

Adsorption of Dursban (Chlorpyrifos) Pesticide by Loam Soil from Limuru, Kenya: Apparent Thermodynamic Properties

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ABSTRACT

The adsorption phenomenon of chlorpyrifos by suspended loam soil particles from Limuru, Kenya in an aqueous solution was studied using a model which assumes the adsorption/ desorption relations: $nX + S \rightleftharpoons SX_n$, $K = [SX_n]/[X]^n[S]$ and $\ln[x]_{ads} = \ln(nK') + n\ln[x]_e + [sx_n]_w$, where X is the chemical species of interest; S is the substrate; K is the adsorption/desorption equilibrium constant; SX_n is the particle-pesticide complex. The apparent adsorption equilibrium constant; $[X]_{ads}$ is concentration of X in adsorbed state in suspension. $[X]_e$ is the concentration of X in solution at equilibrium and $[SX_n]_w$ is the pesticide adsorption site complex in the suspension at equilibrium. The amount of chlorpyrifos adsorbed was determined against variation of mass of sediment, concentration of chlorpyrifos and contact time using UV-Visible spectrophotometer at 254nm. The data obtained in this study best fitted the quasi-langmuir adsorption isotherm with regression values of up to 0.992. The calculated values of the apparent K , n and $\Delta G'$ were found to be 118.665, 0.244 and -11.7946kj/mol respectively. The negative value for $\Delta G'$ confirmed the fact that adsorption reaction occurs spontaneously as expected. Moreover, adsorption of chlorpyrifos onto suspended/dissolved sediment particles decreased with increase in mass of the substrate.

Key words: Adsorption, pesticide, chlorpyrifos, adsorption equilibrium constant, UV-Visible spectrophotometer

DURSBAN PESTICIDE (CHLORPYRIFOS)

Dursban is the registered trademark of Dow AgroSciences' pesticide chlorpyrifos. It acts on the nervous system of insects by inhibiting acetylcholinesterase. Although almost all household uses of chlorpyrifos were banned under a June 2000 agreement between Dow and other manufacturers and the Environmental Protection Agency (EPA 2000). Chlorpyrifos is still used as a broad spectrum insecticide for the treatment of crops, lawns, ornamental plants and domestic animals. EPA (1997) reported that most of the chlorpyrifos poisonings results from misuse or inappropriate use by pest control operators.

Chlorpyrifos low solubility, volatility and strong affinity for colloidal matter are among the physical and chemical properties which influences its fate and mobility in the environment[1] When in the environment, chlorpyrifos can undergo abiotic hydrolysis, photo-degradation and biodegradation ([2]. It exists in the atmosphere primarily in vapor phase, but can transform into other forms. It is not persistent in water due to volatilization and strong adsorption to particulate matter [1,3,4,5]. It is white in colour, odorless and belongs to the organophosphates family.

It boils at approximately 100⁰ C @100kPa with a specific gravity of 1.03g/ml at 20⁰C. It disperses as a suspension in water but dissolves in acetone and it's not corrosive. The active ingredient of Dursban SL is the organophosphate compound chlorpyrifos ([6]. The health effects of Dursban SL have been studied using toxicity tests conducted on animals [7]. Excessive exposure may cause organophosphate type cholinesterase inhibition whose symptoms may include pallor, nausea, vomiting, diarrhea, abdominal cramps, headaches, dizziness, eye pain, blurred vision, constriction or dilation of the eye pupils, tears, salivation, sweating and confusion. Severe poisoning will affect the central nervous system, producing in coordination, slurred speech, loss of reflexes, weakness, fatigue, involuntary muscle contractions, twitching, tremors of the tongue or eyelids, and eventually paralysis of the body extremities and the respiratory muscles [8]. In severe cases there may also be involuntary defecation or urination, psychosis, irregular heartbeats, unconsciousness and convulsions [8]. Chlorpyrifos is highly toxic to birds, freshwater fish, aquatic invertebrates and estuarine and marine organisms. Chlorpyrifos is also highly toxic to honeybees and should not be used when bees are actively collecting pollen and nectar. Chlorpyrifos is

moderately toxic to pets and livestock and has low toxicity to earthworms[9].

Environmental Fate

Chlorpyrifos adsorbs strongly to soil particles and it is not readily soluble in water. It is therefore immobile in soils and unlikely to leach or to contaminate groundwater [5]. At termiticide use rates the half-life approximates 380 days depending on sunlight, soil type and climatic conditions [10]. Absorbed chlorpyrifos is subject to degradation by UV light, chemical hydrolysis and by soil microbes [11]. If chlorpyrifos enters water bodies, it binds to organic particles in the water and sediment. The concentration of chlorpyrifos that dissolves (approx. 1ppm) is hydrolyzed rapidly in twelve hours to six days depending on pH [2]. Both absorbed and dissolved chlorpyrifos may be lost from water through volatilization and to a lesser extent photo degradation [12,13]. Chlorpyrifos is degraded eventually into carbon dioxide and simple organic molecules.

