

# Adsorption and Leaching of Deltamethrin Pesticide in Alluvial Soil Under Laboratory and Field Conditions

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## ABSTRACT

This study was carried out to assess the adsorption and leaching activities of deltamethrin pesticide in soil and water. Experiments in the lab and in the field were used to better understand these processes and the factors that influence them. Sections of the adsorption experiment were separated into kinetic and steady-state. Pseudo-first and second-order models were used to evaluate the kinetic data. Deltamethrin kinetic adsorption on soil was shown to be pseudo second order, with a rate constant of 4.625 mg/g/h. Using the Langmuir and Freundlich isotherms, it was determined that Freundlich's isotherm was well-observed, with adsorption capacities of 0.164-0.861 mole per gramme, based on the equilibrium data. In the lab, leaching experiments were carried out in 30-cm-long plastic columns. After adsorption, 500 ml of water was used to elute a known amount of deltamethrin insecticide from the column. It was discovered that the deltamethrin concentration fell from 0.405 ng/l in the first portion of the water to 0.0601 ng/l in the last portion of the water and 2.584 ng/l in the first section of column soil to 0.278 ng/l in the third section of column soil. Deltamethrin's leaching capability was tested in the field to a depth of 30 cm, and its concentration declined as soil depth increased. In the first piece of soil, it was 10.518 ng/l, and in the third, it was 0.354 ng/l. It was discovered in this investigation that deltamethrin insecticide leached to 30 cm depth because to minimal organic matter, sandy texture and basic pH.

**Keywords:** Adsorption; Deltamethrin; Leaching; Soil; Water

## INTRODUCTION

Pesticides have a devastating effect on wildlife because they destroy insects, invertebrates, birds, and mammals. The runoff from agricultural fields, horticultural regions, and residential gardens pollutes the environment. Pesticides are washed into neighbouring water sources by rainwater, polluting the water supply. Because pesticides fall into various categories with varying impacts on living things, it's difficult to establish precise judgments (Viran et al., 2003; Velisek et al., 2006; Yildirim et al., 2006; Dinu et al., 2010).

For pest management, synthetic pyrethroids have become increasingly popular as an alternative to organochlorine pesticides because of their superior efficacy and shorter soil life. Insects are quickly paralysed by Deltamethrin [(S)-a-cyano-3-phenoxybenzyl (1R, 3R)-3-(2, 2, dibromovinyl)-2, 2-dimethylcyclopropanecarboxylate], which is based on the structure of natural pyrethroids (Xue and Xu, 2006; Chen et al., 2002; Zhao et al., 2008). Due to the fact that deltamethrin is a lipophilic molecule, it is not water soluble and consequently extremely stable. It is used in agriculture to control apple and pear suckers, the plum fruit moth (apple and pear), caterpillars on brassicas, peas moth (apple and pear) and the aphids (apples, peaches) and the aphid moths (apples) and the aphid moths (apples) and the aphids (apples) and the aphid moths (apples), and in public health to treat ectoparasitic and malaria disease (Soderlund et al., 2000; Anand et al., 2006; Yadav et al., 2001).

Choreoathetosis, hyperexcitability, and salivation are the main adverse consequences of deltamethrin (Ray et al., 2000). The aquatic animals amphibians, crustaceans, mollusks, plankton, fish, bees, vertebrates, mammal species, and chickens have been reported to be very poisonous to deltamethrin in laboratory conditions (Hernández-Moreno et al., 2010; Senger et al., 2005; Amweg et al., 2005; Bradberry et al., 2005). Under acute exposure, it is also hazardous or even deadly to earthworms (Yajuan et al., 2007).

The knowledge of this type of dissipation effects was important because due to enhanced persistence of pesticides in soil, the environmental or food chain contamination will be increased. For this purpose, this study was carried to know laboratory and field persistence, leaching, and adsorption of deltamethrin in soil.

