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Keywords: pesticides, solubility, pollution, ground water contamination

Abstract
The adsorption and leaching studies of molinate, carbofuran and propiconazole on silty clay soil were conducted under laboratory conditions. Propiconazole ($K_f$ value = 52.94 litres/kg) was the most strongly adsorbed pesticide by silty clay soil as compared to molinate ($K_f$ value = 10.22 litres/kg) and carbofuran ($K_f$ value = 6.59 litres/kg). The $1/n$ values of molinate (0.99) showed that the ability of molinate to be adsorbed into silty clay soil decreased when the concentration of molinate in solution increased. Carbofuran and propiconazole tend to be adsorbed more into silty clay soil when their concentrations in solution increased. Soil columns with a length of 60 cm were erected and the pesticides were leached with distilled water for 7 days (molinate = 1.03 kg/ha, carbofuran = 0.42 kg/ha and propiconazole = 0.042 kg/ha). No residues of molinate (<1.0 ng/ml), carbofuran (<3.2 ng/ml) and propiconazole (<0.1 ng/ml) were detected in the leachate.

Introduction
Soils all over the world are exposed directly or indirectly to chemicals and it is a major issue to be able to assess how the chemicals will be distributed and degraded in the soil environment. Adsorption, an important process which determines the risk of chemicals to pollute the environment, is defined as the ability of soils to retain the chemicals so that they do not runoff or leach which may lead to pollution of surface and groundwater (Thorstenen et al. 2001). Adsorption is a process in which the pesticide forms chemical bonds with colloidal materials, such as soil organic matter and clay particles. Adsorption is an extremely important process affecting the fate of pesticides (Stenersen 2004; Polyrakis 2009).

Apart from the organic matter and clay contents, the adsorption process is influenced by size, shape, configuration, molecular structure, chemical functions, solubility, polarity, environmental temperature and the acid-base nature of the pesticide molecule itself (Arias-Estevez et al. 2006; Gevao et al. 2000; Muller et al. 2007). Therefore, adsorption is the key in controlling pesticide advective-dispersive, transport, degradation and bioaccumulation (Kafia and Shaw 2008).

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The Muda Irrigation Scheme, which is located in the north-western part of Peninsular Malaysia, is the largest rice production area in Malaysia. Based on the annual rainfall pattern, this granary area has 3 seasons, namely, the dry season from December to March (average rainfall less than 100 mm/month), the moderate season from April to July (average rainfall 200 mm/month) and the wet season from August to November (average rainfall 200 to 300 mm/month) (Ho 1998).

The herbicide molinate (S-ethyl hexahydro-1H-azepine carbothioate) is widely used for controlling barnyard grass (Echinochloa sp.) in paddy fields (Sabater and Carrasco 1998). Molinate has low persistency in soil environment with a field half-life of 5 – 21 days and reported to be poorly bound to soils and thus, may be mobile and present a risk to groundwater contamination (Kamrin 1997). In Malaysia, a formulation of molinate together with propanil was used to suppress the population of sprangletop (Leptochloa sp.), broadleaf signalgrass (Brachiaria platyphylla) and sedges (Cyperus sp.) (DOA 2004).

Carbofuran (2,3-dihydro-2,2-dimethylbenzofuran-7-yl methylcarbamate) is a broad-spectrum carbamate insecticide that kills insects, mites and nematodes on contact after ingestion (Kamrin 1997). Paddy farmers in Malaysia intensively apply carbofuran to control the population of leaffolders and stemborers (DOA 2004). Carbofuran has been reported to be moderately persistent in soil, with a field half-life of 30 – 120 days. Carbofuran binds weakly to soil particles and therefore, it is very mobile in sandy loam, silty clay and silty loam soils and slightly mobile in muck soils (Kamrin 1997).