The structure of chlorpyrifos is as shown.

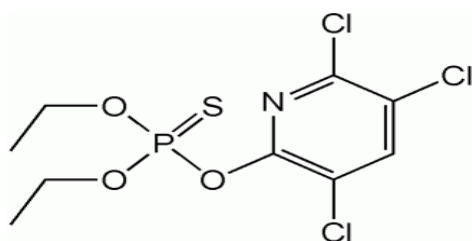


Figure 1: structure of chlorpyrifos

Chlorpyrifos is released in agricultural, home and garden soil during direct soil or foliar treatment [5]On the soil surface, dursban undergoes photo-induced reactions. Laboratory photo-degradation of dursban on soil surfaces with UV light at 254nm from mercury lamps demonstrated that hydrolysis, de-chlorination and oxidation take place simultaneously [14]The products of oxidation and dehalogenation undergo further photolysis to form chloropyridiniols and o,o-diethyl phosphorothioic acid. The oxon is less stable and hydrolyzes more rapidly than chlorprifos and doesn't accumulate in the soil.

The adsorption phenomenon

The theory behind the adsorption process has been reported by [15]. Here we present the adsorption kinetics of Chlorothalonil onto Nairobi river sediments based on the adsorption model of a binary dilute solution [16]. The apparent thermodynamic data is also calculated.

The characteristic adsorption of pesticide by soils or sediments can be described by the Freundlich empirical isotherm [17]

$$C_{ads} = k_F C_e^n \dots\dots\dots(1)$$

Where k_F the Freundlich constant, C_{ads} is concentration (mg/ml) of the pesticide adsorbed by the soil/sediment in a colloidal solution and C_e is the concentration of the pesticide in the solution (mg/ml) at equilibrium [18, 19]. The adsorption process of pesticides on soils was reviewed by [16]Several factors need to be considered in conducting adsorption studies. Firstly, what is the kinetics involved, particularly the magnitude of the adsorption and desorption rate constants and also the energies involved. Do the latter depict weak or strong nature of interaction between the solute and the adsorbents? Secondly, what are the initial and equilibrium conditions and how do the chemical composition and/or structure of both the adsorbent and the pesticide affect the results?

In order to obtain the adsorption/desorption, equilibrium, thermodynamic and kinetic data, there is need to come up with a functional adsorption/desorption equilibrium model, from which the apparent equilibrium constant and kinetic information can be calculated. Assuming that the adsorption of pesticide solute by the colloidal/sediment or both particles occurs during the shaking period, implying when the sediment is in suspension, then the adsorption/desorption equilibrium can be described as follows

$$nX + S \rightleftharpoons SX_n \dots\dots\dots(2)$$

$$K = [SX_n] / [X]^n [S] \dots\dots\dots(3)$$

On re-arrangement;

$$[SX_n] = K[X]^n [S] \dots\dots\dots(4)$$

Where X is the pesticide molecule of interest; S is the adsorbent/substrate or adsorption site on the sediment or colloidal particle in solution and K is the adsorption/desorption equilibrium constant.

SX_n is the particle-pesticide adsorption complex. Also, one notes that S is a solid whose mass is very large compared to that of the solute. Therefore, the $[S]$ can customarily be taken to be unity thereby reducing equation 4 to;

$$[SX_n] = K[X]^n \dots\dots\dots(5)$$

And on taking logs we have;
 $\log[SX_n] = \log K + n \log[X] \dots \dots \dots (6)$

It means, since equation (6) is linear, the value of K , the equilibrium constant, and n , the number of pesticide molecules adsorbed, can be obtained from the slope and intercept of the $\log[SX_n]$ versus $\log[X]$ plots respectively. In addition, the standard Gibbs free energy of activation ΔG , can be estimated by use of the conventional equation;
 $K = e^{-\Delta G/RT} \dots \dots \dots (7)$