**Experimental:** 2.1. Chemicals Commercial deltamethrin was purchased from the local market in Hyderabad-Sindh, Pakistan. Bayer Crop Science provided a 99.4% purity grade for deltamethrin. This method was used to prepare the Deltamethrin stock solution and various working solutions by diluting the stock solution with water.

**Study Area:** National Center for Excellence in Analytical Chemistry, University of Sindh, Jamshoro, Sindh, Pakistan, was chosen as the study location. The experimental field's okra crop was planted in the first week of November 2010 on an area measuring 60 feet by 60 feet. Okra was treated with deltamethrin at the recommended amount of 250 cc per acre one month after planting. It was sprayed with deltamethrin twice a week for a total of sixteen times until harvest.

**Soil Sampling:** 0-15 cm soil samples were gathered for lab research. Samples were homogenised, crushed, and air-dried before being analysed. Cool, dry polypropylene bags held soil samples. In the results and discussion section, Table 1 shows the soil's physicochemical properties. Glass electrodes and hydrometers were used to measure soil pH in a 1:1.25 soil-to-water solution (Jackson, 1967). Walkley-Black determined organic matter (Walkley and Black, 1934). The study sampled four random okra plots. Each location's soil samples were taken at 0 to 10 cm, 11 to 20 cm, 21 to 30 cm, and 31 - 60 cm. The samples were labelled and frozen at -10 °C until extraction. In a lab experiment, pesticide leaching and soil adsorption were examined. Field studies revealed pesticide residue and leaching.

**Kinetic Adsorption Study:** 5 g of soil was combined with 100 ml of 100 ng/l deltamethrin in a 250 ml conical flask for kinetic adsorption. This combination was shaken for 24 hours at 130 rpm. At 0, 0.25, 0.5, 1, 2, 4, 8, 16, and 24 hours, 5 ml flask samples were obtained. The obtained samples were extracted three times with 5 ml of ethyl acetate, then passed through anhydrous sodium sulphate to eliminate moisture before GC-ECD analysis.

**Equilibrium Adsorption Study:** 5 g of soil was mixed with 100 ml of 0.25, 1, 2, 5, 10, 25, 50, and 100 ng/l deltamethrin in 250 ml conical flasks for equilibrium adsorption. These mixes were shaken at 130 rpm for 4 hours at room temperature (kinetic study equilibrium time). After 4 hours, 5 ml of each flask sample was centrifuged at 3000 rpm for 10 minutes; the supernatant was extracted with ethyl acetate (as stated in kinetic adsorption study),

and remaining pesticide content was measured by GC-ECD. A blank solution was also made to test deltamethrin adsorption on conical flask walls. Both kinetic and equilibrium experiments were conducted three times.

**Column leaching study:** The 30 cm x 6 cm PVC column with a 0.60 m nylon membrane. Wool on nylon membrane prevents column dirt loss. First day, dirt was soaked in distilled water and left overnight. The next day, 5 mg of deltamethrin dissolved in 5 ml ethyl acetate was added to the column surface. The column was eluted with 500 ml of distilled water at 100 ml.h<sup>-1</sup> using a peristaltic pump. After elution, 10 cm pieces of column soil were split to measure pesticide adsorption. Three times repeated to get reproducible results.

**Extraction of soil and water samples:** In a 250 ml stoppered flask, 50 g air-dried dirt was combined with 50 ml ethyl acetate. The sample was equilibrated for 2 hours on a rotary shaker, then filtered. In a 250 ml separating funnel, 100 ml of column-eluted water was combined with 50 ml ethyl acetate. Five minutes of vigorous shaking ensured thorough mixing of two layers. After separating two layers, pesticide-residue-containing ethyl acetate was dried with anhydrous sodium sulphate. These extracts (soil and water) were concentrated to 5 ml with nitrogen and analysed with GC-ECD.