Propiconazole formulated together with difenoconazole are used in Malaysian rice fields to suppress the population of Helminthosporium oryzae, Rhizoctonia solani and Rhyncosporium oryzae (DOA 2004). Propiconazole has been reported to be very persistent in clay loam and sandy loam soils with half-lives of 336 and 277 days respectively (Bromilow et al. 1999).

The use of soil columns to simulate pesticide movement in soil for soil mobility studies are well documented (Farahani et al. 2008). Apart from carbofuran, studies on the adsorption and leaching of molinate and propiconazole in tropical agricultural soils under laboratory conditions are scarcely reported and thus, the present study was performed to address this. In addition, leaching study and quantifying the adsorption of molinate, carbofuran and propiconazole in Muda agricultural soil will lead to an improved understanding of the behaviour of these pesticides in rice agro-ecosystems.

Materials and methods

Soil sampling

Soil was collected from a non-recycled area located in Kampung Pengkalan Kundor, Alor Setar, Kedah, Malaysia (06°02.925’S, 100°22.289’E). A non-recycled paddy area means this area uses freshwater from the dam to irrigate paddy fields. Soil samples were collected at a depth of 0 – 15 cm from the soil surface. After air-drying and gentle manual disaggregation, the soil was passed through a 2 mm sieve and stored in non-contaminating plastic bags at – 20 °C prior to analyses. Soil samples were prepared in duplicate to determine the physicochemical properties of the soil (Table 1).

Chemicals

All chemicals used in this study were of analytical grade, unless otherwise stated. Pesticide standards were purchased from Dr. Ehrenstorfer, Germany, with purity greater than 98%. A 1,000 µg/ml standard stock solution for each pesticide was...
prepared by adding 0.002 g of pesticide standards in 20 ml ethyl acetate. A series of standard diluted solutions of the 3 pesticides with concentrations of 1.0, 10.0 and 100.0 µg/ml were established from the standard stock solution.

**Pesticide adsorption equilibria**

Two studies, namely, determination of equilibrium time and multiple-point adsorption isotherm were conducted. The multiple-point adsorption isotherm was used to determine the Freundlich adsorption coefficient (Kf) which is widely used to measure the sorption of chemicals on certain adsorbents (Muller et al. 2007). Adsorption data were calculated using the linearized Freundlich equation as shown below:

\[
\ln C_s = \ln K_f + \frac{1}{n} \ln C_w
\]

where Cs is pesticide adsorbed per mass unit soil (mg/kg), Cw is the equilibrium solution concentration (mg/litre), Kf is the Freundlich Coefficient (litre/kg), and 1/n is a measurement of intensity of sorption and reflects the degree to which sorption is a function of concentration (Thorsten 2001). When n = 1, adsorption of chemicals would be linearly propotional to the equilibrium concentration and the distribution coefficient (Kd) would be appropriate to use (Neera 2005). Apart from the Kf values, Koc, Kom and Log Kow values were also calculated using the equations as follows:

\[
K_{oc} = K_f / \% \text{ OC}
\]

\[
K_{om} = K_f / \% \text{ OM}
\]

\[
K_{oc} = 1.724 K_{om}
\]

\[
\log K_f = 0.52 \log K_{ow} + 0.62
\]

where Koc is organic carbon coefficient, Kom is organic matter coefficient, Kow is octanol-water partition coefficient, OC is soil organic carbon content and OM is soil organic matter content (Krishna and Philip 2008).

**Determination of equilibrium time**

The equilibrium time was determined according to Ngan (2002). A volume of 10.0 ml of 0.01 M CaCl₂ solution was added to 2 g soil and pre-equilibrated for about 2 h before the soil solution was spiked with 10.0 ml of 1.0 µg/ml concentrated pesticide standards. Triplicate samples were shaken at 150 rpm for 2, 4, 8, 24, 48 and 72 h at 28 °C and then centrifuged at 3,000 rpm for 20 min. The supernatants were transferred to glass tubes and stored in the refrigerator at 4 °C prior to analyses.

