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Fate of Diuron in Selected Agricultural Soils

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ABSTRACT. *Adsorption, leaching and plant uptake of diuron were studied in ten surface soils collected from different locations of Sri Lanka. Adsorption was studied by equilibrating soils samples with varying concentrations of diuron. Adsorption data were fitted to Linear, Freundlich and Langmuir isotherms. Diuron leaching in soils was studied using packed soil columns at two different bulk densities, i.e., 1.0 and 1.5 Mg m^{-3}, as well as using organic manure amended and un-amended soils. Plant uptake of diuron was estimated by using 1 and 4 weeks old Guinea-A (Panicum maximum L.) plants grown in pots filled with diuron treated soils. Microbial degradation was studied using the soil sampled from Nuwara Eliya, having the highest organic matter content. Losses of diuron due to volatilization were also estimated.*

In seven soils, the adsorption data fitted well to Linear isotherms, indicating that the amount adsorbed increases linearly with increasing diuron concentrations. However, in the other three soils, with low clay and organic matter contents, the adsorption data fitted well to Langmuir isotherm, indicating that adsorption sites for diuron are limited in these soils. Leaching losses of diuron in these three soils were also found to be much higher. In all soils, the amount of diuron leached was significantly higher at a bulk density of 1.0 Mg m^{-3} than at 1.5 Mg m^{-3}, whereas, application of compost significantly reduced leaching losses. Losses of diuron due to volatilization were negligible, unless directly exposed to solar radiation. Microbial degradation was undetectable within the short period of seven days, even in the soil from Nuwara Eliya with high organic matter content. In all soils, plants took up major proportion of the applied diuron.

The fate of diuron is influenced by soil properties such as soil bulk density and the organic matter content. Manipulation of such properties by various management practices could reduce leaching losses that may lead to groundwater pollution.

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INTRODUCTION

Diuron [3-(3,4-dichlorophenyl)-1, 1-dimethyl urea] is a pre-emergent, selective herbicide. It is usually applied to soil at the rate of 2-4 kg (a.i.) ha^{-1} depending on the severity of the weed infestation. However, the sensitivity of different weeds to diuron is variable and in many instances total weed control has been achieved by application of heavy doses. The activity of diuron in soil has been reported as 4-8 months (Worthing, 1987) depending on the prevailing environmental conditions and soil type. High persistence of diuron may lead to adverse effects on soil macro and micro fauna and flora.

Diuron is a polar aromatic compound and therefore, its ability to retain in the soil colloidal system may not be as high as an ionic compound such as paraquat (Ratnayake and Kumaragamage, 1996). This non-ionic nature increases the mobility of diuron, thus increasing the possibility to contaminate groundwater.

Fate of any pesticide applied to soil is governed by chemical, physical and biological transformations. Several experiments that have been carried out to study such transformations of substituted-urea herbicides such as sulfonyl-ureas and phenyl-ureas (Grover, 1975; Bowmer and Adeney, 1978; Miller *et al.*, 1978; Attaway *et al.*, 1982; Wang *et al.*, 1985; Shelton *et al.*, 1996), revealed that these transformations are highly influenced by soil and environmental conditions.

Therefore, this study was carried out to investigate, (a) the fate of diuron applied to Sri Lankan soils in terms of gaseous and leaching losses, microbial degradation, plant uptake and adsorption by soil particles and, (b) the effects of soil compaction and organic manure application on leaching losses of diuron.

MATERIALS AND METHODS

Soils

Ten surface soil samples (0-15 cm) from different locations of Sri Lanka, namely, Polonnaruwa, Kundasale, Gampaha, Puttalam, Kandy, Mawanella, Maha Illuppallama, Matale, Galaha and Nuwara Eliya were collected. These soils belong to soil orders of Ultisol, Entisol, Inceptisol and Alfisol. Important physical and chemical properties were determined using standard methods. Texture of the soils used was determined by pipette method (Gee and Bauder, 1986) and the textural class was determined using the textural triangle.