**Analytical technique:** GC-ECD evaluated deltamethrin residue. A 7890A GC with ECD was used. 30 m 0.320 mm 0.25 m HP-5 GC column. GC has 7683 autosampler and 7683B injector. Operating conditions: injector port temperature 250 °C, injection volume 1l in a split mode (50:1), nitrogen as carrier gas at 60 mL/min; oven temperature programme, initial 70 °C, increased at 30 °C/min to 210 °C (2 min), then increased to 250 °C at 25 °C/min (2 min), and finally increased at 30 °C/min to 290 °C and held for 5 min. Analysis takes 16.6 minutes. ECD was 310°C. All analyses were autosampler-injected.

**Percent recovery:** Standard solutions of 0.1, 0.5, and 1 ng/l deltamethrin were sprayed onto 50 g of blank soil. To ensure an equitable dispersion of pesticide, the soil was carefully stirred and then left overnight to let the pesticide to fully absorb. Deltamethrin was then isolated and tested as described above. Deltamethrin standards ranging from 0.01 to 2 ng/l concentration were run on GC-ECD for calibration purposes. Soil and water deltamethrin recovery percentages were 87.43 ± 1.2 percent and 83.15 ± 1.09 percent, respectively.

**RESULTS AND DISCUSSION**

**3.1. Influence of soil physicochemical parameters on deltamethrin pesticide adsorption and leaching**

Soil and pesticide chemistry affect pesticide adsorption. Adsorption affects pesticide leaching, transmission, runoff, and degradation. Adsorption affects pesticide-soil interactions. Pesticide adsorption depends on soil texture, organic matter, cation exchange capacity, pH, moisture, and electrical conductivity. Clay soil's wide spaces improve pesticide adsorption. Sand particles had fewer vacant sites than silt or clay, hence column and field tests confirmed deltamethrin leaching. In a column experiment, 30cm of deltamethrin was eluted with water. Deltamethrin travelled the same distance in both studies. Sand and low organic stuff created this. Organic matter increases soil pesticide adsorption due to more adsorption sites. Organic matter has a bigger surface area than mineral soil, increasing its potential to absorb contaminants and decreasing bioactivity. Bansal said organic matter increases soil carbon and electrical conductivity while lowering pH. (Bansal, 2010). His research showed a relationship between soil organic carbon, cation exchange capacity, and pH. Pesticide chemisorption uses stronger cation exchange processes in acidic soils, hence adsorption is greater. Imidacloprid adsorption was stronger at lower pH and/or temperature (Ping et al., 2010). pH 8.46 reduced adsorption and increased leaching (in the basic range). Water molecules compete with insecticides for binding sites in wet soil. Increasing soil osmotic potential prolongs adsorption contact, enhancing water retention. High-leaching, low-

adsorption soils have less organic matter and a lighter texture. Low-organic-matter, acidic soils have been studied for pesticide adsorption, however Sindh, Pakistan's soils are alkaline. Pesticide adsorption and leaching are affected by soil organic matter, cation exchange capacity, texture, and electrical conductivity. Table 1 indicates soil parameters.

Table 1: Physicochemical properties of the soil.

Parameter	Value
pH	8.46± 0.01
Electrical Conductivity (µS cm <sup>-1</sup> )	560 ± 0.25
Cation Exchange Capacity (meq/100g)	18± 0.21
Organic Matter (%)	0.899 ± 0.01
Total Organic Carbon (%)	0.522 ± 0.001
Sand (%)	74.75 ± 0.68
Silt (%)	18.15 ± 0.24
Clay (%)	7.1 ± 0.17
Classification	Sandy Loam

**Kinetic adsorption study:** Pesticide residence time at the solid-solution interface is determined by the pace at which the pesticide's solute is removed from the solution. Figure 1 depicts the two distinct phases of kinetic adsorption: the fast phase lasting up to two hours, and the slow phase lasting longer than that. The deltamethrin content in the soil changed very little after four hours. In 24-hour sorption trials, atrazine and isoproturon were removed from solution in under an hour (Beck and Jones, 1996). Endosulfan and deltamethrin have a comparable elimination time of two hours (Kumar and Philip, 2006; Parkpian et al., 1998). As a result of this, deltamethrin adsorption was initially limited to the surfaces. Slow migration and diffusion were followed by deltamethrin's rapid filling of empty spaces in soil particles (Gao et al., 1998).

