Adsorption and Desorption of Paraquat in Two Malaysian Agricultural Soils

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Adsorption and desorption of paraquat (1, l’-dimethyl-4,4’-dipyridylum dichloride) in two tropical soils was determined under laboratory conditions. The two soils were taken from rice fields located in the North West of Perak state. The adsorption equilibrium time was 2 hours for both soil types. This adsorption equilibrium time was used to determine the effect of concentration on adsorption. The high Freundlich adsorption distribution coefficients $K$ for paraquat of 321.91 L/kg and 325.66 L/kg were obtained in the clay loam and clay soils, respectively. The adsorption coefficient ($K_a$) of clay loam and clay soil were found to be 885.53 L/kg and 772.40 L/kg with solution concentration of 100 µg/L and soil- solution ratio (1:5) at 30°C. The mechanism of adsorption of paraquat involves ionic and charge transfer bonds and the $K_a$ value of the herbicide may therefore not be applicable. Low desorption was recorded in the clay loam and clay soils after the first desorption process (35%). Subsequent desorption processes, however, failed to displace the paraquat cation from either type of soil. The adsorption of paraquat was not affected by temperature (30°C/ 40°C).

**Key words:** Adsorption, desorption, temperature, paraquat, soil.

**Introduction**

It is a known fact that herbicides give rise to serious health problems when not used properly (Nakamura et al., 2000). The adsorption/desorption phenomena of pesticides in soils are of great importance from the environmental point of view. Pesticide sorption affects other processes like transport, degradation, volatilization and bioaccumulation, which influence the final fate of these compounds in the soil (Kumar and Philip, 2006).

The pesticide soil sorption coefficient $K_a$ and the soil organic carbon sorption coefficient $K_{oc}$ are basic parameters for describing the environmental fate and behavior of pesticides in soil. Desorption is a key process affecting the mobility of pesticide molecules in soils. Work in the past has shown a strong relationship exists between the desorption process and the desorption rate as well as the potential mobility of pesticides in soil (Haung and Weber, 1998). Paraquat (1, l’-dimethyl-4,4’-dipyridylum dichloride) has been used widely as a non-selective aquatic and terrestrial herbicide. For weed control, paraquat is applied at the rate of 0.28 to 1.12 kg/ha (1/4 to 1 lb per acre); for desiccation it may be used twice (Hall, 1995). Paraquat is classified as a class II herbicide (moderately hazardous) (WHO, 2003). Once paraquat enters the soil environment, it is rapidly and strongly bound to clay minerals and organic matter and becomes biologically inactive (Ricketts, 1999).

When paraquat molecules bind to sites on clay and penetrate the inter-lattice regions of the expanding clay particles, the herbicide persists for some time because it is no longer available for exchange with other cations (Weber and Coble, 1968). Clays, as efficient natural adsorbents, are one of the main components of soils and possess a negative charge that is compensated for by exchange cations, on their surfaces, such as Na$^+$ and Ca$^{2+}$.
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(Akcay and Yurdakoc, 2000). Paraquat is considered safe for many agricultural uses because the compound is easily photodegradable with low mobility in clay and organic rich soils. However, its ecological risk may be expected because it is strongly bound to erode of sediments that may be transported to surface water (Vinten et al., 1983).

The experiment was designed to determine the adsorption/desorption characteristics of the compound under laboratory conditions, which may be extrapolated to natural conditions. The objective of this study was to investigate the adsorption and desorption of 14C-paraquat and to determine the fate of paraquat in two types of Malaysian soils.

Materials and methods

Soils and Chemicals

Soil samples, collected from a rice-growing area in Kerian district, located in the North West Perak, were air dried and sieved through a 2-mm sieve. They were classified as clay loam and clay, respectively, through mechanical analysis (Table 1). It was found that the clay content in the clay soil was more than 1.3 times higher than that of the clay loam soil but the carbon content in the clay loam soil was more than 2.8 times higher. All soil data were recorded on dry weight basis. The method as described by Allison (1965) was employed for determining the organic carbon content. The bulk density of the soils was also recorded.

Radio-labelled [ethyl-1-14C] paraquat obtained from the Institute of Isotopes, Budapest and non-labelled paraquat obtained from Dr. Ehrenstorfer Germany, were used in the study. The radioactive concentration of the radio-labelled paraquat was 100 µCi with a specific activity 32.3 mCi/mmol. The radio purity of the supplied labelled compound was pre-checked by radio-TLC and found to be more than 95%.

Experimental Procedure

One hundred µCi in 0.5 mL distilled water radio-labelled [ethyl-1-14C] paraquat with a specific activity of 4646.58 KBq/mg (32.3 mCi/mmol) was diluted by adding 9.5 mL distilled water and this was labelled as RSS. Then a standard solution of 1850 KBq/mg (RSS2) was prepared by pipetting 5 mL of RSS into a 1 L volumetric flask.