The saturated hydraulic conductivity (Ks) was measured by the constant head method. Glass columns with an inner diameter of 4 cm were filled with soil to attain bulk densities of 1.0 and 1.5 Mg m^{-3} and a water head of 5 cm was maintained. Once the steady state flow condition was reached, the flux of each column was measured at five minutes intervals.

To determine the CEC, soils were saturated with ammonium acetate (pH=7) for 24 h and washed with excess isopropyl alcohol and distilled with magnesium oxide. Ammonia liberated was trapped in 2% boric acid and determined by titrating with hydrochloric acid (Rhoades, 1982). The pH of the soil suspension (1:2.5 deionized water) was measured using a pH meter. Walkey and Black wet oxidation method (Nelson and Sommers, 1982) was used to determine the organic matter content of soils.

Adsorption experiment

The adsorption experiment was conducted by equilibrating 25 g of oven dried soil samples with 100 ml of diuron, each having concentrations of 5, 10, 50, 100, 200,300, 400 and 500 mg l^{-1} at 30±1°C. To reach equilibrium between the liquid and solid phases, samples were shaken for one h. Soil solution was then separated by centrifugation at 30,000 rpm for 10 min. An aliquot of 25 ml of the supernatant solution was pipetted into a 250 ml separating funnel and diuron was extracted with four portions of 25 ml chloroform solution. The chloroform extract was then evaporated with a gentle stream of heated air using a hot air gun and the residues were dissolved in 25 ml of methanol. Any remains of water were removed by treating with 5 g of anhydrous Na_2SO_4. The supernatant solution was separated by centrifugation at 20,000 rpm for 5 min and diuron concentration was measured using a double beam UV–spectrophotometer (Shimadzu UV 1601) at optical densities of 213 nm and 250 nm.

Volatilization study

A bottom sealed glass capillary tube filled with a small quantity of diuron was heated in a oil bath until the chemical melts, to determine the melting point of the compound. Triplicate samples of diuron (100 g) were heated to 30°C and 50°C using an electric hot–plate for 3 h or kept in open environment (30°C) for 12 h. Loss of weight was measured by using an electronic balance and the change in concentration was determined by spectroscopic method. Vapour pressures at these two temperatures were measured using a digital manometer (Digitron P 200 H).

Leaching experiment

A column experiment was carried out to investigate the leaching behaviour of diuron in different soils. Leaching columns (20 cm dia.) were packed with soils maintaining two different bulk densities of 1.0 and 1.5 Mg m^{-3}, respectively. Soils were treated with diuron at the rate of 4 kg (a.i.) ha^{-1}, after which columns were leached with de–ionized water. The amounts of diuron recovered in the leachate samples (10 ml) were detected spectroscopically using a UV visible spectrophotometer. Each treatment was replicated twice.

To investigate the effects of organic–matter on leaching of diuron, compost produced using urban waste was added to soils at a rate of 10% (w/w) and the leaching experiment was repeated twice. Analysis was done using UV spectroscopy.

Microbial degradation

This study was carried out using only the soil from Nuwara Eliya, as it had the highest organic matter content, and therefore, the highest microbial activity. Ten samples, each of 100 g, were sterilized with chloroform for 48 h (control) and treated with diuron at the rate of 4 kg (a.i.) ha^{-1}. In addition, ten unsterilized soil samples were also treated with diuron at the same concentration, and were incubated at 30°C for 7 days. The difference in the diuron concentration in the two sets of soil solution extracts was taken as the effect of microorganisms on degradation of diuron. The concentrations were determined using UV spectroscopy and Gas Liquid Chromatography (GLC; Shimadzu GC 14B).