Considering the assumption that the adsorption of chlorothalonil by colloidal and/or sediment particles occurs during the shaking (suspended particles) and also that all the adsorbed pesticide goes to the sediment on settling, then the concentration of pesticide adsorbed to the suspended particles $[X]_{ads}$ can be obtained using equation 8 below;

$$[X]_{ads} = [X]_i - [X]_e \dots \dots \dots (8)$$

Where $[X]_i$ represents the initial pesticide concentration before a known mass of sediments is added, and $[X]_e$ is the equilibrium pesticide concentration. Also, agitation facilitates the settling down of the sediments and thus the separation of dissolved and adsorbed pesticides. Since n molecules of pesticide are associated with a single adsorption site, then $[SX_n]$ is given by;

$$[SX_n] = \frac{1}{n} ([X]_i - [X]_e) \dots \dots \dots (9)$$

$$[SX_n] = \frac{1}{n} [X]_{ads} \dots \dots \dots (10)$$

[21,15]demonstrated the existence of a colloidal bound fraction when a pesticide is shaken with water containing sediment. They also showed that the colloidal bound fraction in suspension after settling was significantly small compared to the bound fraction in the sediment thus justifying the assumption made regarding the determination of $[SX_n]$ using $[X]_{ads}$ above. Note that $[SX_n]$ is the concentration of the colloidal bound fraction in suspension at settling equilibrium, since not all the pesticide is adsorbed. Therefore, on modifying equation 10 to show the total adsorbed pesticide we have;

$$[X]_{ads} = nK'([X]_e + [SX_n]_w)^n \dots \dots \dots (11)$$

Where K' is the apparent adsorption equilibrium constant and $[SX_n]_w$ is the concentration of the colloidal bound fraction in suspension at settling equilibrium. On taking logarithm equation 11 yields a linear expression;

$$\ln[X]_{ads} = \ln(nK') + n \ln([X]_e + [SX_n]_w) \dots (12)$$

Assuming that equilibrium exists between the colloidal bound fraction in the sediment and that in the suspension, then equation 2 becomes:

$$nX + S \leftrightarrow (SX_n)_w \leftrightarrow (SX_n)_{sediment} \dots \dots \dots (13)$$

It is apparent from equation 13 that a steady state exists with respect to $[SX_n]_w$ at settling equilibrium. Moreover, a plot of $\ln[X]_{ads}$ versus $\ln([X]_e + [SX_n]_w)$ in equation 12 will not affect the value n in equations 6 and 10, but will affect the value of nK' . Therefore, the value of K obtained is not a true equilibrium constant, but rather an apparent equilibrium constant (K').

EXPERIMENTAL MATERIALS AND REAGENTS

The following materials, instruments and reagents were used: UV-Visible spectrophotometer (UV-1700 model), Analytical balance (Fischer scientific A-160), dursban (analytical standard 97.5% pure), Orbital shaker, Glass bottles, Distilled water, Stop watch and 85% Acetone, loam soil from Limuru, Ndeiya location, Kenya.

PROCEDURE

1. Available nutrient elements (P, K, Na, Ca, Mg and Mn): Mehlich Double Acid Method (Tran, T. S. et al.,1993, Mehlich, A. 1953)

The oven - dry soil samples were extracted in a 1:5 ratio (w/v) with a mixture of 0.1 N HCl and 0.025 N H₂SO₄ [22].

Elements such as sodium, calcium and potassium are determined with a flame photometer while phosphorous, magnesium and manganese were determined – calorimetrically [23].

2. Total organic carbon: Calorimetric method (Gislason, E.A et al., 2005)

All organic C in the soil sample are oxidized by acidified dichromate at 150⁰C for 30 minutes to ensure complete oxidation. Barium chloride was added to the cool digests. After mixing thoroughly digests are

allowed to stand overnight. The concentration was read on the spectrophotometer at 600 nm.

3. Total nitrogen: Kjeldahl method (Jan-Åke Persson et al., 2008)

Profile	Properties	Profile	Properties
Soil depth cm	Top	Calcium milliequivalent (me)%	44.4
Soil pH-H ₂ O (1:2.5)	6.50	Magnesium me%	3.1
Elect. Cond. mS/cm	0.3	Potassium me%	1.5
Carbon %	2.7	Sodium me%	3.6
Sand %	40	Sum me%	52.6
Silt %	40	Base %	100+
Clay %	20	ESP	14.4
Texture Class	L	Total nitrogen %	0.25
Cat. Exch. Cap. me%	24.8	Phosphorus ppm	44
Zinc ppm	62.9	Iron ppm	96.2
Copper ppm	1.22		

Interpretation and Fertilizer Recommendation

The soil reaction (pH) is satisfactory for crops' growth. Soil fertility is good. Soil organic matter is sufficient. During the land preparation apply 1 ton/acre of well decomposed manure or compost.

Soil samples were digested with concentrated sulphuric acid containing potassium sulphate, selenium and copper sulphate hydrated at approximately 350°C. Total N is determined by distillation followed by titration with H₂SO₄.