**Multiple-point adsorption isotherm**

The procedure to determine the multiple point adsorption isotherms was in accordance to Ngan (2002). Two grams of soil was added to 10 ml of 0.01 M CaCl₂ solution and then the soil solution was spiked with 0.05, 0.1, 0.5, 1.0, 2.0 and 5.0 µg/ml of pesticide standards. Triplicate samples were shaken at 150 rpm for 24 h and then centrifuged at 3,000 rpm. The supernatants were collected and pesticide concentrations in the supernatants were determined. Adsorption was calculated as the difference between initial and final concentration of pesticide residues in the solution. Blank samples which contained pesticide standards and CaCl₂ solution but no soil were also prepared to study the adsorption of pesticides to the glass tubes.
Leaching study
The leaching study was conducted according to Ngan (2002). Columns for the leaching study were erected with 4 glass tubings (15 cm length x 2.5 cm ID) to create the whole column of 60 cm. Soil was added and compacted to a length of 45 cm and the column was covered with aluminium foil to minimize photo-degradation process. The soil column was saturated with 300 ml distilled water for 7 days. However, only 38.7 – 50.1 ml of water was eluted from the column after day 7. This might be due to the high clay content of the soil. A 5 g soil sample spiked with molinate, carbofuran and propiconazole was added to the top of the column prior to the watering. Two water volumes, 169.1 and 338.2 ml, which simulate two rainfall distributions (172 and 344 mm) were used in this study. These rainfall amounts reflected the average rainfall received by Muda Irrigation Scheme during moderate and wet season per month. The distilled water was passed through the column and leachate was collected in a 75 ml flask for 7 days. An aliquot of 10 ml of leachate was filtered for determination of pesticide concentration. All the experiments were carried out in triplicates.

Pesticides analysis
All pesticides were determined and quantified by gas chromatography (GC) On Hewlett Packard (HP) (Palo Alto, CA) model 6890 equipped with NPD and µ-ECD detectors and fitted with HP DB05MS column (30 m length x 0.25 mm ID x 0.25 µm film thickness). Molinate and carbofuran residues were quantified using NPD detector while carbofuran was determined using µ-ECD detector. The operating conditions for molinate was: column 340 °C; injector 300 °C and detector 310 °C. Carrier gas used in this study was helium. The limit of determination of molinate, carbofuran and propiconazole in water matrix were 1.0, 3.2 and 0.01 ng/ml respectively.

Results and discussion
Equilibrium time and multiple-point adsorption isotherm
Molinate, carbofuran and propiconazole reached equilibrium after 48 h, as shown in Figure 1. Propiconazole was the most rapid to reach the equilibrium (after 8 h) as compared to molinate and carbofuran. About 93% of propiconazole was adsorbed into the soil after 8 h of incubation while about 65% and 47% of molinate and carbofuran were adsorbed after 24 h respectively. Time (t) needed for certain chemicals to reach equilibrium from one phase to another phase (e.g, from aqueous phase to solid phase) can indicate the potential of the chemical to pollute the environment. Chemicals that adsorbed fast on soil/other adsorbents have low possibility to contaminate surface water through runoff process due to its short time existence in aqueous phase.

The parameters for $K_f$, $1/n$, $K_{oc}$, $K_{om}$ and Log $K_{ow}$ are shown in Table 2 while the Freundlich adsorption isotherm used to reflect the adsorption of molinate, carbofuran and propiconazole are shown in Figures 2, 3 and 4 respectively. The slope ($1/n$) values for the 3 pesticides varied between 0.99 and 1.21. Therefore, the $K_f$ values were chosen as the parameters for comparison in order to minimize the effect of isotherm non-linearity and also to have more meaningful comparison (Neera 2005).

