



Research article

Adsorption-desorption and leaching behavior of diuron on selected Kenyan agricultural soils

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ABSTRACT

In this work, the adsorption-desorption dynamics of diuron in three typical Kenyan agricultural soils, Nzoia (NZ), Thika (TH) and Machakos (MK) was investigated. The equilibrium adsorption data, tested against three classical nonlinear adsorption isotherms, was best described by the Freundlich model. The Freundlich adsorption constant, (K_F), increased in the order MK > TH > NZ soil. Additionally, the negative Gibb's free energy values indicate the adsorption processes were thermodynamically spontaneous and physical. Multiple linear regression analysis indicated that the adsorption-desorption behavior was controlled by the clay and phosphorus contents of the soil. Phosphorus negatively affected the adsorption of diuron and promoted desorption. The groundwater ubiquity score (GUS) indicated that diuron movement rating in MK soil was 'moderate' while the movement in TH and NZ soils was 'high'.

1. Introduction

Contamination of water resources with pesticides and other organic pollutants, especially in regions largely dependent on groundwater for potable water is of great environmental concern (Hall et al., 2015). The use of agrochemicals is a leading source of pesticide-contaminated waters. Though governmental authorities regulate the registration and usage of pesticides, an understanding of pesticide transport, fate and leaching potential are necessary for assessment of possible threat to groundwater quality (Dusek et al., 2010). Diuron (*N*-(3,4-dichlorophenyl)-*N*-dimethylurea) is extensively used as a soil-applied herbicide for control of pre-emergent and post-emergent weeds. Noteworthy, diuron is classified as a known carcinogenic compound (US-EPA, 1999). Owing to its stability in the environment (Dores et al., 2009), groundwater contamination by diuron has been reported as a significant environmental concern in Brazil (Ellmache et al., 2009). Similar findings have been reported in Dutch coastal waters (Lamoree et al., 2002) as well as in France (IFEN, 2002) and the United Kingdom (UK-EPA, 2002). Though

diuron has been in use in Kenya for decades, the paucity of data on its occurrence in water resources indicates the far-reaching possible effects of exposure to diuron and pollution levels remain unknown. The groundwater pollution potential is determined by the degree of sorption/desorption dynamics of the herbicide on soils besides degradation rates. Several studies have reported the adsorption pattern of diuron in soils with diverse conclusions (Burns et al., 2008; Chaplain et al., 2008; Wang and Keller, 2009). The variances in results reported underscore the role of soil characteristics and experimental conditions such as temperature and pH as driving factors affecting diuron adsorption. Soil hydrophobicity and organic matter content have been singled out as factors controlling the sorption of diuron in soil (Burns et al., 2008; Chaplain et al., 2008). Microbial degradation of diuron was reported with as low as 25% removal in 35 days (Ngigi et al., 2011). Though widely used in Kenya, the lack of empirical data on the adsorption/desorption, leaching behavior of diuron and potential compromise of groundwater quality is the motivation of this work. The objective of this study was to evaluate the sorption, desorption and leaching characteristics of diuron as

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influenced by various soil properties in three soils from commercial farming areas of Kenya namely, Nzoia (NZ), Thika (TH) and Machakos (MK). The leachability of diuron was classified using the groundwater ubiquity score (GUS) (Gustafson, 1989).

2. Materials and methods

2.1. Soil sampling and characterization

Soil samples were collected in June 2016 from fields within Nzoia at an altitude of 1788 m, (0° 53'2" N, 35, 4' 0" E), Thika at an altitude of 1815 m, (0° 4' 55" N 34° 50' 49" E), and Machakos at an altitude of 1912 m, (0° 53'2" N, 35, 4' 0" E) where diuron has been extensively applied at a rate of 0.5–1.0 kg/ha (active ingredient) for over 15 years. Fields for sampling were identified through a random stratified sampling technique and soil samples were collected from 0–15 cm depth. All the soil samples were placed in sterile amber bottles then placed in a cooler at 4 °C for transport to the laboratory for further use in leaching, adsorption and desorption studies. Before the experiments were started, the soil samples were thoroughly prepared through crushing, homogenization, and sieving. The soil samples were characterized using standard protocols for soil characterization and the properties are listed in Table 1. Soil pH was measured in a suspension with 1:1 (w/v) ratio of soil to 0.01 M CaCl₂. Percent clay fraction was determined by the pipette method (Day, 1965). Organic carbon content (Chapman, 1965) and cation exchange capacity (Chapman, 1965) were determined. These measurements were made on a representative sample taken from the bulk sample collected from the field. Residual levels were determined prior to soil spiking and confirmed to be below quantification limits.

2.2. Reagents and chemicals

Diuron (purity 99.8 %) and its metabolites (purity 99.5 %) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Calcium chloride solutions (0.01M) were prepared by dissolving in distilled water. All Analytical grade reagents including anhydrous sodium sulphate and HPLC grade solvents (Methanol, Water, Acetonitrile, Dichloromethane) were purchased from Sigma Aldrich. Stock solutions of diuron and its metabolites were prepared in methanol and working solutions prepared by appropriate dilution of the stock solutions.

2.3. Adsorption and desorption experiments

The sorption of diuron was through batch equilibrium and determined according to the EEC protocol and as reported by other researchers (Schwab et al., 2014). Here, 10 mL 0.01 M CaCl₂ aqueous solution

Table 1. Physico-chemical characteristics of Machakos soil, Thika soil and Nzoia soil.

	Machakos soil (MK)	Thika soil (TH)	Nzoia soil (NZ)
OC (%)	2.70 ± 0.11	2.52 ± 0.025	2.24 ± 0.042
N (%)	0.18 ± 0.002	0.13 ± 0.001	0.65 ± 0.012
pH	5.31 ± 0.092	5.52 ± 0.076	5.97 ± 0.081
Cation exchange capacity (Meq/100g)	0.103 ± 0.002	0.066 ± 0.001	11.80 ± 0.150
Cu (ppm)	1.10 ± 0.014	0.48 ± 0.011	0.82 ± 0.012
Clay (%)	92.00 ± 0.784	94.00 ± 0.991	10.90 ± 0.628
Sand (%)	6.0 ± 0.085	4.0 ± 0.048	53.8 ± 0.035
Silt (%)	2.0 ± 0.046	2.0 ± 0.029	36.3 ± 0.017
P (ppm)	126.71 ± 0.87	180.82 ± 1.54	140.31 ± 1.14
Fe (ppm)	134.11 ± 1.25	135.76 ± 2.14	139.81 ± 1.85
Mg (ppm)	246.42 ± 2.24	243.51 ± 1.88	214.31 ± 1.11
Ca (ppm)	821.65 ± 3.45	858.46 ± 2.98	789.01 ± 1.78
Zn (ppm)	13.53 ± 0.26	11.12 ± 0.12	1.37 ± 0.041

containing standard diuron (99.8% pure), at various concentrations of 0.1, 1, 2 and 5 mg L⁻¹, respectively, were added to 3 g of each soil in 15 mL Teflon centrifuge tubes covered with aluminium foil to avoid direct light (Qui et al., 2016). The rate of application was tailored to the field applications (Lalah and Wandiga, 1996). The samples were shaken continuously on a rotary shaker at 100 rpm at room temperature (25 ± 2 °C) for 24 h, a period established from trial experiments for equilibration. The samples were centrifuged and the residual diuron in the resultant supernatants determined using HPLC.

Desorption studies were conducted immediately after adsorption. The supernatant was decanted after centrifugation and replaced with an equal amount of free 0.01 M CaCl₂ solution. The samples were equilibrated again for 24 h, centrifuged and residual diuron in the aqueous phase determined (Kaur et al., 2016). The experiments were always conducted in triplicates. Control experiments involved shaking and centrifuging soil samples with pesticide-free 0.01 M CaCl₂ solution and also shaking and centrifugation of pesticide solutions in 0.01 M CaCl₂ solution without soils.

2.4. Leaching studies in the laboratory

Leaching studies were performed in triplicate, based on the EEC standard procedure (Lalah and Wandiga, 1996). The soil samples were homogenized and sieved through a 2-mm pore sieve. The sieved soil samples were packed in glass columns (I.d of 45 mm) to the height of 500 mm with a glass wool plug at the bottom. Each soil column was saturated with 0.01M calcium chloride solution by passing the solution through it by capillarity for 12 h. The columns were then allowed to drain freely overnight with the 0.01M CaCl₂ solution. The dry mass of the soil in each column was 400.5 g. The equivalent of 10 mg L⁻¹ diuron in the soil was prepared by dissolving an appropriate amount of the standard in 0.01 M CaCl₂ which was added on top of the soil column. Leaching was monitored for 8 h, draining with 1.15 L of 0.01 M CaCl₂ at a flow rate of 2.4 mL min⁻¹ which is the average field application flow rate. After 8 h, the volume of the leachate was measured before partitioning with 250 mL dichloromethane for analysis of diuron and its metabolites residues. The wet soil in the glass column was carefully removed and sub-divided into 0–7 cm, 7–14 cm, 14–21 cm, 21–28 cm, 28–35 cm and 35–42 cm portions using a ruler and extracted for residues by use of methanol and analysis as explained above. The aim of sub-dividing the soil portions to 42 cm was to observe and understand chances of underground leaching by the compound.

2.5. HPLC analysis of extracts

Extracts were analysed by HPLC (LC-10AT VP Shimadzu) equipped with SPD-20A UV detector at 254 nm and 125 × 4 mm Crom Saphir 110 C₁₈ 5 µm column. The HPLC measurement conditions included a pressure of 107 bar, a mobile phase of (isocratic) acetonitrile: water: methanol (40: 40: 20), a flow rate of 1 ml/min and an injection volume of 5 µl.

2.6. Data analysis

The adsorption equilibrium data were fitted to Langmuir (1918) (Equation 1), Temkin (Temkin and Pyzhev, 1940) (Equation 2) and Freundlich (1906) (Equation 3) models in their nonlinear forms.

$$\text{Langmuir model: } q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \quad (1)$$

Where q_e is the amount of diuron adsorbed at equilibrium (mg kg⁻¹), C_e is the residual diuron concentration in the solution at equilibrium (mg L⁻¹), Q_m is the Langmuir maximum adsorption capacity (mg kg⁻¹) and K_L is the Langmuir constant related to the free energy of adsorption (L kg⁻¹). The Langmuir isotherm equation postulates monolayer adsorption of

adsorbate molecules, with no lateral interactions, onto a homogeneous adsorbent surface.

$$\text{Temkin model: } q_e = B_T(A_T C_e) \quad (2)$$

where B_T and A_T are Temkin constants. Temkin isotherm model allows for adsorbate-adsorbate interactions for the adsorbed molecules. Additionally, the model assumes that the heat of adsorption (ΔH_{ads}) of adsorbed molecules in the layer reduces linearly with increased surface coverage.

$$\text{Freundlich model: } q_e = K_F C_e^{1/n} \quad (3)$$

The Freundlich isotherm describes a multilayer adsorption process onto a heterogeneous adsorbent surface without lateral interaction. The best-fitting model was determined by the coefficient of determination (R^2) is given by Eq. (4):

$$R^2 = \frac{\sum_{i=1}^n (q_{\text{exp}} - q_{m,\text{cal}})^2}{\sum_{i=1}^n (q_{\text{exp}} - q_{m,\text{cal}})^2 + \sum_{i=1}^n (q_{\text{exp}} - q_{\text{cal}})^2} \quad (4)$$

where q_{cal} is the model predicted equilibrium concentration adsorbed, q_{exp} is the experimentally determined equilibrium concentration adsorbed and $q_{m,\text{cal}}$ is the mean of q_{cal} .

The free energy change (ΔG , kJ mol⁻¹) related to the adsorption process was estimated using Eq. (5):

$$\Delta G = -RT \ln K_{OC} \quad (5)$$

where R is the gas constant (8.314 J K⁻¹ mol⁻¹), T is temperature (K), and K_{OC} is the distribution coefficient on organic carbon related to the percent carbon (%C) and the sorption coefficient, K_d (L/Kg) by the Equations (6) and (7) (Hall et al., 2015):

$$K_d = \frac{C_s}{C_w} \quad (6)$$

$$K_{OC} = \frac{K_d}{\%C} \times 100 \quad (7)$$

The Hysteresis coefficient, H (Equation 8), was calculated for the adsorption-desorption isotherms using the following relation (Liu et al., 2010):

$$H = n - \text{desorption}/n - \text{adsorption} \quad (8)$$

where n -desorption and n -adsorption are the Freundlich coefficients calculated from the desorption and adsorption isotherms, respectively.

3. Results and discussion

3.1. Soil characteristics

The physicochemical characteristics of the MK, TH and NZ soils are listed in Table 1. It can be seen that Machakos soil had the highest %OC, Mg and Zn content, and the least P. Thika soil had the highest phosphorus and % clay fractions while Nzoia soil had the highest CEC, Fe, sand and silt contents. The characteristics of the soil are known to affect the adsorption-desorption and leaching dynamics of pesticides in soil (Sergio et al., 2019).

3.2. Adsorption isotherms

The limit of detection for the compound was 0.0004 mg/g and linearity was 0.997. The adsorption equilibrium data were fitted to three two-parameter adsorption isotherms viz Langmuir, Freundlich, and

Temkin isotherm models to examine the pesticide-soil interactions and the parameters obtained by the nonlinear regression method. The equilibrium data were best fitted by the Freundlich model with coefficients of determination closest to unity (Table 2). In contrast, the curve fit by the Temkin and Langmuir model were subordinate with $R^2 \leq 0.785$ and ≤ 0.538 , respectively (Tables 2 and 3) and are therefore not discussed. The poor predictive power of the Langmuir and Temkin models for the experimental data is shown in Figure 1. The tested models fitted the data in the order Freundlich > Temkin > Langmuir. Compliance with the Freundlich model implies multilayer adsorption on heterogeneous adsorbing surfaces. The magnitude of the Freundlich isotherm exponent $1/n$ is an index of the degree of the favorability of an adsorption process (Liu et al., 2010). In the present work (Table 4), all the n values were below 1, varying between 0.836 and 0.964, an indicator that adsorption of diuron on TH, MK, and NZ soils was less favorable. Similar observations were reported for adsorption of diuron on Kenyan agricultural soils from Ahero and Chiromo regions (Lalah and Wandiga, 1996). Additionally, the n parameter values obtained also indicate the adsorption curves were nonlinear (Conde-Cid et al., 2019), though the nearness to unity suggests a tendency towards linearity. This observation pinpoint that the number of energetically favorable adsorption sites vacant for diuron uptake decreases as the concentration of the pesticide is increased corresponding to heterogeneous adsorbent surfaces (Sukul et al., 2008).

Additionally, $n < 1$ values correspond to the S-type isotherm (Figure 1) which suggest that diuron may adsorb onto the fine soil fractions such as silt and clay (Albers et al., 2008). This implies that the amount of clay and silt fractions in the soils could significantly account for the variance in the adsorption capacity of the soils. The adsorption isotherm for sorption of diuron on MK soil is shown in Figure 1, a representative of a similar trend for the other two soils. The effects of the soil characteristics on the adsorption processes were examined using multiple linear regression to verify the role of clay fraction against other parameters.

Table 2. Langmuir isotherm parameters for diuron.

Isotherm parameters	Q_m mg kg ⁻¹	K_L (L kg ⁻¹)	R^2
TH soil	3.333	2.118	0.533
NZ soil	2.802	1.740	0.538
MK soil	4.243	3.064	0.525

Table 3. Temkin isotherm parameters for diuron.

Isotherm parameters	B_T	A_T (L kg ⁻¹)	B_T (ln A_T) kJ mol ⁻¹	b_T kJ mol ⁻¹	R^2
TH soil	2.145	13.511	5.584	1.155	0.785
NZ soil	1.903	10.663	4.504	1.302	0.785
MK soil	2.761	17.503	7.903	0.897	0.769

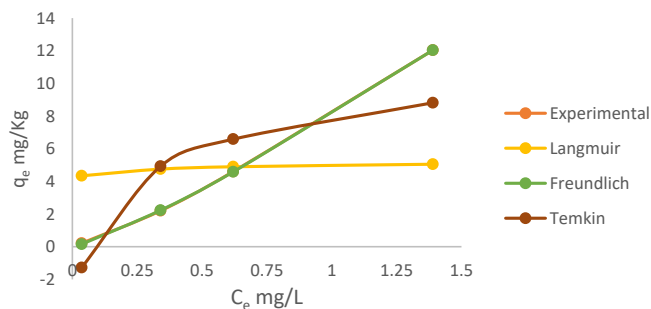


Figure 1. Adsorption isotherms for diuron sorption on Machakos soil (The data points for “experimental” and “Freundlich model” do overlap).

Table 4. Adsorption Freundlich isotherm parameters and Gibbs free energy for diuron.

Isotherm parameters	1/n	K_F ($L^n \text{ mg}^{1-n} \text{ kg}^{-1}$)	n	K_{oc} (L/Kg)	ΔG (kJ mol^{-1})	R^2
MK soil	1.196	8.116 ± 0.047	0.836 ± 0.0098	239.7	-13.575	0.999
TH soil	1.037	4.387 ± 0.023	0.964 ± 0.0112	143.3	-12.300	0.999
NZ soil	1.083	3.095 ± 0.011	0.923 ± 0.0156	121.7	-11.897	0.999

Additionally, Freundlich's adsorption affinity factor (K_F) values in this study were in the range of 3–8 $L^n \text{ mg}^{1-n} \text{ kg}^{-1}$. Earlier, [Lalah and Wandiga \(1996\)](#) obtained K_F values of about 15 $L^n \text{ mg}^{1-n} \text{ kg}^{-1}$ for two aforementioned Kenyan soils from Ahero and Chiromo regions despite the soils having clay and organic carbon fractions much lower than the soils in the present work.

In terms of adsorption energetics, the negative ΔG values ([Table 4](#)) confirm that the adsorption of diuron onto the NZ, MK and TH soils was a thermodynamically spontaneous process. The relatively low magnitude of ΔG values support a physisorption mechanism ([Kaur et al., 2016](#)).

3.3. Desorption dynamics of diuron on soil

Desorption reaction is an index of pesticide mobility in soil and is an important parameter in the prediction of potential groundwater contamination for highly desorbed compounds or risk to the succession crop in case of poorly desorbed pesticides. Diuron desorption studies were done in batch mode and the results are presented in [Table 5](#). The desorption equilibrium data were suitably modeled by the Freundlich equation with high coefficients of determination, R^2 . Here, NZ soil (with the least clay content) posted the highest desorption Freundlich coefficient K_F . The calculated desorption K_F values were 10.9, 8.24 and 30.35 for MK, TH and NZ soils, respectively.

3.4. Effect of soil properties on adsorption/desorption

An understanding of the sorption–desorption dynamics of pesticides in the soil is critical for determining their transport and fate in soil. To account for and predict diuron adsorption-desorption dynamics as a function of the soil characteristics, multiple linear regression was performed with the Freundlich coefficient (K_F) as a dependent variable, and the MK, TH, and NZ soil properties as the independent variables. The performance of the multiple linear regression was evaluated using root mean square error (RMSE) ([Equation 9](#)) and coefficient of determination (R^2) as proposed by [Dos Santos et al. \(2019\)](#) and [Eqs. \(10\) and \(11\)](#) were obtained.

$$RMSE = \frac{1}{n} \sum_{i=0}^n (y_i - x_i)^2 \quad (9)$$

where n is the number of observations, y_i is the value of K_F (adsorption or desorption) measured in soils, and x_i is the value of K_F predicted by [Eqs. \(10\) and \(11\)](#).

$$K_F = 0.05 \%clay - 0.071 P + 12.479 \quad (RMSE = 0.0014, R^2 = 1, p < 0.05) \quad (10)$$

$$K_F = -0.246 \%clay - 0.039 P + 38.642 \quad (RMSE = 0.0327, R^2 = 1, p < 0.05) \quad (11)$$

From the equations, it could be seen that the total (100%) variance of K_F was attributed to the independent variables % clay and phosphorus content while the rest of the soil characteristics had an insignificant effect on the sorption-desorption dynamics of diuron in the Kenyan soils. This observation is contrary to the study by [Liu et al. \(2010\)](#) that reported CEC had a significant positive effect on diuron adsorption on Chinese soils.

In this work, a comparison of the coefficients in the equation revealed that the % clay content had a significant additive effect on diuron adsorption, while phosphorus had a comparable but slightly high negative effect on the adsorption. Therefore, low phosphorus and high clay content favored adsorption in MK soil while high P and low clay content were responsible for the low adsorption affinity in NZ soil. Though TH soil had the highest phosphorus content, the higher than NZ K_F value is due to high % clay content that offset the adsorption retarding effects of phosphorus. The positive effect of clay on the adsorption of diuron was reported by [Sergio et al. \(2019\)](#). Relative to each other, phosphorus accounted for a slightly higher fraction of the variance of adsorption K_F . The study revealed that phosphorus impedes diuron. However, the exact mechanisms involved are a phenomenon hitherto unexplained and requires further investigation since diuron is non-ionizable in soil solution. Similar phenomenon was reported by [Conde-Cid et al. \(2019\)](#) and [Wang et al. \(2010\)](#) for adsorption of tetracycline in agricultural soils.

Contrarily, the soil % clay had a significant negative effect on diuron desorption and explained a higher percentage of the variance in desorption K_F from the coefficients in the desorption model equation.

Clay and phosphorus contents are the determining factors that affect the adsorption-desorption pattern of diuron on the Kenyan soils. Clay content is known to have a positive influence on the adsorption of organics in soil ([Conde-Cid et al., 2019](#)). This explains why MK soil had the highest adsorption capacity for diuron conjoined with low P content. Noteworthy, adsorption-desorption of diuron on the soils were independent of the soil pH. This is in agreement with recent findings reported by other authors ([Conde-Cid et al., 2019](#)). However, the same studies showed that the adsorption of diuron is dependent on the solution pH (CaCl_2 solution).

A further multiple linear regression was done to predict the adsorption Freundlich linearity index (n) as a function of MK, NZ and TH soil characteristics. Again, the variance of n was accounted for the phosphorus and % clay contents ([Equation 12](#)). From the coefficients in the equation, phosphorus had a significant positive effect on the linearity index (n) while % clay content had a significant negative effect. Overall, phosphorus accounted for a greater fraction of the variance of n .

$$n = -0.00067 \%clay + 0.00239 P + 0.595 \quad (RMSE = 0, R^2 = 1, p < 0.05) \quad (12)$$

The predicted K_F and n values from the model were compared with those obtained from the adsorption experiments as shown in [Table 6](#). The overlap of the data points proves that the proposed model perfectly predicted the adsorption and desorption K_F and n constants consistent

Table 5. Desorption Freundlich isotherm parameters for diuron.

Isotherm parameters	1/n	K_F ($L^n \text{ mg}^{1-n} \text{ kg}^{-1}$)	n	R^2	Hysteresis, H
MK soil	10.031	10.9 ± 0.085	0.099 ± 0.001	0.941	0.119
TH soil	1.923	8.244 ± 0.120	0.520 ± 0.007	0.999	0.539
NZ soil	2.263	30.346 ± 0.185	0.442 ± 0.008	0.999	0.479

Table 6. Experimental and predicted Freundlich adsorption isotherm parameters for diuron.

Isotherm parameters	K_F ($L^n \text{ mg}^{1-n} \text{ kg}^{-1}$) (predicted)	K_F ($L^n \text{ mg}^{1-n} \text{ kg}^{-1}$) (Experimental)	n-predicted	n-Experimental
MK soil	8.083	8.116 ± 0.047	0.836	0.836 ± 0.0098
TH soil	4.341	4.387 ± 0.023	0.964	0.964 ± 0.0112
NZ soil	3.062	3.095 ± 0.011	0.923	0.922 ± 0.0156

with the coefficient of determination of unity and RMSE of zero. This could also be due to the relatively low number of observations ($n = 3$). Kaur et al. (2016) also reported the effect of soil characteristics on the adsorption-desorption of pretilachlor in three soils of Punjab, India.

3.5. Hysteresis analysis

Hysteresis phenomenon in adsorption-desorption of pesticides in soils has extensively been reported in the literature (Conde-Cid et al., 2019; Kumar and Philip, 2006). Hysteresis effect implies a restrained level of reversibility during adsorption of pesticides which depends on the properties of the pesticide molecule and the physicochemical characteristics of the soil. Typically, hysteresis values close to unity imply that the rate of desorption is equal to the rate of adsorption; hence, there is no hysteresis. Contrarily, a hysteresis index value below 1 denotes that the desorption rate is less than the rate of adsorption, thus hysteresis occurs (Tang et al., 2009). In this study, the hysteresis index was less than 1 (Table 5) for all three soils examined an indicator that the desorption rate was slower than adsorption. The value of the hysteresis index for the soils was in the order $TH > NZ > MK$ a testament that the MK soil exhibited the highest hysteresis effect. Encapsulation of diuron molecules within the clay matrix, such as interlayer spaces, as shown in the multilinear linear regression of desorption K_F , is the driving force and predominantly accounts for the observed adsorption-desorption hysteresis. In the MK and TH soils, with high and comparable % clay content, the adsorption-desorption hysteresis was mainly controlled by phosphorus content. On the other hand, the adsorption-desorption hysteresis in NZ soils was strongly controlled by % clay content. The results indicate there is potential to groundwater contamination with diuron and may be enhanced by the simultaneous application of phosphate fertilizers.

3.6. Leaching

The leaching of diuron in the soils was examined using column experiments and the distribution of diuron in the soil column and occurrence in leachate determined. Figure 2 represents the distribution of

diuron in Nzoia, Thika and Machakos soils. The percent recoveries of diuron in the soils were 57.9, 57.0 and 52.3 % for the MK, TH and NZ soils, respectively. In terms of leachate concentrations, the amount of diuron as a percent of the initial concentration (10ppm) detected in the leachates was 39.7, 37.2 and 46.6 % for MK, TH, and NZ leachates, respectively. Notably, NZ soil gave the highest percentage of diuron in the leachate, a testament of high mobility of diuron in NZ soil and consistent with the adsorption-desorption studies. Percentage loss, by mass balance, could be due to losses during sample preparation or degradation.

Additionally, the Groundwater Ubiquity Score (GUS) (Gustafson, 1989) was used to compare the leachability of diuron in the three soils. This GUS approach (Equation 13) uses the sorption coefficient (K_{oc}) value and half-life ($t_{1/2}$) of a chemical to determine its potential to contaminate groundwater. The diuron half-life and K_{oc} values used in this study were obtained experimentally for each soil. Diuron half-life under field conditions was 53.72, 55.89 and 67.94 days in TH, MK, and NZ soil, respectively (Muendo et al., 2020). The leaching risks in the three soils were classified based on pesticide movement ratings (Table 7) described by Kerle et al. (2007).

The GUS index is obtained by the relation (Hall et al., 2015):

$$GUS = \log t_{1/2} \times (4 - \log K_{oc}) \quad (13)$$

The calculated GUS values for the soils were 2.83, 3.19 and 3.51 for MK, TH, and NZ soil, respectively. Accordingly, diuron movement rating

Table 7. GUS values and corresponding pesticide movement rating.

GUS Value	Pesticide movement rating
Less than 0.10	Extremely low
0.10–1.00	Very low
1.00–2.00	Low
2.00–3.00	Moderate
3.00–4.00	High
More than 4.00	Very high

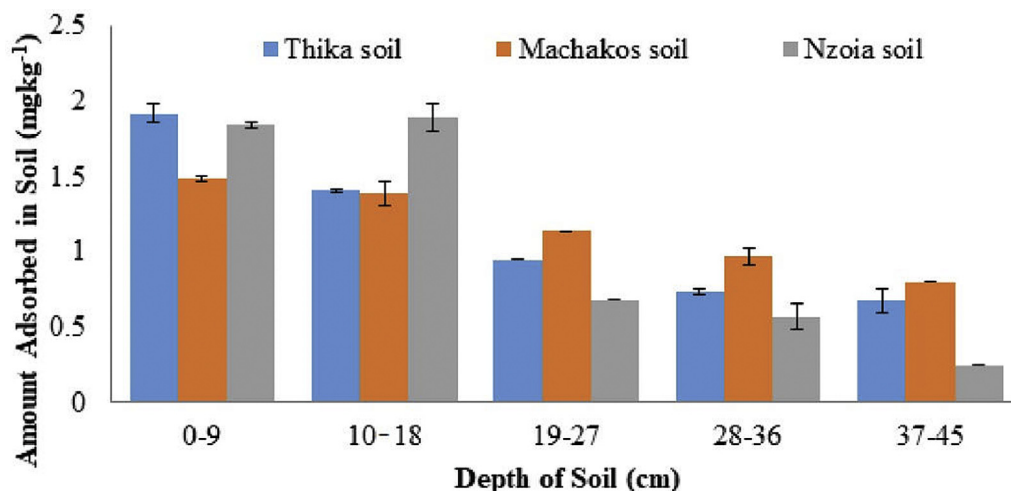


Figure 2. The distribution of diuron with soil depth in NZ, TH and MK soils (Initial concentration = 10 mg kg⁻¹).

in MK soil was classified as 'moderate' while the movement in TH and NZ soils was 'high'. This implies that the likelihood of groundwater contamination with diuron is highest in TH and NZ soils. Similar findings of high leachability risk of diuron were reported for Brazilian soils (Sergio et al., 2019). It is noted that despite their variance in adsorption affinity (K_F) (Table 6), TH and NZ soils had the same diuron movement rating. This is due to the high phosphorus content in TH soil and low clay content in NZ soil.

4. Conclusion

Clay content had a positive effect on diuron adsorption while phosphorus is the only soil parameter shown to have a negative effect on adsorption onto the Kenyan soils. The adsorption was thermodynamically spontaneous and the energy values correspond to a physical process. From the GUS index, diuron movement rating in MK soil was classified as 'moderate' while the movement in TH and NZ soils was 'high'. The results show that to protect groundwater from diuron contamination, diuron application in soils with low clay and high phosphorus contents should be applied with restriction.

Declarations

Author contribution statement

Boniface M. Muendo: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Victor O. Shikuku: Analyzed and interpreted the data; Wrote the paper.

Zachary M. Getenga: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data.

Joseph O. Lalah; Shem O. Wandiga: Conceived and designed the experiments.

Michael Rothballer: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data.

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Data availability statement

Data included in article/supplementary material/referenced in article.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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