Plant Uptake of Diuron

To estimate diuron uptake by plants, a pot experiment was carried using Guinea-A (*Panicum maximum* L.) as the indicator plant. Three treatments used included a control with no vegetation in the pot, seedlings (1 week old) and mature plants (4 weeks old). Three replicates were allocated to each soil and pots were treated with diuron at the rate of 4 kg (a.i.) ha^{-1}. Before treating with diuron, pots were irrigated up to the field capacity of the soil and no further irrigation was done until the end of the experiment. After one week, 100 g of soil from the top 10 cm was obtained and the soil solution was extracted with water. Residual diuron concentration was analyzed by UV spectroscopy. The difference in concentrations in the soil extracts of pots with plants and without plants was used to estimate the plant uptake, assuming that other transformations are not affected by the presence of plants.

RESULTS AND DISCUSSION

Texture of the soils varied from sandy to clay loam with low to moderate CEC values ranging from 1–10.5 $cmol_c\ kg^{-1}$. All soils were acidic with pH values less than 7. Soil taken from Nuwara Eliya exhibited the lowest pH of 4.2 while Aralaganwila soil had a pH close to 7. Organic matter contents were generally low varying between 0.7% and 1.5%, except for the soils from Nuwara Eliya which contained 3.2% of organic matter (Table 1).

Table 1. Important physical and chemical properties of the soils.

Location	Soil Order	Textural Class	CEC $cmol_c kg^{-1}$	pH	OM (%)
Polonnaruwa	Alfisol	Sandy loam	6.5	6.9	1.4
Maha-Illuppallama	Alfisol	Clay loam	7.0	6.8	1.1
Puttalam	Entisol	Sand	1.0	6.1	N.D.
Matale	Alfisol	Clay loam	10.5	6.8	1.2
Kundasale	Ultisol	Clay loam	4.0	6.0	1.3
Kandy	Inceptisol	Sandy clay loam	4.5	5.2	0.7
Mawanella	Ultisol	Sandy loam	4.5	6.0	1.1
Galaha	Ultisol	Clay loam	7.5	5.0	0.8
Gampaha	Ultisol	Loam sand	3.5	5.6	1.5
Nuwara Eliya	Ultisol	Clay loam	9.5	4.2	3.2

N.D. = Not detected

Adsorption of Diuron

The importance of individual constituents on pesticide sorption is usually evaluated by studying the sorption behaviour on selected soil fractions (Huang *et al.*, 1984; Hermosin and Cornejo, 1989; Cox *et al.*, 1993; Laird *et al.*, 1994), or by investigating changes in sorption after removing soil constituents such as Fe oxides, clay or organic matter. However, the objective of this research was to study the fate of diuron in soil, and as such, adsorption experiment was conducted using soils as they were, without removing any fraction of its components.

The adsorption data were fitted to three isotherms, namely, Freundlich isotherm (Equation 1), Linear isotherm (Equation 2) and Langmuir isotherm (Equation 3).

$$Cs = K_L\ Ce \quad (1)$$

$$\frac{Cs}{Ce} = \frac{1}{bQ} + \frac{Ce}{Q} \quad (2)$$

$$\ln(Cs) = \ln K_f + n \ln(Ce) \quad (3)$$

where,

Ce = Equilibrium solution concentration (mg l^{-1})
Cs = Equilibrium solid phase concentration (mg kg^{-1} soil)
Q = Langmuir sorption maximum (mg g^{-1})
n = Adsorption intensity constant
b = Enthalpy related sorption constant (l mg^{-1})
K_f = Sorption capacity constant (l mg^{-1})
K_L = Linear partition coefficient (l mg^{-1})

In seven soils, the adsorption data fitted well to Linear isotherms (Figure 1), indicating that the amount adsorbed increases linearly with increasing diuron concentrations. These soils generally had higher organic matter and clay contents. In three soils sampled from Polonnaruwa, Puttalam and Gampaha, which showed sandy textures (Table 1) with low organic matter contents, the adsorption data fitted well to Langmuir isotherm (Figure 2), indicating that adsorption sites for diuron are limited in these soils.