A working standard solution of labelled [ethyl-1-14C] paraquat and non-labelled paraquat, with a measured specific activity of 0.18 KBq/µg was further prepared. An equilibration time was determined using 1.0 mg litre-1 solutions of paraquat in 0.01 M calcium chloride solution (0.18 KBq/µg) of the 14C-labelled paraquat, mixed with non-labelled analytical grade materials.

Determination of Adsorption Equilibrium Time

Two g of soil were weighed into each test tube. Then 10 mL of the non-labelled and 14C-paraquat solution (RSS2) were added to the test tube. The tubes with their contents were shaken using a reciprocation shaker at 150 rpm and a constant temperature of 30°C at intervals of 10, 15, 30, 45, 60,120, 240, 360, 480 and 720 minutes. The tubes (in triplicate) were taken out of the reciprocation shaker at the specified intervals and centrifuged at 3000 rpm for 20 minutes. An aliquot solution (1 mL) was sampled with a micropipette and placed in a 20 mL scintillation vial. The scintillation cocktail (PICO. FLUOR™ 15, purchased from Packard) was added prior to radioassay using a Liquid Scintillation Counter (TriCarb Model TR 2550 AB). The procedure in principle followed OECD Guidelines 106 (2000) but the temperature of shaking was higher 30°C, as this reflects the temperature of tropical Malaysia.

Determination of Desorption Equilibrium Time

Solutions of paraquat at the concentration of 100 µg/L were prepared using 1.85 kBq of the 14C-labelled and non-labelled analytical grade materials. The solutions (10 mL) were placed in tubes, each tube containing 2 g of soil. All treatments were carried out in triplicate. A procedure similar to that used in the determination of equilibration time was followed. At the end of centrifugation, an aliquot of the supernatant (1 mL) was radio assayed. The remaining supernatant was discarded and replaced by a fresh solution of 0.01 M CaCl2 (10 mL). The tubes were shaken again on a shaker at the provisory specified conditions, at intervals of 3, 6, 17, 32, 35, 40, 57, 60 and 65 hours. The tubes (in triplicate) were sampled at the completion of each interval and subjected to centrifugation. An aliquot solution (1 mL) was radio assayed by LSC.
Effect of Concentration on Adsorption

A series of concentrations of the mixture of the 14C-labelled and non-labelled paraquat solutions of 0.1, 0.2, 0.5, and 1 µg/mL were prepared in triplicate. Solutions of different concentrations of the above 14C-labelled and non-labelled paraquat mixtures were added to the centrifuge tubes containing 2 g of clay loam and clay soil, respectively. The tubes were shaken on a reciprocation shaker at equilibrium time (above study) for both soil types. The temperature and shaking rate were set at 30°C and 150 rpm, respectively. The next process was centrifugation at 3000 rpm for 20 minutes. One mL of the supernatant from the centrifuge tubes (in triplicate) was then sampled and placed in a scintillation vial of 20 mL capacity. Ten mL of the scintillation cocktail were put into this vial prior to addition of 1 mL of the supernatant and radio-assayed using LSC. The concentration of paraquat adsorbed to the soil was calculated as:

\[
\frac{(C_B - C_s)V_s}{M}
\]

Where \( C_B \) and \( C_s \) are the blank and supernatant solution concentration, \( V_s \) the solution volume, and \( M \) the soil mass. Adsorption isotherms were fitted to the Freundlich model in log form:

\[
\log \frac{x}{m} = \log k_f + \frac{1}{n} \log C_{eq}
\]

Where \( x/m \) is the concentration of paraquat adsorbed to the soil (µg/g), \( C_{eq} \) the equilibrium concentration of paraquat in solution (µg/mL), and \( k_f \) (intercept) and \( 1/n \) (slope) the adsorption parameters calculated from the liner regression.

Desorption Studies:

Solution of paraquat at concentration 100 µg/L (10 mL) were placed in tubes containing 2 g soil. The tubes were placed on the reciprocation shaker (150 rpm) in triplicate, at 30°C for 2 hours. The tubes were then centrifuged at 3000 rpm for 20 minutes. An aliquot (1 mL) of the supernatant was radioassayed.

The remainder of the supernatant was discarded and fresh 0.01 M CaCl2 solution was added. The tubes were shaken as described earlier to attain equilibrium and subsequently placed in a centrifuge tube for the second desorption study. After centrifugation, an aliquot (1 mL) of the supernatant was radioassayed. The process was carried out in triplicate. The quantity of pesticide adsorbed after every desorption stage was evaluated. The results of the desorption were expressed as percentage of the initially adsorbed concentration. After the fourth desorption stage, the soil samples were air dried, homogenized and 0.2 g samples were taken from each tube and radioassayed using a biological oxidizer.