4. Soil pH (1:1 soil-water)

Soil pH was determined in a 1:1 (w/v) soil-water suspension with pH meter.

5. Available trace elements (Fe, Zn & Cu): Extraction with 0.1 M HCl [24]

The oven - dry soil samples were extracted in a 1:10 ratio (w/v) with 0.1 M HCl. The elements were determined using an (AAS) atomic spectrophotometer

6. Cation Exchange Capacity (CEC) pH 7.0 and Exchangeable Ca, Mg, K, Na. The soil sample was leached with 1N ammonium acetate buffered at pH 7. The leachate was analyzed for exchangeable Ca, Mg, K and Na. The sample is further leached with 1N KCl, and the leachate is used for the determination of the CEC. Elements such as sodium and potassium were determined with a flame photometer and calcium and magnesium was determined using AAS (atomic absorption spectrophotometer). CEC was determined by distillation followed by titration with 0.01M HCl [25].

Adsorption procedure

A stock solution of 1000 mg/L of dursban was made and concentrations of 20, 40, 60, 80 and 100 mg/L obtained by appropriate dilutions. Absorbance values were obtained for these solutions at 254 nm and calibration curves obtained.

To investigate the existence of the adsorption/desorption equilibrium, 0.1g, 0.5g, 1.0g, 1.5g and 2.0g of the dried sediment were shaken with 10ml of 2mg of dursban aqueous solution for 60 minutes. The sediment was then allowed to settle for 72 hours. The aqueous phase was decanted, and filtered through a Whatman A40 filter paper, in order to obtain concentration of dursban in the clear aqueous solution. $[X]_e + [SX]_w$ was determined by UV-Visible spectrophotometer at 254 nm. To determine the values of ΔG , n and K , 0.5g of the dried sediment was shaken with 10ml distilled water spiked at 10,20,30,40 and 50 μ g/ml level of dursban. The samples in quadruplicate were shaken for 15, 30, 45 and 60 minutes using an orbital shaker. The concentration of the dursban in the clear solution was determined as described above.

RESULTS AND DISCUSSION

The properties of the samples were analyzed and their properties were recorded in table 1 below

Table 1: Properties of the loam soil used in adsorption experiment

Calibration curve

The curve obeyed Beer's law in the investigated range of 1 to 10ppm (low concentrations). Wavelength range was range 200-400nm with a lambda maximum of 254nm. UV-Visible was used for this study.

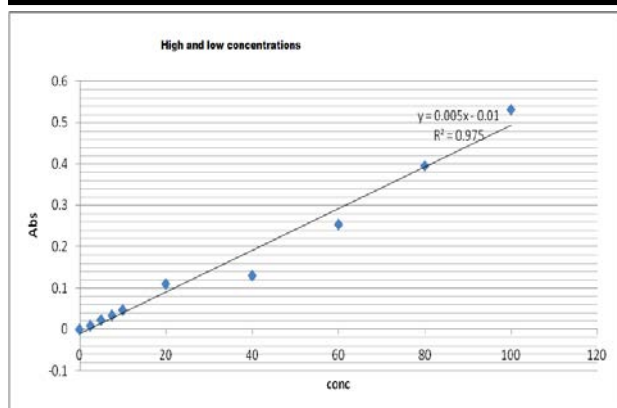


Fig 2: A plot of absorbance versus concentration

When the amount of loam soil was varied and 20 µg/ml of dursban added, the result obtained indicated that as adsorption surface area increases, the amount of residues adsorbed increases too. This had been reported by [15,29] for adsorption of pesticide residue by river sediments.

According to figure 2, the amount of the chlorpyrifos remaining in solution and/or suspension decreases exponentially as the amount of soil increases. This is consistent with equation 11 above, and confirms:

- a) The existence of an adsorption/desorption equilibrium in the system.
- b) The predictions of the adsorption/desorption equilibrium model presented above.

An elaborated picture is obtained when the data obtained is plot as shown graphically in figure 2

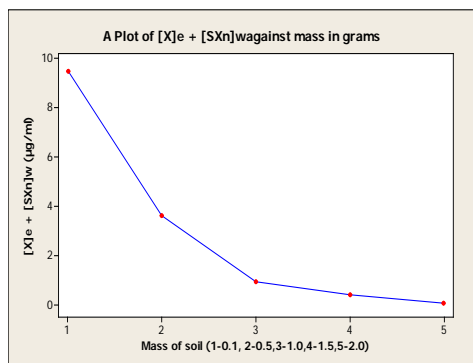


Fig 2: plot of $[X]_e + [SX_n]_w$ versus mass of loam soil

The amount of time the pesticide and soil are in contact is an important parameter in adsorption kinetics of an adsorbate at a given initial concentration [26]. The effect of contact time on adsorption of chlorpyrifos by loam soil was investigated for 60 minutes figure 4. The kinetic studies were carried at different spike levels of 10, 20, 30, 40, 50µg/ml at

room temperature, 25°C. Figures 3 illustrate the percentage amount of chlorpyrifos adsorbed against contact time.