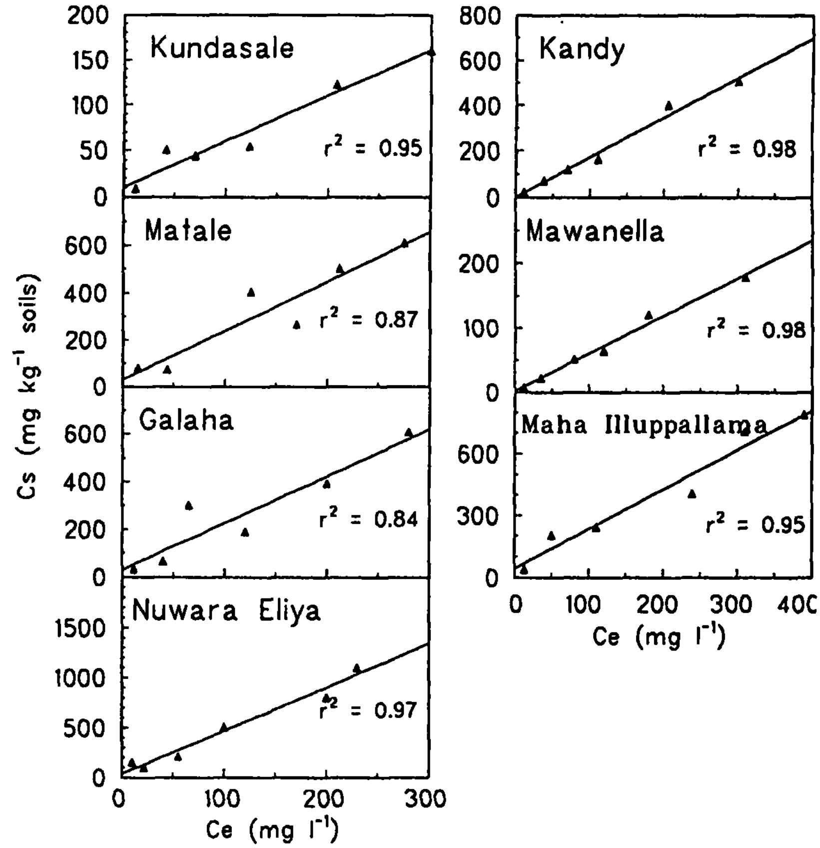

Figure 1. **Linear isotherms for diuron adsorption.**

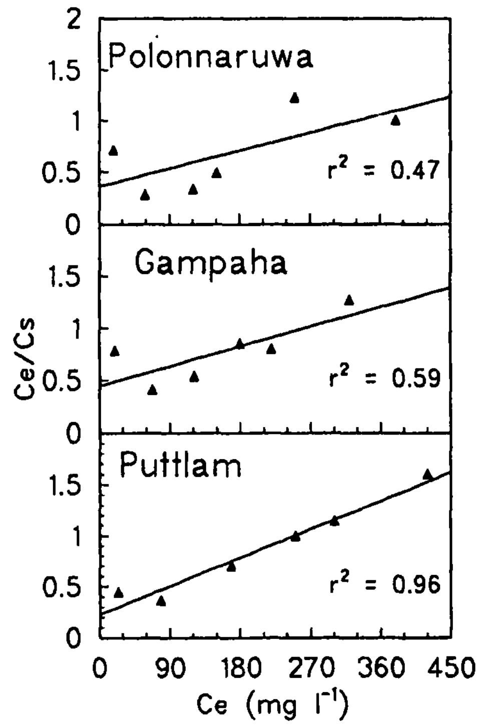

Figure 2. Langmuir isotherms for diuron adsorption.

The adsorption parameters (Table 2) indicated that out of the seven soils that gave the best fit to Linear isotherm, soil from Nuwara Eliya which had the highest organic matter content, showed the highest adsorption, with a linear partition coefficient of 4.32. However, adsorption parameters when regressed with soil properties such as CEC, pH, and organic matter and clay contents did not show a significant correlation with any of the soil properties. In the ten soils studied the organic matter content was varying within a narrow range of 0.7–3.2 and the adsorption parameters showed a linear relationship although it was not statistically significant at $p<0.005$.

Table 2. Model parameters and coefficients of determination for different isotherms.

Location	Linear Isotherm		Langmuir Isotherm		
	r^2	K_L	r^2	Q	b
Polonnaruwa	-	-	0.47	516.80	0.005
Maha Illuppallama	0.95	1.92			
Puttalam	-	-	0.96	322.58	0.014
Matale	0.87	2.09			
Kundasale	0.94	0.50			
Kandy	0.98	1.74			
Mawanella	0.98	0.58			
Galaha	0.61	1.96			
Gampaha		-	0.59	477.10	0.005
Nuwara Eliya	0.97	4.32			

Leaching of Diuron

Leaching is a significant means of transporting solutes in most soils beyond the root zone. However, leaching is a function of solubility of the compound as well as the volume of water that passes through the profile. Solubility of diuron in water at 25°C was found to be only 39 mg l^{-1} while at 50°C it was only 46 mg l^{-1}. Although diuron is a relatively less soluble compound, the commercial product which is a flowable powder mixes with water readily than the pure compound.

When diuron leachate in soil columns with two different bulk densities of 1.0 and 1.5 Mg m^{-3} were considered, a significant relationship was observed between soil bulk density and leaching of diuron. When the bulk density was 1.0 Mg m^{-3}, the amount of diuron leached (as a % of added) was significantly higher ($p<0.05$) than when the bulk density was 1.5 Mg m^{-3} in all soils (Table 3). The average flux of water through soil columns at bulk densities of 1.0 and 1.5 Mg m^{-3} were 4.3 and 1.7 ml cm^{-2} min^{-1}, respectively.

Table 3. The amount of diuron leached (mean) from soil columns at two bulk densities.

Location	Amount leached as a % of the amount added	
	Bulk Density 1.0 Mg m^{-3}	Bulk Density 1.5 Mg m^{-3}
Polonnaruwa	38.2	20.5
Maha Illuppallama	13.2	5.8
Puttalam	92.1	78.8
Matale	15.4	7.6
Kundasale	21.4	12.3
Kandy	18.6	10.3
Mawanella	17.5	9.7
Galaha	10.4	4.3
Gampaha	61.4	43.0
Nuwara Eliya	11.2	5.2

Leaching pattern among the ten soils at bulk density of 1.5 Mg m^{-3} showed considerable differences. In soils with high clay contents, such as those sampled from Kundasale, Maha Illuppallama, Galaha and Matale, the maximum concentration of diuron in leachate fractions was detected after about 0.9–1.2 pore volumes were leached. In sandy soils such as soils sampled from Puttalam and Polonnaruwa, maximum concentration occurred when about 0.3–0.5 pore volumes were leached. However, the leaching pattern of the ten soils at a bulk density of 1.0 Mg m^{-3} was similar and maximum leaching occurred between 0.5–0.8 pore volumes. Similarly when the soils were treated with organic matter there was a marked reduction in average amounts leached, which was statistically significant at $p< 0.01$ (Table 4).

Table 4. Effect of organic matter application on leaching of diuron.

Location	Amount leached as a % of the amount added	
	Without organic matter	With organic matter
Polonnaruwa	38.2	12.2
Maha Illuppallama	13.2	1.2
Puttalam	92.1	56.8
Matale	15.4	1.6
Kundasale	21.4	3.1
Kandy	18.6	2.3
Mawanella	17.5	2.5
Galaha	11.2	1.0
Gampaha	61.4	34.6
Nuwara Eliya	10.4	1.0

Significant decreases in the amounts of diuron leached with the addition of organic manure shows the potential of using organic matter to reduce leaching losses and minimize groundwater pollution. However, in this study only one rate (10% w/w) of organic manure application was studied, whereas the field level applications are usually made at the rate of 5–10 tons ha^{-1}. Usually, such applications are made on the surface after plant beds are prepared and incorporated into the soil to a depth cf about 10–15 cm. Therefore, the rate of organic matter application is comparable with the tested rate. The results indicate that diuron leaching could be reduced considerably by application of organic manure such as compost, at the recommended rate.

Volatilization of diuron

Volatilization is the gaseous loss of material and in tropical regions, where atmospheric temperature is relatively higher, losses due to volatilization is higher. Although urea is a very volatile compound, the volatility of substituted urea, such as diuron, were found to be very low. The melting point of diuron is around 160°C, and the vapour pressures at 30°C and 50°C were found to be 0.37 m Pa and 0.41 m Pa, respectively. Hence, under field conditions, loss of diuron by volatilization can be considered to be negligible. However, when diuron samples were kept in an open environment at 30°C exposed to solar radiation, the weight increased possibly due to the adsorption of moisture from the atmosphere. In addition, the change in concentration (mg l^{-1}) was significant ($p<0.05$). This indicates that although loss of diuron as a gas is very limited, under the direct influence of solar radiation it can be degraded. Therefore, such exposures in the field may lead to loss of diuron by photo–chemical reactions.

Microbial degradation of diuron

Studies conducted to investigate the influence of micro–organisms on urea substituted herbicides have shown variable results. According to Wang *et al.* (1985), monuron at a rate <10 ppm had been microbialy degraded, while linuron and diuron had been mineralized at the rate of 500 mg l^{-1} but not at 2 g l^{-1}. This indicates that linuron and diuron are more resistant to microbial degradation than monuron.

In this study, however, residual diuron concentration in the sterilized and unsterilized soil samples analyzed after 7 days of treatment showed a mean concentration difference of 16 mg l^{-1} which was not statistically significant. This indicates that microbial degradation during 7 days is very low and undetectable in the soil studied. When soil solutions of both treatments were analyzed by GLC, two unknown compounds were detected in addition to diuron in the unsterilized soil samples, but not in the sterilized soil samples. These could be the metabolites of microbial degradation of diuron. Further studies are needed to characterize those compounds.

Plant uptake of diuron

The main targets of diuron are weeds, and considerable quantity of diuron is expected to be absorbed by the vegetation. Grover and Hance (1969) reported that the adsorption of phenyl-urea and s–atrazine herbicides on roots was greater than on soil particles.

Diuron recovered from soils in pots with seedlings was lower than the control and the difference was statistically significant except for the soils obtained from Nuwara Eliya and Galaha (Table 5). This indicates that in certain soils, diuron is preferentially retained by soil than getting absorbed by plants. The usual pattern observed when there are plants in the field is the preferential partitioning from soil to plants.

Table 5. Plant uptake of diuron by Guinea-A grass.

Location	Recovered from Soil Solution (%)			Estimated Plant Uptake (%)	
	Control	With seedlings	With mature weeds	With seedlings	With mature weeds
Polonnaruwa	34.2	22.1 **	8.1	87.9	91.9
Maha Illuppallama	9.0	4.4*	N.D.	95.6	≈ 100
Puttalam	82.6	74.0*	N.D.	26.0	≈ 100
Matale	10.4	5.2*	N.D.	94.8	≈ 100
Kundasale	13.4	9.5*	N.D.	91.5	≈ 100
Kandy	12.7	6.0*	N.D.	94.0	≈ 100
Mawanella	15.2	5.3*	N.D.	95.7	≈ 100
Galaha	6.2	5.4	N.D.	95.6	≈ 100
Gampaha	73.1	63.0*	N.D.	37.0	≈ 100
Nuwara Eliya	6.8	5.0	N.D.	95.0	≈ 100

N.D. - Not Detected
* - Difference between control and the treatment was significant at $p=0.05$
** - Difference between control and the treatment was significant at $p=0.01$

CONCLUSIONS

Fate of diuron was very much influenced by soil properties. Adsorption was favoured in soils with high clay and organic matter contents resulting in less leaching losses in such soils. In sandy soils, considerable losses due to leaching were observed. Losses due to leaching was significantly influenced by bulk density and application of organic manure. Thus, manipulating such soil properties by management practices could help to reduce leaching losses that could lead to groundwater pollution.

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