In general, $1/n$ (slope) values for pesticides were 1 or <1, indicating C-shaped or L-shaped sorption isotherms. C-shaped sorption isotherms are independent of the initial sorbate concentration while L-shaped isotherms are characterized by the decrease in the sorption of pesticide molecules as the aqueous concentration of sorbate in solution increased (Neera 2005). However, if the $1/n$ >1, it shows greater adsorption of pesticides
Figure 1. Adsorption of molinate, carbofuran and propiconazole in soil versus time

Figure 2. Freundlich isotherm for molinate

Figure 3. Freundlich isotherm for carbofuran

Figure 4. Freundlich isotherm for propiconazole

Table 2. K_f, 1/n, r^2, K_oc, K_om and Log K_ow values for the various pesticides

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Molinate</th>
<th>Carbofuran</th>
<th>Propiconazole</th>
</tr>
</thead>
<tbody>
<tr>
<td>K_f (litres/kg)</td>
<td>10.22</td>
<td>6.59</td>
<td>52.94</td>
</tr>
<tr>
<td>1/n</td>
<td>0.99</td>
<td>1.21</td>
<td>1.04</td>
</tr>
<tr>
<td>K_oc (litres/kg)</td>
<td>538.03</td>
<td>347.14</td>
<td>2,786.32</td>
</tr>
<tr>
<td>K_om (litres/kg)</td>
<td>312.08</td>
<td>201.35</td>
<td>1,616.19</td>
</tr>
<tr>
<td>Log K_ow</td>
<td>0.75</td>
<td>0.38</td>
<td>2.12</td>
</tr>
<tr>
<td>r^2</td>
<td>0.9966</td>
<td>0.8809</td>
<td>0.9116</td>
</tr>
</tbody>
</table>

into the soil when pesticide concentrations exist in higher range (Thorstensen et al. 2001).

The results showed that the ability of molinate to be adsorbed into silty clay soil decreased when the concentration of molinate in solution increased, while carbofuran and propiconazole tend to be adsorbed more into the soil when their concentration in solution increased. The K_f values of molinate, carbofuran and propiconazole were 10.22, 6.59 and 52.94 litres/kg respectively. These findings reflected that carbofuran is weakly adsorbed.
Adsorption and leaching of pesticides in agricultural soils into silty clay soil as compared to molinate and propiconazole.

Currently, studies on the adsorption of molinate are very scarce. Distribution coefficient (Kd) values of molinate in various soil textures in Europe and United States ranged from 0.74 – 2.04 litres/kg (average = 1.53) (European Commission 2003). Kf value for molinate obtained from this study was higher as compared to the reported Kd values. This might be due to different soil textures used in determining the Kf and Kd values (European Commission 2003).

An adsorption study conducted on 43 Sri Lankan soil textures reported that the Kd values for carbofuran ranged from 0.11 – 41 litres/kg (average = 0.83) (Liyanage et al. 2006). Study conducted by Krishna and Philip (2008) showed that Kf values of 4 Indian soil textures ranged from 0.911 – 11.41 litres/kg with highest Kf value of carbofuran in compost soil (11.41 litres/kg) as compared to clay soil (8.29 litres/kg), red soil (3.53 litres/kg) and sandy soil (0.91 litres/kg). Lalah and Wandiga (1996) found that Kf values of carbofuran in Kenyan soils ranged from 15.14 – 15.49 litres/kg. Adsorption of carbofuran in lateritic soils in Taiwan reported that Kf values of carbofuran in 4 soil textures ranged from 0.22 – 0.8 litres/kg (Hsieh and Kao 1998). The Kd values for carbofuran ranged from 0.9 – 1.2 litres/kg and 2.7 – 2.9 litres/kg in Bagan Datoh and Labu soils respectively (Farahani et al. 2008).

Kf value of carbofuran in silty clay soil reported in this study was higher from the values reported by Farahani et al. (2008) and Hsieh and Kao (1998). However, it was lower when compared to Kf values reported by Krishna and Philip (2008), Liyanage et al. (2006) and Lalah and Wandiga (1996).

