Chloroformate (FMOC-Cl) were purchased from Merck.

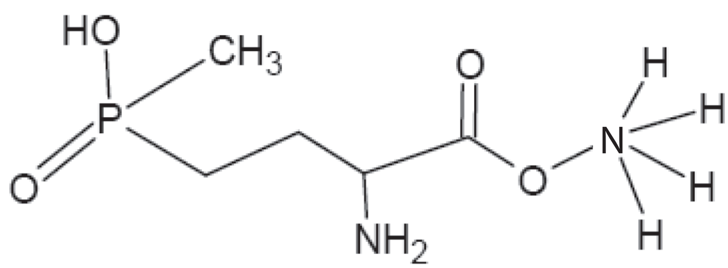


Fig. 1: Chemical structure of GLUF

TABLE 1

Basic properties of glufosinate ammonium

Molecular formula	Molecular mass	Solubility in H_2O	pK_a
$C_5H_{15}N_2O_4P$	198.19	>500g/L at 20ºC	9.15 ± 0.07

Source: Pesticide Action Network, North America. http://www.pesticide.info.org

Stock standard solutions (400 ug/mL) of GLUF as well as mixed diluted standards were prepared with HPLC-grade water. Acetone, 0.125 M borate buffer solution and 0.01M FMOC-Cl in acetone were used to perform derivatization prior to HPLC analysis.

Collection of Soil Samples and Characterization

The soils in this study represent the soil types under oil palm cultivation in Malaysia. The samples were collected from several locations that were not exposed to GLUF application. Five types of soil with different soil texture were chosen for this study. Soil samples chosen were identified as Inceptisol (Selangor Series), Oxisol (Munchong Series), Ultisols (Rengam and Serdang Series) and Histosol (peat) according to USDA Soil Taxonomy. Soil samples were collected at two different depths: topsoil (0-15 cm) and subsoil (15-30 cm). Collected soils were air dried and passed through a 2-mm sieve.

Soil texture of each soil was determined using the pipette method of Day (1965) using Calgon as the dispersing agent; the textural class was determined using the USDA soil textural triangle. The cation exchange capacity (CEC) was determined by the leaching method, using 100 mL ammonium acetate (1M NH_4OAc) (Thomas, 1982). Soil organic carbon was determined by the Walkley and Black method, (1984). One gram of soil was weighed into an Erlenmayer flask to measure organic carbon (OC). The pH of the soils was recorded based on the soil-water suspension 1:1(v/v) using Beckman Digital pH meter. The clay mineral contents were analysed by X-ray diffraction technique (XRD). Important soil properties are listed in Table 2 and the results of XRD analysis are shown in Table 3.

TABLE 2

Particle size distribution and chemicals characterization of soils used in this study

Soils series	Depth (cm)	Texture	OC (%)	OM (%)	pH (H_2O)	CEC (cmol(+)kg^{-1})	Clay	Silt (%)	Sand
Selangor	0-15	Silty clay	2.75	4.79	4.31	15 .76	55.64	42.14	1.88
	15 -30	Clay	1.94	3.38	4.11	12 .66	64.93	36.54	0.51

Sorption and Desorption Studies

Sorption isotherms were carried out using the batch equilibrium technique which permits convenient evaluation of parameters that influence the adsorption process (OECD 2000). The analyses were performed with 7 different concentrations of the active substances (GLUF) in triplicates. Two g of each soil were weighed into 50 mL propylene centrifuge tubes. Then, 20 mL of deionized water containing 0.25, 0.5, 1, 1.5, 3, 5 and 10 ug/mL of GLUF were added. The tubes were equilibrated at room temperature for 24 hours after which they were centrifuged for 30 min at 3500 rpm. Then, the supernatant was removed and the equilibrium concentration (Ce) of GLUF was determined in the supernatant by HPLC.

Adsorption isotherms were fitted to linear and Freundlich equations (logarithmic form). In linear form: Cs = Kd Ce, where Kd is a constant. For Freundlich equation: log Cs = log Kf +1/nf log Ce. The amount of herbicide adsorbed (Cs, μg/g) was calculated from the difference between the initial (Cini, μg/L) and the equilibrium concentrations of pesticide in solution (Ce, μg/L).