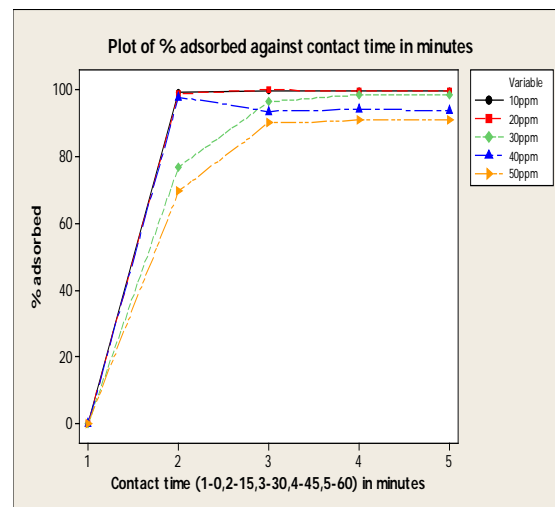


Figure 3: % chlorpyrifos adsorbed versus contact time in minutes

Equilibration is achieved around the 30th minute. This implies that no matter how much time you shake the samples, the amount of chlorpyrifos adsorbed doesn't increase significantly. This is illustrated in figure 3 above.

Adsorption isotherm models

Langmuir, Freundlich, Temkin, and Quasi - Langmuir models were used to assess the adsorption of chlorpyrifos on the various soils.

Freundlich Equation

To check adherence of the adsorption data with the Freundlich isotherm model, i.e.

$$q_e = KF C_e^{1/n}$$

This implies a plot of $\ln q_e$ was plotted against $\ln C_e$

The data in table 2 shows the Freundlich equilibrium constant values from the plots.

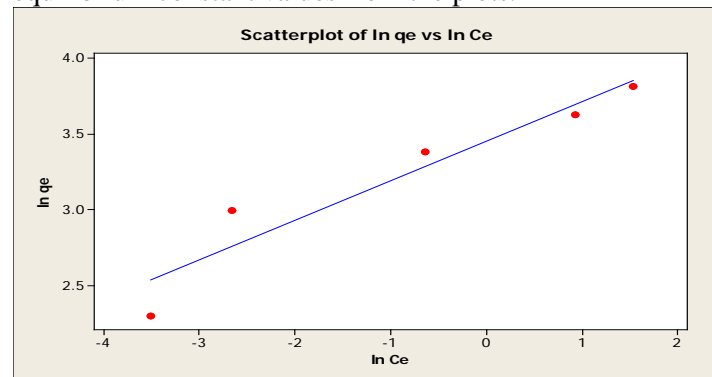


Figure 4: Scatter plot of $\ln q_e$ versus $\ln C_e$ for chlorpyrifos

Table 2: Freundlich isotherm parameters for chlorpyrifors at different contact times

Time in minute	n	ln K _F	R ²
15	0.1998	2.964	0.858
30	0.2022	3.447	0.701
45	0.2805	3.449	0.904
60	0.2914	3.469	0.912

Langmuir Model

The Langmuir (Langmuir, 1918) model assumes that uptake of pesticide molecule occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed molecules. The Langmuir equation may be written as:

$$C_e/q_e = 1/K Q^0 + C_e/Q^0$$

A plot of C_e/q_e versus C_e should give a straight line with intercept: 1/ K Q⁰ and slope: 1/ Q⁰

The obtained values from the plots are presented below

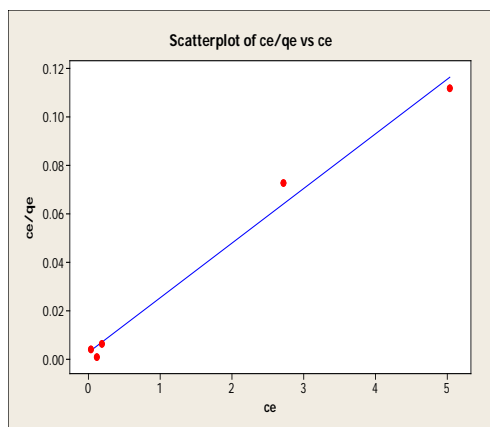


Figure 5: Scatter plot of c_e/q_e versus c_e for chlorifors

Table 3: Langmuir isotherm parameters

Time in minute	1/ Q ⁰	1/ K Q ⁰	R ²
15	0.019000	0.01557	0.908
30	0.022172	0.004877	0.991