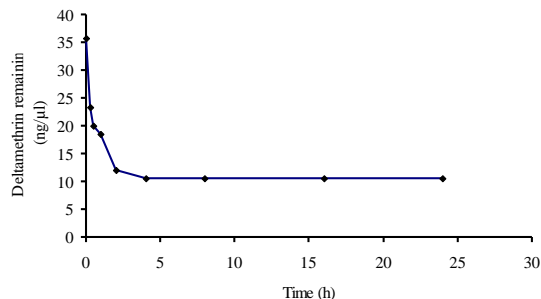


Figure 1: Kinetic adsorption of deltamethrin.

**Pseudo first order model:** First order rate constant was calculated by equation 1.

$$\log (q_e - q_t) = \log q_e - k_1 \cdot t / 2.303 \quad (1)$$

Pseudo second order model

Data was also examined through pseudo second order model given by Ho and McKay. Second order rate constant was calculated by equation 2.

$$t/q_t = 1/k_2 \cdot q_e^2 + t/q_e \quad (2)$$

Pseudo-second order models in chemisorption are better than pseudo-first order models because they take into account the valency forces that interact adsorbent and adsorbate during the process. The adsorption of deltamethrin pesticide was studied by Al-Qoodah and found that deltamethrin absorption followed pseudo-second-order kinetics rather than the first order model, as a result (Al-Qodah et al., 2006). Table 2 lists the rate constants for both orders.

Equilibrium adsorption study

Langmuir isotherm model: We performed adsorption isotherm experiments with an equilibrium time of 4 hours at a temperature of 28 °C. The isotherm constants and maximum adsorption capacity of deltamethrin at nine different concentrations were calculated using Langmuir and Freundlich isotherm models. These

concentrations ranged from 0.25, 0.5, 1, 2, 5, 10, 25, 50, and 100 ng/ml, respectively. Because the adsorbed layer is only one molecule thick, this model deals with monolayer and homogenous adsorption. Adsorption occurs at fixed and identical places. Equation 3 depicts this model's linear form.

$$C_e/C_{ads} = 1/Q_b + C_e/Q \quad (3)$$

Freundlich isotherm model: In addition to monolayer formation, Freundlich isotherms are associated with non-ideal and reversible adsorption processes. As a result, non-uniform distribution of adsorption heat and affinities over the heterogeneous surface is used in multilayer adsorption. Equation 4 provides the linear version of this model.

$$\log Q_e = \log A + (1/n) \log C_e \quad (4)$$

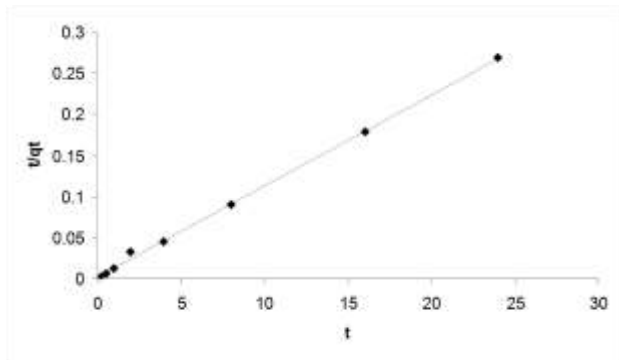


Figure 2: Pseudo second order plot of deltamethrin.

Table 2: Adsorption rates of deltamethrin.