Effect of Temperature on Adsorption:

The experiment was carried out with the concentration of herbicide 100 µg/L and incubation temperature of 30, 35 and 40°C. Each treatment was triplicated. An aliquot solution (1 mL) was radio assayed using LSC. Statistical analysis of the above experiments was conducted with single factor analysis of variance (ANOVA). The P values that were less than 0.05 were considered significant.

Results and discussion

Adsorption/Desorption:

Preliminary studies showed that 14C-labelled paraquat attained equilibrium at 2 hours in both the soil types, and this result was used in the investigation on adsorption characteristics. Tsai et al. (2003) reported that adsorptive equilibrium for paraquat was attained within 60-120 minutes in clay soil.

The soil sorption coefficient (Kd) was used to describe the binding strength of paraquat to soil. Adsorption of paraquat to the clay loam (r2=0.76) and clay (r2=0.86) soils was found to follow a Freundlich adsorption isotherm (Figures 1 and 2). Kd values of 321.91 and 885.53 (1 kg-1) were observed for the clay loam, and 325.65 and 772.40 (1 kg-1) for the clay respectively; 1/n values were 1.43 and 1.31 at respectively (Table 2). The 1/n values observed for the both soil types were more than unity, indicating that the relative adsorption increased with increasing solution concentration. This indicates high adsorption of paraquat to both clay loam and clay soils, as reported in previous studies (Cheah et al., 1997). Paraquat adsorbs easily to predominantly negatively charged soil colloids. The mechanism of adsorption of paraquat involves ionic and charge transfer bonds (Calvert, 1980).
Fig. 1: Freundlich adsorption isotherm of paraquat in clay loam soil

Fig. 2: Freundlich adsorption isotherm of paraquat in clay soil

\[ y = 1.4291x + 7.4735 \quad \text{R}^2 = 0.7886 \]

\[ y = 1.3127x + 7.7576 \quad \text{R}^2 = 0.8567 \]

K\text{oc} is defined as the distribution coefficient (k\text{d}) for a particular soil/pesticide combination divided by the organic carbon content of the soil. Thus, once a pesticide’s K\text{oc} value is determined for a soil or a group of soils, the k\text{d} values can be estimated for different soils by multiplying the K\text{oc} value by the organic carbon content. Since ionic pesticides such as paraquat bind to soil primarily by electrostatic mechanisms involving both mineral and organic matter, the K\text{oc} parameter is not as useful for these compounds.

The amounts of 14C-labelled paraquat adsorbed at the different concentration levels on to the clay loam and clay soils are shown in Table 3. The amount of 14C-labelled paraquat adsorbed onto the clay loam was 4.55, 11.31, 28.21 and 51.73 (µg/g) at initial concentrations of 0.1, 0.2, 0.5 and 1 µg/mL, respectively, and in the clay soil, the amount of paraquat adsorbed was 4.52, 11.28, 28.20 and 51.59 at the same respective concentrations.

Results showed that adsorption onto the two types of soil was very similar but adsorption on to the clay loam soil was slightly stronger than that onto the clay soil, probably due to the higher organic matter content. The amount of paraquat adsorbed onto the clay loam and clay soil, obtained from the triplicate samples, were analyzed using analysis of variance (ANOVA). The statistical analysis of variance confirmed that the amount of paraquat adsorbed was significantly affected by the different concentrations in both soil types (P< 0.05), confirming the results of Wapakorn et al. (2006).

However, the tightly bound paraquat can be removed only by disturbing the soil structure indicating a dependence on the rigidity and spatial dimensions of the pore structure of the soil, that is, the tightly bound paraquat becomes trapped in the lattice structure of the soil particles. Weber et al., (1965) have shown by x-ray analysis that paraquat is held in the lattice of montmorillonite with the plane of the ring parallel to the silicate sheet. Knight and Tomlinson (1967) has also done x-ray crystallography of clay fractions containing adsorbed paraquat.

Table 4 shows desorption of paraquat from clay and clay loam soil samples after four successive desorption processes. The insignificant desorption of paraquat from the soil suggests strong binding of paraquat to the adsorption sites. It appears that the total percentage desorption from either clay or clay loam soils was less than 0.4% (Table 4), thus unfolding the strength of the bonds that hold paraquat to clay and clay loam. This showed that paraquat molecules are strongly adsorbed on soil particles, and this consequently reduces its downward mobility.