A study conducted by Thorstensen et al. (2001) found that Kf values of propiconazole in loam and sandy loam soils ranged from 27 – 36 litres/kg while Wu et al. (2004) reported that Kf values of propiconazole on sediment existing in runoff water was two times higher (30.9 and 38.8 litres/kg) when compared with the Kf values of the soil (17.5 litres/kg). The difference in Kf values reported by Wu et al. (2004) might be due to the higher organic matter content in sediment as compared to the soil. Kf values of propiconazole in 2 Indian soils have been reported to range from 1.28 – 2.59 litres/kg (Neera 2005). These low Kf values might be due to high sand content in both soils. Kf value of propiconazole in silty clay soil was found to be higher than the reported values, probably due to high clay content in the soil. For silty clay soil, the Kf values increased in pesticides in the order: propiconazole > molinate > carbofuran.

Apart from Kf and Kd values, Koc, Kom and Kow values are also used to predict the adsorption and transport of pesticides in soil environment. In general, pesticides with high Koc, Kom and Kow values adsorb strongly to soil particles. Koc and Kom values can validate the adsorption of non-polar pesticides as compared to polar pesticides. This might be due to the high affinity of organic matter to hydrophobic pesticides. Furthermore, organic matter dominates the adsorption of pesticides on soil when the organic matter content in that particular soil is less than 1% (Muller et al. 2007). The Koc values of the pesticides increased in the order: propiconazole > molinate > carbofuran.

According to the classification of availability of pesticide movement by McCall (1980), it showed that carbofuran is moderately mobile in silty clay soil (Koc = 150 – 500) while molinate and propiconazole is classified as slightly mobile in silty clay soil (Koc = 500 – 2000). The Log Kow value of propiconazole was the highest as compared to molinate and carbofuran. According to Nicholls et al. (1988), herbicides with Kow values ranging from 0.5 – 3.0 are strongly adsorbed herbicides, while organophosphorus insecticides with Kow < 1, is poorly bound to soil particles and is likely to leach to ground and surface waters. Fungicides
with $K_{ow}$ values $> 5$ are strongly adsorbed and have low potential to pollute the environment. From the classification made by Nicholls et al. (1988), it can be considered that molinate and propiconazole are strongly bound to silty clay soil while carbofuran is poorly bound to silty clay soil and has high potential to pollute the ground and surface waters in the plot where the soil samples were taken.

**Leaching of pesticide residues**

No residues of molinate, carbofuran and propiconazole were detected in the leachates collected after 7 days of watering (Table 3). It was also found that the soil columns were not fully saturated when only about 35.4 – 48.7 ml of leachate water was collected at the end of the experiment. This might be due to the compaction of the soils in the columns. Furthermore, the soil used in this study had high clay content with low permeability compared to soils with lower clay content (Weiner 2000).

Soil column study which involved two Italian agricultural soils with high sand content (41.5 – 71%) reported that carbofuran was very mobile in these soils in which the carbofuran and its metabolites, 3-ketocarbofuran and 3-hydroxycarbofuran, were detected in the leachate (Fava et al. 2007). A field study conducted by Awasthi et al. (1984) found that carbofuran was detected at 3 soil depths, namely, 0 – 7.5, 7.5 – 15.0 and 15.0 – 22.5 cm. Most of the residues were detected on the soil surface (0 – 7.5 cm).

Leaching studies conducted on Bagan Datoh and Labu soils (column length 30 cm) showed that carbofuran was very mobile in sandy clay and silty clay loam soils when its residues were detected in the leachate up to 81.4% from the total carbofuran applied (Farahani et al. 2008). Carbofuran was detected in two Kenyan soils (column length 27 cm) in the range of 29.0 – 33% of total carbofuran applied (Lalah and Wandiga 1996). Contrasting results obtained through this study might be due to: 1) soil sample had high clay content, 2) compaction of the soils in the glass tubings and 3) soil column was longer when compared to previous studies.

To date, reports on the mobility of molinate under laboratory conditions are very limited. A field study conducted by Deuel et al. (1978) in rice plots reported that molinate residues were detected at depths of 7.6 – 15, 15 – 23 and 23 – 30 cm. However, the detection of molinate in the lower soil depths might be due to cross contamination during surface soil and water sampling. A study on the degradation of molinate under anaerobic conditions found that molinate residues distributed evenly (0.06 ppm) at 3 different soil depths, namely, 0 – 2, 2 – 4 and 7 – 14 cm (Imai and Kuwatsuka 1988). Therefore, it can be considered that molinate was slightly mobile in mineral soil with 13.2% clay content.

Soil column experiment involving 2 agricultural soils collected from New Delhi and Punjab district reported that no residue of propiconazole was detected in the leachate water (Neera 2005). The residue was detected at 10 – 15 cm soil depth in Punjab and up to 20 cm soil depth in New Delhi. In the 2 soil columns, most of the residues were found on the surface area (0.0 – 5.0 cm). Lysimeter study conducted in Korean rice field reported that about 0.0005 – 4.4% of total applied $^{14}$C-propiconazole was detected in lysimeter water and this showed that propiconazole was slightly

### Table 3. Pesticide concentrations in leachate under two rainfall distributions

<table>
<thead>
<tr>
<th>Rainfall distribution</th>
<th>Molinate (ng/ml)</th>
<th>Carbofuran (ng/ml)</th>
<th>Propiconazole (ng/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>172 mm</td>
<td>&lt;1.0*</td>
<td>&lt;3.2*</td>
<td>&lt;0.1*</td>
</tr>
<tr>
<td>344 mm</td>
<td>&lt;1.0</td>
<td>&lt;3.2</td>
<td>&lt;0.1</td>
</tr>
</tbody>
</table>

*Limit of determination
mobile in loam and loamy clay soils (Kim et al. 2002).

Conclusion
Propiconazole was the most rapid pesticide adsorbed by silty clay soil followed by molinate and carbofuran. The 1/n values showed that the ability of molinate to be adsorbed into silty clay soil decreased when the concentration of molinate in solution increased. Carbofuran and propiconazole tend to be adsorbed more into the soil when their concentration in solution increased. Propiconazole was the less mobile pesticide in silty clay soil as compared to molinate and carbofuran based on the Kf, Koc, Kom and Log Kow values obtained from this study. No residues of molinate, carbofuran and propiconazole were detected in leachate after 7 days of watering. These could be due to the high clay content in the soil samples, compaction of soil in the glass tubings and the soil column being longer than in the previous studies.

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References


Adsorption and leaching of pesticides in agricultural soils

**Abstrak**
Kajian penjerapan dan larut lesap molinat, karbofuran dan propikonazol pada tanah lempung berlodak telah dijalankan di bawah keadaan makmal. Propikonazol (nilai Kf = 52.94 liter/kg) adalah pestisid yang paling kuat terjerap pada tanah lempung berlodak berbanding dengan molinat (nilai Kf = 10.22 liter/kg) dan karbofuran (nilai Kf = 6.59 liter/kg). Nilai 1/n pestisid molinat (0.99) menunjukkan bahawa keupayaan molinat untuk terjerap pada tanah lempung berlodak menurun apabila kepekatan molinat dalam larutan meningkat. Bagi karbofuran dan propikonazol, keupayaan kedua-dua pestisid untuk terjerap pada tanah lempung berlodak meningkat apabila kepekatan kedua-duanya dalam larutan meningkat. Turus tanah sepanjang 60 cm telah didirikan dan pestisid telah dilarut lesap ke dalam turus ini dengan air suling selama 7 hari (molinat = 1.03 kg/ha, karbofuran = 0.42 kg/ha dan propikonazol = 0.042 kg/ha). Tiada residu molinat (<1.0 ng/ml), karbofuran (<3.2 ng/ml) dan propikonazol (<0.1 ng/ml) dikesan dalam air larut lesap yang dielut keluar dari turus tanah.