Quasi- Langmuir Model

Quasi-Langmuir model is used as a compromise between Langmuir and Freundlich models, which can be written as (Redlich and Peterson, 1959):

$$q_e = \frac{KRP C_e}{1 + \alpha RP C_e^\beta}$$

A special case of Langmuir would give the same linear equation as follows

$$1/q_e = (1/K_a q_m) 1/C_e + 1/q_m$$

45	0.022470	0.003286	0.990
60	0.029820	0.002838	0.953

Temkin Isotherm Equation

The Temkin isotherm equation assumes that the heat of adsorption of all the molecules in layer decreases linearly with coverage due to adsorbent-adsorbate interactions, and that the adsorption is characterized by a uniform distribution of the bonding energies, up to some maximum binding energy)[27] The Temkin isotherm is represented by the following equation

$$q_e = \frac{RT}{b} \ln(K_T C_e)$$

This can be rearranged linearly as

$$q_e = B_T \ln K_T + B_T \ln C_e$$

Therefore a plot of q_e against ln C_e is linear. From the plots, the data in table t1 was obtained

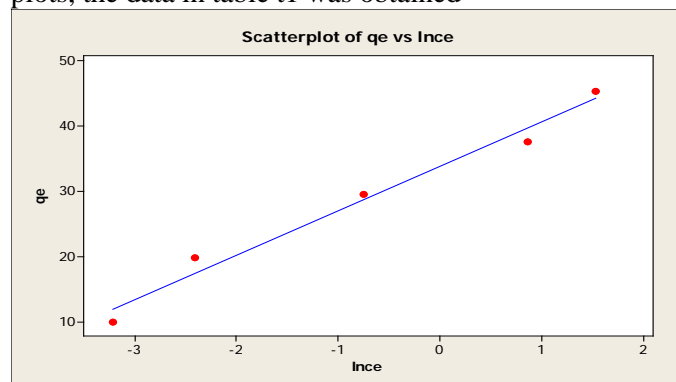


Figure 6: Scatter plot of q_e against ln C_e

Table 4: Temkin isotherm parameters.

Time in minute	B _T	B _T lnK _T	R ²
15	4.624	21.91	0.811
30	5.171	34.63	0.852
45	6.803	33.90	0.979
60	6.298	33.90	0.975

This means a plot of 1/q_e versus 1/C_e is linear with 1/K_aq_m slope and intercept as 1/q_m

Table 5: Quasi-Langmuir isotherm parameters

Time in minute	1/K _a q _m	1/q _m	R ²
15	0.005945	0.03490	0.969
30	0.003105	0.02249	0.992
45	0.002980	0.02343	0.983
60	0.002207	0.02451	0.981

Based on the higher regression values in quasi-Langmuir isotherms, the experiment was found to

follow this model. Freundlich isotherm model plots and quasi-Langmuir isotherms for different shaking time were used to calculate the apparent thermodynamic values.

The result for different shaking time is illustrated logarithmically in figures 4 which is a plot of $\ln[x]_{ads}$ versus $\ln [X]_e + [SX_n]_w$. The obtained scatter plots have regressions (R^2) ranging from 0.71-0.91. This confirms that adsorption of chlorpyrifos observes Freundlich adsorption model. The obtained plots parameters were further used to obtain apparent thermodynamic properties.

Table 6 shows the values of the apparent thermodynamic properties calculated from Freundlich

and quasi-Langmuir adsorption isotherms. Adsorption/desorption equilibrium constant, K' of **118.665**, was obtained from the log plots (figures 4). Langmuir constant of 142.510 was obtained from $K_c = C_{Ae} / C_e$ where C_e is the concentration at equilibrium and C_{Ae} is the amount adsorbed on solids at equilibrium. This illustrates that despite the model used, the apparent thermodynamic properties obtained are almost the same. The mean value of n is: **0.244** and the mean $\Delta G'$ for the adsorption of chlorpyrifos is **-11.7946 KJ/mol** and **-11.6809 KJ/mol** for Freundlich and Langmuir isotherms respectively for the loam soil. This demonstrates that pesticide residues are spontaneously absorbed by non-target environmental samples.