Therefore, paraquat has very limited mobility in clay loam and clay soils. The low desorption was recorded for the both soil types at the first desorption process: 0.03 µg. The low desorption observed in both soil types may have been caused by the calcium chloride used in the experiment. At a high concentration of 750 g/L, calcium chloride has been reported to cause an immediate elution of 10% of paraquat from a sandy loam (Calderbank, 1968). A total amount of 35% of 14C paraquat was desorbed from the clay loam and clay soil after four successive desorption processes.
Table 4 shows the high $k_{des}$ value at the first stage of desorption for both types of soil and explains the low desorption process later as the molecules strongly adsorb onto the soil particles. Biological oxidation of the soils have revealed high amounts of soil-bound paraquat residues of 90% in the clay loam and clay soils. The effect of temperature on adsorption of ¹⁴C-labelled paraquat on the clay loam and clay soil was also studied. The concentration of the paraquat solutions was 100 µg/L. Results showed the total amount of paraquat adsorbed on clay loam and clay soils was not affected significantly ($P=0.05$) by the temperature increase from 30°C to 40°C (data not shown). These observations are similar to the findings (Weber et al., 1965; Akhavein and Linscott, 1968; Damianakis et al., 1970) where it was found that there was no apparent effect of temperature on the adsorption of paraquat onto soil particles.

### Table 1: Physico-chemical properties of the clay loam and clay soils

<table>
<thead>
<tr>
<th>Soil Type</th>
<th>pH</th>
<th>Total C (%)</th>
<th>Coarse Sand (%)</th>
<th>Fine Sand (%)</th>
<th>Silt (%)</th>
<th>Clay (%)</th>
<th>Bulk density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay Loam</td>
<td>5.82</td>
<td>5.94</td>
<td>3.13</td>
<td>31.04</td>
<td>26.76</td>
<td>39.07</td>
<td>1.29</td>
</tr>
<tr>
<td>Clay</td>
<td>6.17</td>
<td>2.10</td>
<td>8.20</td>
<td>13.03</td>
<td>28.51</td>
<td>50.26</td>
<td>1.24</td>
</tr>
</tbody>
</table>

### Table 2: Adsorption, desorption and organic carbon distribution coefficients of pesticides in clay loam and clay soils

<table>
<thead>
<tr>
<th>Parameter (1 kg⁻¹)</th>
<th>Clay loam</th>
<th>Clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_b$</td>
<td>321.91</td>
<td>325.65</td>
</tr>
<tr>
<td>$K_d$</td>
<td>885.53</td>
<td>772.40</td>
</tr>
<tr>
<td>$1/n$</td>
<td>1.43</td>
<td>1.31</td>
</tr>
<tr>
<td>$r^*$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$K_{des}(1 kg⁻¹)$</td>
<td>1410.33</td>
<td>1410.00</td>
</tr>
<tr>
<td>$K_{oc}$ (1 kg⁻¹)</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>$K_{r}$ (1 kg⁻¹)</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>

*Except for 1/n.

NA: Not available as desorption did not occur.

### Table 3: The amount of adsorption (µg/g) and the percentage adsorption of ¹⁴C-labelled paraquat in clay and clay loam soils

<table>
<thead>
<tr>
<th>Soil Type</th>
<th>Initial amount (µg/mL)</th>
<th>Amount adsorbed (µg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay loam</td>
<td>0.1</td>
<td>4.55 (±0.003)</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>11.31 (±0.002)</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>28.21 (±0.003)</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>51.73 (±0.005)</td>
</tr>
<tr>
<td>Clay</td>
<td>0.1</td>
<td>4.52 (±0.002)</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>11.28 (±0.002)</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>28.20 (±0.001)</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>51.59 (±0.005)</td>
</tr>
</tbody>
</table>

### Table 4: Desorption of paraquat in clay loam and clay soils

<table>
<thead>
<tr>
<th>Clay loam</th>
<th>Clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>Desorption (%)</td>
<td>Desorbed (µg)</td>
</tr>
<tr>
<td>------------</td>
<td>-------------</td>
</tr>
<tr>
<td>1</td>
<td>0.35 (±0.00)</td>
</tr>
<tr>
<td>2</td>
<td>0.00 (±0.00)</td>
</tr>
<tr>
<td>3</td>
<td>0.00 (±0.00)</td>
</tr>
<tr>
<td>4</td>
<td>0.00 (±0.00)</td>
</tr>
<tr>
<td>Total desorbed</td>
<td>0.35</td>
</tr>
</tbody>
</table>

Standard deviation (±)

Mean and standard deviation from 3 replicates, adsorption (at equilibrium) = 8.489 µg.

**Conclusion:**

In conclusion, it can be stated that paraquat molecules are strongly bound to soil components such as clays and organic fractions, thus permitting less desorption and consequently decreasing the lateral and downward movement of paraquat into surface water.

**References**


WHO, 2003. International Statistical Classification of Disease & Related Health Problems, 10th revision, Toxic effects of pesticides, T60; Sequelae of toxic effects of substances chiefly nonmedical as source TO: