

Adsorption of Paraquat in Selected Sri Lankan Soils

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ABSTRACT. *Adsorption of paraquat to soil particles strongly influences the fate of the chemical in soils, its efficacy in controlling target weeds and its potential for adverse effects on non-target organisms. This study was conducted to investigate the magnitude and nature of paraquat adsorption in some Sri Lankan soils as related to soil properties and to study the downward movement of paraquat in few selected soils.*

Soils with different physical and chemical properties were collected from twelve locations of Sri Lanka. An adsorption experiment was conducted by equilibrating soil samples with increasing concentrations of paraquat solutions and determining the paraquat concentration of the supernatant solution. The adsorption data were fitted to different adsorption isotherms. The relationship between adsorption parameters and soil properties were analysed. An elution experiment was conducted using soil columns with three selected soils based on texture. Elution curves were plotted and percentage of paraquat eluted was calculated.

The adsorption data in most soils fitted well to Linear and Freundlich isotherms, indicating that with increasing paraquat concentrations, the amount adsorbed increases linearly or exponentially. In soils having very low cation exchange capacities (<10 cmol(+)/kg), the adsorption data fitted well to Langmuir isotherm, which assumes that a maximum adsorption occurs when all adsorption sites are occupied. The elution experiment indicated that in clay and loamy soils, the downward leaching was very low, while in sandy soils, almost all of the paraquat applied was eluted.

The results indicate that retention of paraquat is substantial even in soils with a moderate capacity to adsorb cations (CEC >10 cmol(+)/kg) which may reduce potential adverse effects on non-target organisms. Application of

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paraquat to sandy soils, may lead to ground water pollution with possible adverse effects on non-target organisms.

INTRODUCTION

Paraquat (1,1-Dimethyl, 4,4-bipyridine dichloride) is a non-selective herbicide commonly used to control weeds in agricultural crop production in Sri Lanka. In addition to soil, paraquat is readily and strongly adsorbed on to clay minerals and organic particles (Calvett, 1989; Weber and Weed, 1981; Kookana and Aylmore, 1993; Rytwo *et al.*, 1996). According to Koskinen and Harper (1990) the capacity of a soil to adsorb or retain a pesticide is a key parameter controlling the extent to which the chemical will leach through the soils to ground water. Therefore the adsorption process determine both the efficacy of paraquat in controlling target weeds as well as its environmental impact on the soil system.

Adsorption is related to soil properties such as clay content, clay mineralogy and organic matter content (Knight and Tomlinson, 1967; Weed and Weber, 1969). Presence of paraquat residues in soils soon after paraquat application has been reported in lowland rice fields of Sri Lanka (Bandara and Kearney, 1991). However, detail studies on the magnitude and the nature of paraquat adsorption in Sri Lankan soils have not been reported. Such information will help in improving the efficacy of paraquat in controlling weeds as well as in minimizing the adverse effects of paraquat on non-target organisms.

A study was therefore conducted;

1. To investigate the nature and magnitude of adsorption of paraquat in different soils of Sri Lanka as related to their physical and chemical properties.
2. To study the elution of paraquat as related to soil properties in three selected soils.

MATERIALS AND METHOD

Soils

Twelve surface soils (0-15 mm) with varying physical and chemical properties were collected from different locations of Sri Lanka. The samples belong to the soil orders of Ultisols, Alfisols, Inceptisols and Entisols. Soils were analysed for pH (1:2.5 soil:1M KCl), cation exchange capacity (Chapman and Kelly, 1930) organic matter content (Walkley and Black, 1934) and texture (Bouyoucos, 1936).

Analytical grade Paraquat (98%) was used as an aqueous solution for soil treatment.

Adsorption Experiment

A preliminary kinetic study was conducted to investigate the time taken to reach the maximum adsorption level. A paraquat solution of 100 ppm was equilibrated with 10 g of different soils until no further adsorption is detected.

An adsorption experiment was conducted by equilibrating 10 g of soil samples with 25 ml of solution containing increasing concentrations of paraquat for 2 hrs. Paraquat levels used were 0, 3.125, 6.25, 12.5, 25, 50, 100 mg per liter and each level was replicated twice. After equilibration, the amount of paraquat in the supernatant was determined by a colorimetric method (Ashley, 1970). The amount of paraquat adsorbed was calculated by the difference between the initial and final concentrations.

The adsorption data (mean values) were fitted to Linear, Langmuir, and Freundlich isotherms described by equations 1, 2 and 3 respectively by the least squares method.

$$C_s = K_L C_e \quad (1)$$

$$\frac{C_s}{C_e} = \frac{1}{bQ} + \frac{C_e}{Q} \quad (2)$$

$$\ln(C_s) = \ln K_f + n \ln(C_e) \quad (3)$$

where,

- C_e = Equilibrium solution concentration (mg/l);
- C_s = Equilibrium solid phase concentration (mg/kg soil);
- Q = Langmuir sorption maximum (mg/kg);
- n = Adsorption intensity constant;
- b = enthalpy related sorption constant (l/mg);
- K_f = Sorption capacity constant (l/mg)ⁿ;
- K_L = Linear partition coefficient (l/mg).

The correlation between sorption parameters and soil properties were statistically analysed.

Elution Experiment

Three soils with different soil textures namely Nilambe (Ultisol), Aralaganwila (Alfisol) and Kalpitiya (Entisol) were selected for the elution experiment. Soils were packed into glass columns with a diameter of 7.2 cm and a height of 20 cm. The packing was done so as to obtain the same bulk density observed in the field which was 1.0, 1.2 and 1.5 g/cm³ for Nilambe, Aralaganwila and Kalpitiya soils, respectively. The soils were saturated by adding de-ionized water after which 1 ml of 100 ppm paraquat solution was applied to the surface. The soil columns were eluted with water and 10 ml of eluate fractions were analysed for paraquat colorimetrically. The elution was continued until the paraquat concentration in eluate fractions were undetectable. The total amount of paraquat eluted in each soil was estimated.

RESULTS AND DISCUSSION

The texture of the soils ranged from sand to clay-loam. All soils were strong to slightly acidic in reaction with cation exchange capacities of very low to moderate (Table 1).

Table 1. Physical and chemical properties of the selected soils.

Location	Taxonomy	TEXTURAL CLASS	CEC (me/100g)	pH	OM %
Nilambe	Ultisol	Clay loam	18.9	3.8	1.2
Kamburugamuwa	Ultisol	Sandy clay loam	16.7	6.6	3.0
Hettipola	Inceptisol	Loamy sand	6.4	5.6	1.2
Girandurukotte	Alfisol	Sandy loam	14.8	5.3	0.9
Wattegama	Ultisol	Sandy clay loam	26.0	5.6	2.2
Nuwara Eliya	Ultisol	Clay loam	31.5	3.8	36.6
Yalegoda	Ultisol	Clay loam	23.1	5.7	2.9
Aralaganwila	Alfisol	Sandy loam	16.0	4.8	0.6
Dodangolla	Ultisol	Clay loam	28.8	6.1	0.9
Kalpitiya	Entisol	Sand	1.5	3.2	0.1
Kegalle	Ultisol	Sandy loam	8.7	5.1	1.9
Naula	Alfisol	Clay loam	18.0	6.3	1.5

Adsorption Experiment

The preliminary kinetic study indicated that the rate of paraquat adsorption in all soil samples were very fast and reached the equilibrium within 2 hr. The Coefficient of Determinations (r^2) obtained by fitting the adsorption data to the linear form of different isotherms are shown in Table 2. In most soils, linear isotherm fitted well with the adsorption data. In these soils paraquat adsorption increased linearly with increasing concentrations (Figure 1). For three soils Freundlich isotherm gave the best fitting relationship (Table 2) which indicates that adsorption increases exponentially with increasing concentration (Figure 2a). Thus an adsorption maxima was not observed in soils where adsorption data fitted to either the Linear or the Freundlich isotherms indicating a very high capacity of these soils to adsorb paraquat at the recommended levels (0.4-1.0 kg/ha) applied in the field.

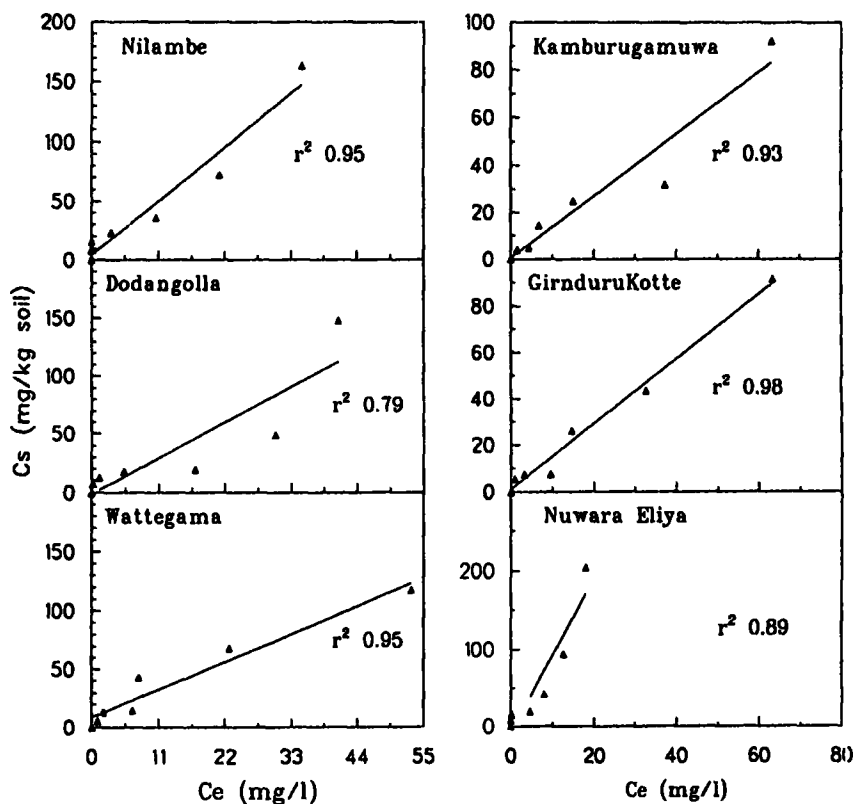


Figure 1. Linear adsorption isotherm for paraquat in six soils.

In sandy soils having low CEC values (<10 cmol(+)/kg), the adsorption data did not fit either to the linear or Freundlich isotherms (Table 2), but gave a good fit to Langmuir isotherm. This isotherm is derived with the basic assumption of an existence of an adsorption maximum corresponding to a monomolecular layer. Thus in soils with cation exchange capacity values <10 cmol(+)/kg, paraquat adsorption may be limited due to lack of exchangeable sites. Similar results have been reported in an earlier study by Rytwo et al. (1996), which indicates that the adsorption is complete upto the CEC of the soil and thereafter becomes limiting.

Table 2. Coefficient of determination and sorption parameters for different isotherms.

Soil	Linear Isotherm		Langmuir Isotherm			Freundlich Isotherm	
	r^2	K_L	r^2	Q	b	r^2	K_f
Nilambe	0.95	4.14	0.51			0.73	
Dodangolla	0.79	2.79	0.28			0.56	
Wattegama	0.95	2.16	0.73			0.87	
Kamburugamuwa	0.93	1.31	0.26			0.83	
Girandurukotte	0.98	1.40	0.14			0.85	
Nuwara Eliya	0.89	9.70	0.21			0.44	
Yalegoda	0.59		0.69			0.78	8.63
Aralaganwila	0.84		0.36			0.94	8.75
Naula	0.94		0.52			0.97	1.10
Kalpitiya	0.33		0.99	6.37	0.19	0.56	
Kegalle	0.43		0.99	125.00	0.61	0.76	
Hettipola	0.49		0.99	41.67	0.37	0.34	

The K_L values of the soils that fitted with the Linear isotherm ranged from 1.31 to 9.70 (Table 2). Highest K_L value was observed in the Nuwara Eliya soil indicating a higher ability to partition paraquat from the solution phase to solid phase.

The parameter K_f in Freundlich isotherm ranged from 1.10 to 8.63. The highest K_f value was recorded for Aralaganwila soil showing a high sorption capacity compared to the other two soils that fitted with the Freundlich isotherm.

Langmuir parameters namely, sorption maxima (Q) and the equilibrium constant (b) ranged from 6.37 to 125, and 0.19 to 0.61,

respectively. The highest value for both parameters were observed in the Kegalle soil. A significant correlation ($r = .96$) was observed between the two Langmuir parameters indicating that soils having high sorption maxima are also having a high equilibrium constant which is a measure of binding energy.

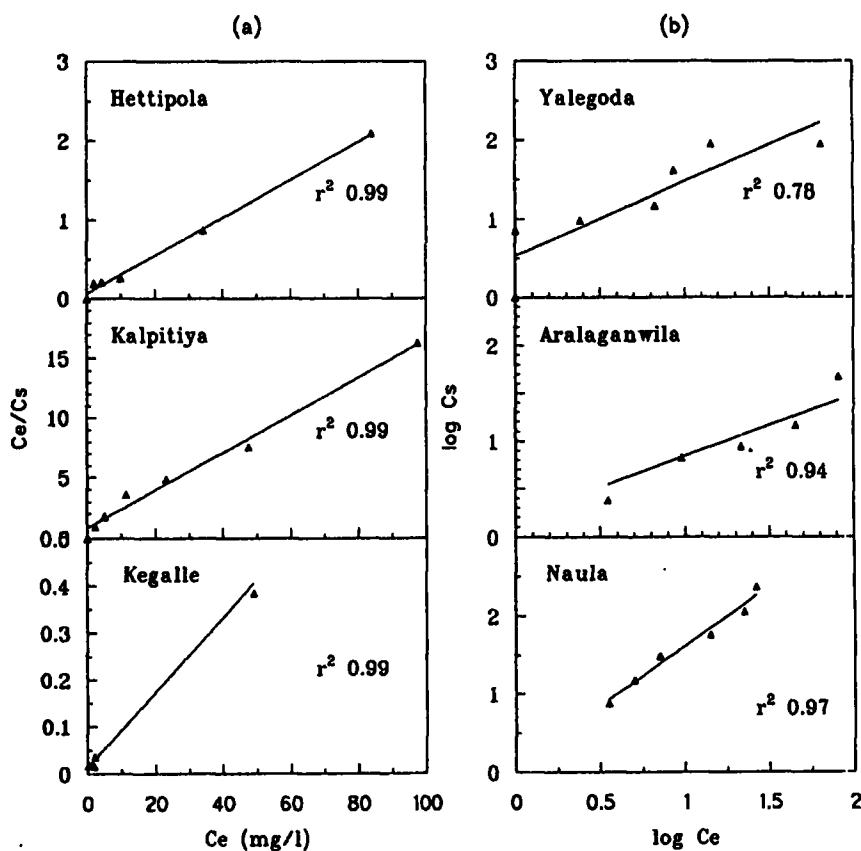


Figure 2. Freundlich adsorption isotherm (a) and Langmuir adsorption isotherm (b) for paraquat in six soils.

The Coefficient of Determination observed for relationship between K_L and soil properties of the six soils showing linear adsorption of paraquat were 0.10^{ns}, 0.20^{ns} and 0.10^{ns} for CEC, OM and clay content respectively. None of the soil properties showed a significant relationship with K_L values. This indicates that for these soils which showed very high capacities to adsorb paraquat at the concentrations usually applied to soil, none of the soil properties studied seems to exhibit a significant effect on paraquat adsorption. However, Rytwo et al. (1996), have reported a linear relationship between the clay content and the paraquat adsorption. In contrast, in this study, the relationship between soil properties and respective adsorption parameter is found to be non significant ($p < 0.05$). The reason may be that in this study adsorption behaviour of either clay or organic matter was not studied in isolation. The soils were used as in the field except for basic laboratory preparations. Nevertheless, on average, the soils with high clay contents (>30%) were found to retain higher amounts of paraquat (95 ± 12 mg/kg) than soils with less clay (78 ± 9 mg/kg).

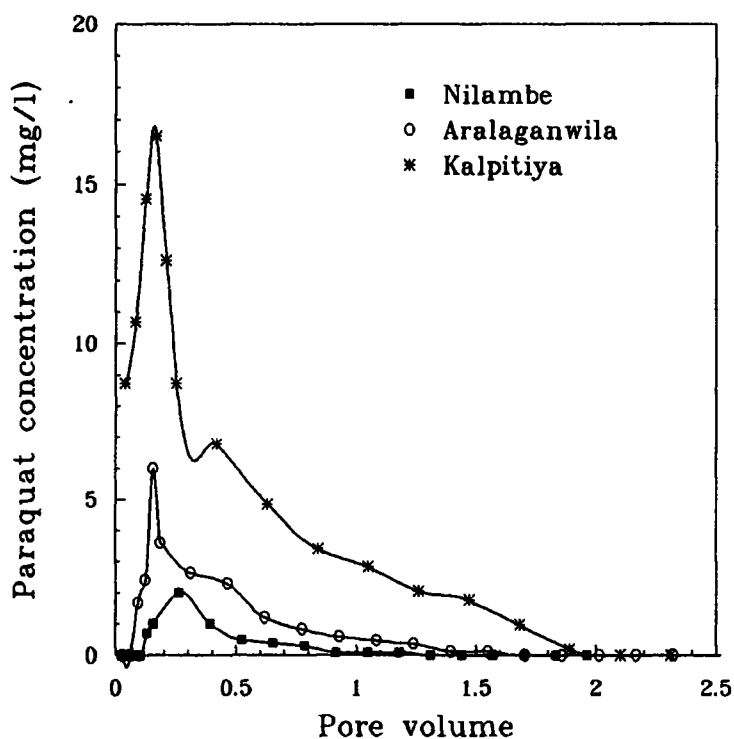


Figure 3. Elution profiles for paraquat in three soils.

Elution Experiment

The elution profiles for paraquat varied substantially in the three soils (Figure 3). In Nilambe soil, which had a higher clay content and CEC than the other two soils, the elution of paraquat started only after 0.1 pore volume had been eluted. In contrast, in Kalpitiya soil the first eluate sample contained a paraquat concentration of 8.5 mg/l. The peak paraquat concentration was reached in all soils when 0.2 - 0.3 pore volume was eluted. However, the peak concentration varied greatly in the three soils. The highest peak concentration of 16.7 mg/l was observed in the Kalpitiya soil while the lowest peak concentration of 2.0 mg/l was observed for the Nilambe soil. The total amounts of paraquat eluted were 6.2%, 22.3% and 94.6% in Nilambe, Aralaganwila and Kalpitiya soils, respectively.

CONCLUSION

From this study it can be concluded that in soils with a moderate to high capacity to adsorb cations (>10 cmol(+)/kg), ground water pollution due to paraquat application is almost negligible. However, application of paraquat to sandy soils with low CEC (<10 cmol(+)/kg) may cause ground water pollution through leaching.

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