Model	Freundlich				Langmuir	
	n	LnnK'	K'	ΔG (kj/mol)	Kc	ΔG (kj/mol)
Time (min)						
15	0.1998	2.964	96.974	-11.333512	34.289	-8.766590
30	0.2022	3.447	155.322	-12.500591	284.568	-14.01437
45	0.2805	3.449	112.189	-11.694598	111.745	-11.69680
60	0.2914	3.469	110.174	-11.649.695	139.439	-12.24595
Mean	0.244+0.05		118.665+22.311	-11.7946+_0.3	142.510+_122.365	-11.681+_2.568

Table 6: Values for n , K' and $\Delta G'$ for the adsorption/desorption of chlorpyrifos by the different soil sample.

Desorption is a special case of thermal dissociation, and therefore transition state theory can be used to obtain the apparent desorption rate constant, K_d , in terms of the apparent adsorption/desorption equilibrium constant, K' , using the relation:

$$K_d' = kT/hK' \dots \dots \dots (13)$$

Where: k is the Boltzmann distribution constant, T is the absolute temperature, h is the planks constant.

From equation 13 K_d is also given by: $K_d' = [X]^n [S] / [SX_n] \dots \dots \dots (14)$

The mean lifetime of a molecule of atrazine in adsorbed state, is given by $1/K_d$ (Atkins, 1978).

Substitution of the appropriate values in equation 13 yields a value of 1.9×10^{-11} s, for the apparent lifetime of a molecule of chlorpyrifos in the adsorbed state. Such apparent life time of the adsorbed state points to physisorption, rather than chemisorption for which room temperature lifetimes of up to 3000 s have been predicted [30]

The exponent n is the number of pesticide molecules associated with a single adsorption site, S , to give the pesticide-site complex SX_n . The value of n of 0.244 suggests that each molecule of chlorpyrifos is associated with an adsorption site. The major adsorption interactions which bind small organic molecules in the soil

Particles are of colloidal dimensions, i.e., 1nm to 1mm [16] Combining equations 9 and 10 one obtains equation 15 which gives the relationship between the apparent equilibrium constant, K' , and the true equilibrium constant, K :

$$K' = \frac{K[X]_e/[X]_e + [SX_n]_w}{\dots\dots\dots} \quad (15)$$

It is apparent that the extent to which K' deviates from K depends on the value of $[SX_n]_w$ and the value of n . The values of K lead to a value for the rate constant for the adsorption reaction, K_{ad} of $1.912 \times 10^{-11}/s$ the adsorption isotherm for loam soils was near linear as shown in figures 9, with Freundlich n values of 0.244. Values of $n < 1$ are indicative of adsorption by heterogeneous media where high energy sites are occupied first, followed by adsorption at lower energy sites, while linear isotherms ($n = 1$) indicate simple partitioning into the amorphous (Weber and DiGiano, 1996).

CONCLUSION

Chlorpyrifos was found to adsorb on loam soil from Ndeiya location, Limuru County, Kenya with a factor of up to 99.2%. The adsorption was found to decrease with increase in mass of soil. The optimum contact time was found to be 30 minutes, and adsorption was found to increase with concentration of chlorpyrifos. The data obtained in this study fitted quasi-langmuir adsorption isotherm model best with high regression values of up to 0.992. As shaking time increased from 15 minutes to 60 minutes, the value of n increased from 0.1998 to 0.2914. The value of ΔG was $-11.7946 \pm 0.3 \text{ kJ/mol}$ and $-11.681 \pm 2.6 \text{ kJ/mol}$ for freundlich and quasi-langmuir isotherms respectively, indicates that adsorption of chlorpyrifos by loam soil is spontaneous.

REFERENCES

1. Felsot A, Dahm PA (1979) Sorption of organophosphorus and carbamate insecticides by soil. *J Agric Food Chem* 27(3):557-563
2. Macalady, D. L. & Wolfe, N. L. 1983. New perspectives on hydrolytic degradation of the organophosphorothioate insecticide chlorpyrifos, *J. Agric. Food Chem.* 31: 1139-1147.
3. Beck, A. J., Johnston, A. E. J. & Jones, K. C. 1993. Movement of non-ionic organic chemicals in agricultural soil. *Critical Rev. Environ. Sci. Technol.* 23: 219-248.
4. McCall PJ, Swann RL, Laskowski DA, et al. 1980. Estimation of chemical mobility in soil from liquid chromatographic retention times. *Bull Environ Contam Toxicol* 24: 190- 195.

5. Racke KD. 1993. Environmental fate of chlorpyrifos. *Rev Environ Contam Toxicol* 13 1: 1- 150.
6. Lide, David R. 1998. *Handbook of Chemistry and Physics* (87 ed.). Boca Raton, FL: CRC Press. 3-126.
7. Muller, Franz, ed. 2000. *Agrochemicals: Composition, Production, Toxicology, Applications*. Toronto: Wiley-VCH. 541
8. California Air Resource Board Cdpr.ca.gov. Retrieved November 20, 2011.
9. US Geological Survey. "Breakdown Products Of Widely Used Pesticides Are Acutely Lethal To Amphibians, Study Finds." *ScienceDaily*. ScienceDaily, 25 June 2007. Retrieved on February 25, 2014
10. Freed VH, Chiou CT, Schmedding DW. 1979. Degradation of selected organophosphate pesticides in water and soil. *J Agric Food Chem* 27:706-708.
11. Atkins P.W. (1978) *Physical Chemistry*, Oxford University 1st edition pg. 938
12. Fontaine DD, Teeter D. 1987. Photodegradation of chlorpyrifos in the vapor phase. Rep. GH-C 1911. Dow Chemical U.S.A., Midland, Michigan. [unpublished study] (As cited in Racke 1993)
13. Blanchet DF, St. George A. 1982. Kinetics of chemical degradation of organophosphorus pesticides; hydrolysis of chlorpyrifos and chlorpyrifos-methyl in the presence of copper(II). *Pestic Sci* 13:85-91.
14. Walia S, Dureja P, Mukerjee SK. 1988. New photodegradation products of chlorpyrifos and their detection on glass, soil, and leaf surfaces. *Arch Environ Contam Toxicol* 17(2):183-188.
15. Zaranyika MF, Mandihza NT (1999) Adsorption of Amitraz by a river sediment: Apparent thermodynamic properties. *Journal of environmental science and health part B – pesticides food contaminants and agricultural wastes* 33 (3) 235-251
16. Burchill S., Greenland D.J. and Hayes M.H.B. (1981), Adsorption of organic molecules, in the chemistry of soil processes, 389-402
17. Graham-Bryce, J. (1981) Behavior of pesticides in soils; the chemistry of soil processes, Greenland and Hayes, NY
18. Halimah, M., Nashriyah, B. M., Yew Ai, T. & Ismail, B. S. 2004. Adsorption and desorption study of C-chlorpyrifos in two Malaysian

- agricultural soils. *Journal of Nuclear and Related Technologies* **1** (1): 31-40.
19. Bowman BT, Sans WW (1977) *Soil Sci. Soc Am.J.* 41: 574-579.
 20. Shahmohammadi-Kalalagh, H. Babazadeh1, A. H. Nazemi2, M. Manshouril (2011) Isotherm and Kinetic Studies on Adsorption of Pb, Zn and Cu by Kaolinite Caspian *J. Env. Sci.* Vol. 9 No.2 pp. 243~255
 21. Singh N, Wahid PA, Murray MVR, Sethunathan N (1990). Sorption-desorption of methyl-parathion, fenitrothion and carbofuran in soils. *J. Environ. Sci. Health B25*(6): 713-728.
 22. Tran, T. S. and R. R. Simard. (1993) Mehlich III-Extractable Elements. In: M. R. Carter, Ed. *Soil Sampling and Methods of Analysis*: 43-49.
 23. Mehlich, A. (1953). Determination of P, Ca, Mg, K, Na, and NH₄. North Carolina Soil Test Division (Mimeo 1953); 23-89.
 24. Gislason, E.A., Craig, N.C. (2005). Cementing the foundations of thermodynamics: comparison of system-based and surroundings-based definitions of work and heat, *J. Chem. Thermodynamics* 37: 954-966
 25. Jan-Åke, Persson, Mårten Wennerholm, Stephen O'Halloran, (2008) *Handbook for Kjeldahl Digestion*: 11- 42
 26. S.Y. Yang and W.L. Chang, (2005). *Soil Sci.*, 170, 55
 27. Carroll, Dorothy (1959). "Ion exchange in clays and other minerals". *Geological Society of America Bulletin* 70 (6): 749-780.
 28. Turner, R.C. and Clark J.S., 1966, Lime potential in acid clay and soil suspensions. *Trans. Comm. II & IV Int. Soc. Soil Science*, 208-215
 29. James Kamau , G.N. Kamau (2012) Adsorption of 2, 4, 5, 6-tetrachloroisophthalonitrile (chlorothalonil) by Nairobi River sediments: adsorption characteristics and related thermodynamic data, *international Journal of BioChemiPhysics*, Vol 20, 25-38
 30. Atkins P.W. (1990) *Physical Chemistry*, Oxford University Press, 4th edition pg. 892