The constants Kf and 1/n are the empirical Freundlich constants. Desorption determination was conducted immediately after the adsorption experiment. First, the supernatant were replaced with 20 ml of distilled water and the mixture was then shaken for 24 hours at room temperature. The suspension was subsequently centrifuged and analyzed similarly as the adsorption experiment. The correlations between the adsorption coefficients and the soil properties were then determined.

Analysis of GLUF

The clear supernatants were analyzed for GLUF. Samples were first derivatised by adding 0.8 ml of borate buffer (0.025 M) and 0.8 ml of acetone together with 0.2 ml of FMOC-CL (0.01 M) solutions into 1 mL of sample. The mixture was swirled and left at room temperature for 30 minutes. After the reaction, the samples were washed with 1 ml of diethyl ether and ready for determination using high performance liquid chromatography (HPLC) equipped with a fluorescence detector (Sancho *et al*. 1994). The HPLC used was a Hewlett-Packard series 1100 consisting of Model 1046A Programmable Flourescence detector (Hewlewtt-Packard) set at 270 nm (excitation) and 315 nm (emission). The analytical column was NH2 Bondapak (3.9 x 300 mm). Acetonitrile: 0.05 M phosphate (pH 6) in water (25:75, v/v) was used as the mobile phase. The pH of the aqueous buffer solution was adjusted with 2M KOH and 1M HCl.

RESULTS AND DISCUSSION

Soil Physico-chemical Properties

Table 2 shows the physico-chemical properties of the soils used in this study. In general, soil pH in the surface was higher than subsurface in all soils and all the soils were acidic with pH ranging from 4.11 to 5.52. Selangor topsoil (0-15 cm) was silty-clay while its subsoil (15-30 cm) was clayey in texture. Selangor topsoil had a higher percentage of organic carbon (OC), organic matter (OM), pH and cation exchange capacity (CEC) compared to the subsoil. Both the topsoil and subsoil of Rengam series was sandy clay in texture. Its topsoil also showed a higher percentage of OC, OM and pH compared to the subsoil. The CEC value of the Rengam soil was higher in the subsoil. Serdang topsoil was sandy loam while its subsoil was sandy clay loam. The OC, OM, pH and CEC were slightly higher in Serdang topsoil compared to its subsoil. Peat showed the highest value of CEC compared to the other 4 soil types due to the higher organic matter content. Selangor soil had the highest CEC content compared to the other mineral soils. while its subsoil had a higher content of clay (65%) compared to the other soils. The subsoils showed a higher percentage of clay content than the topsoils of all the soil types.

TABLE 3

Clay mineral contents in soils used for this study

Soil series	Depth (cm)	Minerals					
		Kaolinite	Quartz	Illite	Montmorillonite	Ver miculite	Gibsite
Selangor	0 - 15	+++	+++	++	+	+	
	15 -30	+++	++	++	+++	+++	
Munchong	0 - 15	++	++				+
	15 -30	++	+	+			+
Rengam	0 - 15	+++	+++				
	15 -30	+++	+++				
Serdang	0 - 15	++	+++				+
	15 -30	++	+++	+			+

* +++ = abundant

++ = present

\+ = traces

Soil Mineralogy

In general, kaolinite mineral and quartz were the most abundant minerals in the soil samples (Table 3). Montmorillonite and vermiculite were only present in the Selangor subsoil. The higher CEC content in Selangor soil can be explained by the higher content of 2:1 layer silicates, montmorillonite and vermiculite. Selangor series soil has high % clay as well as % silt.

TABLE 4

The adsorption and desorption constant of Kd, Kf, n, for all soils.

Soil series	Depth	Sorption					Desorption
		Linear		Freundlich			Average %
	(cm)	K_d	R^2	K_f	R^2	n	desorbed
Selangor	0-15	13.537	0.9848	18.433	0.9553	0.6430	38.280
	15 -30	34.190	0.9950	39.692	0.9955	0.7431	26.753
Munchong	0-15	4.040	0.8321	3.192	0.907	0.9005	78.841
	15 -30	6.046	0.9600	5.445	0.9463	0.8505	45.990
Renggam	0-15	4.801	0.9011	6.563	0.9169	0.7875	74.798
	15 -30	12.640	0.9990	13.237	0.9910	0.8466	41.642
Serdang	0-15	1.764	0.7908	0.412	0.8363	0.7504	98.003
	15 -30	4.991	0. 9801	2.940	0.9996	0.7712	56.094
Peat	0-15	3.841	0.8126	2.370	0.8613	0.3769	83.090

Adsorption of GLUF

Adsorption isotherm data were fitted to the linear and Freundlich sorption equations to compare the adsorption capacity of GLUF on the soil studied. The adsorption isotherm parameters of GLUF by the soils are shown in Table 4. In general, both the linear and Freundlich sorption isotherms fitted the GLUF adsorption data well in all soils as indicated by the R^2 values which are close to 1. Sorption data and values for Kd, Kf, n and R^2 for all soils are shown in Table 4. High Kd and Kf values indicate strong adsorption capacity of the pesticide to the soils. The values for Kd are larger than Kf in Munchong and Serdang Series and peat. In topsoil, Selangor Series soil showed the highest Kd and Kf followed by Rengam, Munchong, peat and Serdang as shown in *Figs. 2* and *3*. High adsorption capacity of Selangor series soil could be explained by its high percentage of clay content compared to the other soils. Effects of clay content on the adsorption of GLUF have been previously reported (Behrendt *et al.* 1990; Autio *et al.* 2004). The high adsorption capacity found on the Selangor series compared to the Serdang series could be explained by its mineral composition. Selangor series soil contained an

(a) (b)

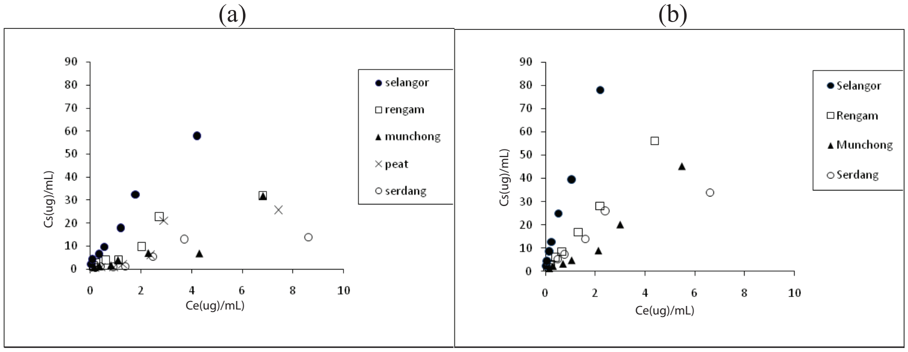


Fig. 2: Linear sorption isotherms of GLUF in (a) topsoil (0-15cm) and (b) subsoil (15-30cm) for the four soils.

(a) (b)

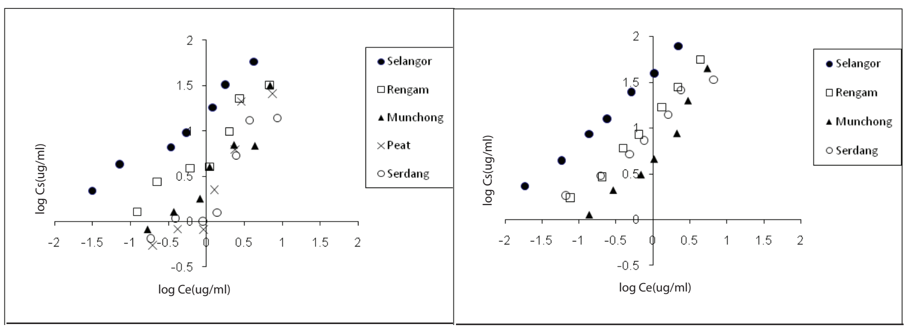
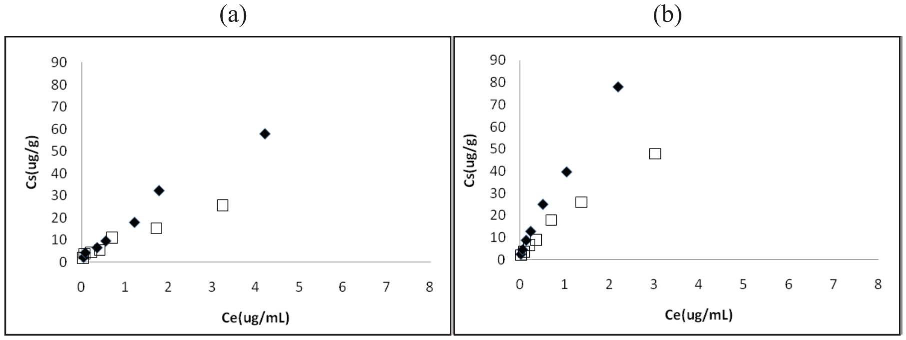


Fig. 3: Log-transformed Freundlich sorption isotherms of GLUF in (a) topsoil (0-15cm) and (b) subsoil (15-30cm) for the four soils

(a) (b)



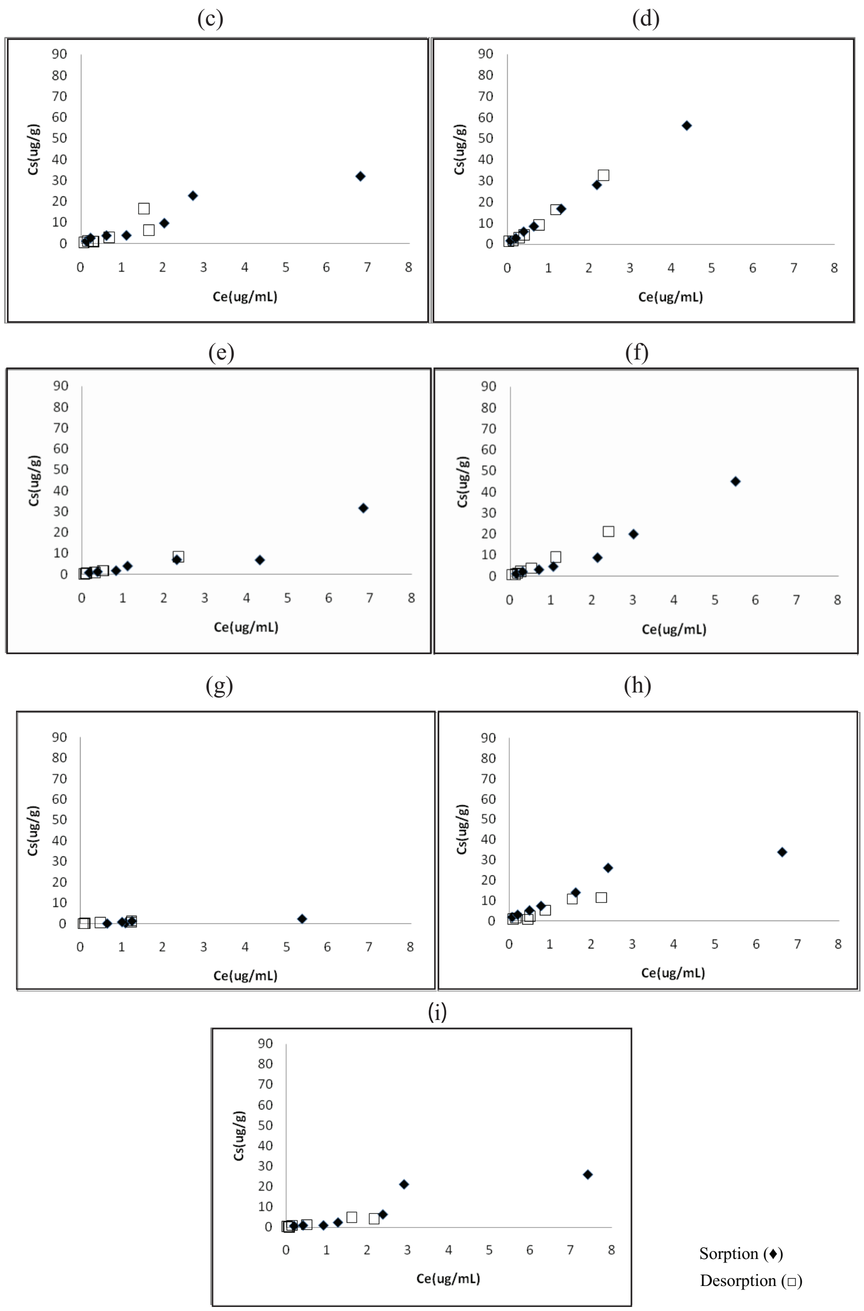


Fig. 4: Sorption and desorption isotherm of GULF in topsoil (0-15cm) and subsoil (15-30cm) of (a) Selangor-topsoil, (b) Selangor-subsoil, (c) Rengam-topsoil, (d) Rengam-subsoil, (e) Munchong-topsoil, (f) Munchong-subsoil, (g) Serdang-topsoil, (h) Serdang-subsoil series soil and (i) peat

abundant amount of kaolinite while Serdang series soil was dominated by quartz and was low in clay content (Table 3). Adsorption of organophosphate pesticides has been reported to be related to organic matter as well as clay content of soils (Khan 1980). However, in this study, peat which is high in organic carbon content, exhibited low GLUF adsorption capacity. This is probably because organic carbon reduces GLUF adsorption by competing with the pesticide molecules for sorption sites on the soil surface. This result is supported by a study done by Autio *et al.* (2004).

As clay content has been reported to be the main factor affecting GLUF adsorption in mineral soils, GLUF adsorption should be higher in Munchong series soil than in Rengam series soil since Munchong series soil has a higher clay content than Rengam series soil. However, the results showed otherwise, which suggest that other factors such as CEC could have also influenced the soils adsorption capacity for GLUF, as Rengam series soil was found to have a higher CEC value than Munchong soil.

Effect of clay content on the adsorption capacity of GLUF is demonstrated by the higher adsorption capacity of subsoils for GLUF than the topsoils in all soils studied (Table 4 and *Fig. 4*). In all soils studied, the subsoil had higher clay content than the topsoil. The correlation between the Kd and Kf values of GLUF and the clay content of the soil was highly significant (Table 5). Table 5 also shows no significant correlation between adsorption capacities of GLUF with CEC, probably, because of the low CEC in highly weathered soil used in the study (Table 2).

TABLE 5

Correlations between soil properties of soils and adsorption isotherm of GLUF (n=3)

Herbicide		% Clay	Organic matter	pH	CEC
GLUF	K_d	0.888*	ns	ns	ns
	K_f	0.903*	ns	ns	ns

* indicates that correlation is significant at P = 0.05 ; ns = not significant

Desorption of GLUF

The average desorption of GLUF was generally higher in the topsoil of all soils studied which was low in clay content compared to the subsoil (Table 4). The highest average desorption was on Serdang series soil followed by peat, Munchong and Rengam series soil. Selangor series soil showed the lowest average desorption percentage among the soils with only 26.75% and 38.28% in the subsoil and topsoil, respectively. Low desorption percentage of Selangor series soil indicates that once GLUF is adsorbed onto the soil colloids, it is strongly bound and its potential to be released into the environment is low. Serdang topsoil which has the lowest adsorption capacity shows the highest average desorption percentage with almost 100% of the herbicide being recovered.

CONCLUSION

As expected, adsorption of GLUF was generally related with clay content. In mineral soils, CEC also plays an important role in the adsorption of GLUF. However, further studies should be conducted to confirm the effects of CEC on soil sorption capacity for GLUF using a wider range of CEC values. The highest adsorption of GLUF was found in Selangor series soil followed by Rengam. Munchong series soil, peat and Serdang series soil. Generally, mineral soils have a higher adsorption capacity of GLUF than peat. Desorption was lowest in soil with a high clay content. Higher desorption was seen in Serdang series soil followed by peat, Munchong, Rengam and Selangor series soil. High desorption recovery of GLUF from the highly weathered soils (Serdang and Munchong) suggests that this compound has potential to be leached into the groundwater.

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