Models applied	Adsorption rate (mg g <sup>-1</sup> h <sup>-1</sup> ) of Deltamethrin
Pseudo first order	1×10 <sup>-3</sup> ± 0.011
Pseudo second order	4.625± 0.02

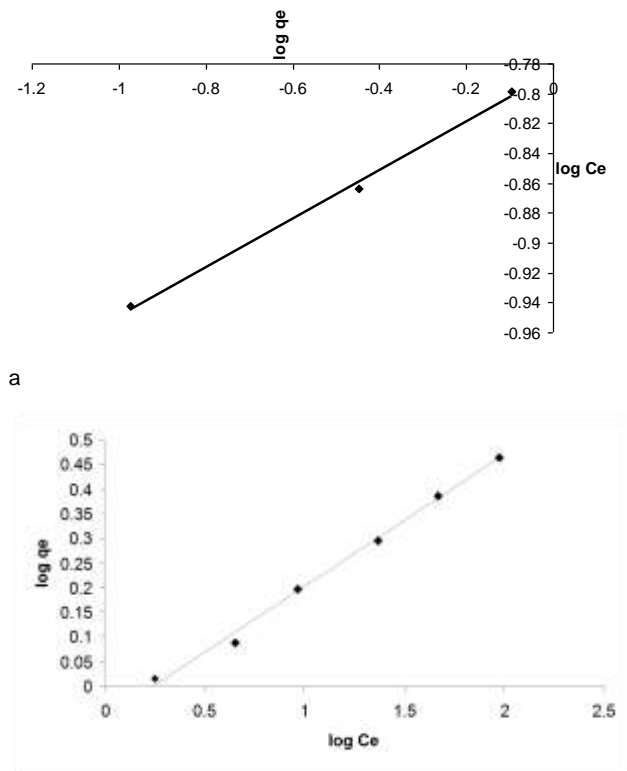


Figure 3: Freundlich isotherm of deltamethrin at (a) lower concentrations (b) higher concentrations

Table 3 shows the parameters of both models. According to the Freundlich isotherm, the n value for deltamethrin is 6.135 and 3.748, which indicates that the process of adsorption was successful because 1–n 10 denotes the favorableness of adsorption (Bilgili, 2006). A tiny amount of blank deltamethrin solution clung to the conical flask's walls, but this was clearly not significant.

Table 3: Equilibrium adsorption isotherm values for deltamethrin pesticide.

Isotherm	Isotherm parameter	Value
Langmuir	Q (mol g <sup>-1</sup> )	0.001528
	b	0.917
	R <sup>2</sup>	0.161
Freundlich (at lower concentration)	A (mol g <sup>-1</sup> )	0.164
	n	6.135
Freundlich (at higher concentration)	R <sup>2</sup>	0.996
	A (mol g <sup>-1</sup> )	0.861
	n	3.748
	R <sup>2</sup>	0.996

### Column leaching study

Deltamethrin in column water was less than in column soil. Every time water was eluted, deltamethrin dropped from 0.405 to 0.0601 ng/l. Due to our soil's lack of organic matter, sandy texture, and great pushing strength, the pesticide eluted 30 cm. We evaluated deltamethrin's adsorption and leaching properties in the first and third soil columns. Results are in Table 4.

Table 4: Deltamethrin leaching and adsorption through column.

Sample (cm)	Deltamethrin concentration found (ng µl <sup>-1</sup> )
Soil- 0-10	2.584 ± 0.02
Soil 11-20	1.05 ±0.011
Soil 21-30	0.278 ±0.002
Water-01	0.405 ±0.002
Water-02	0.305 ±0.001
Water-03	0.0702 ±0.001
Water-04	0.067 ±0.003
Water-05	0.0601 ±0.001

Field study: Deltamethrin has a high soil adsorption, yet it leached 30 cm in our field due to little organic matter, sandy texture, low cation exchange capacity, basic pH, and heavy rain. It's also the soil's top 15 centimetres. As soil sinks deeper, deltamethrin concentrations drop. The first 10 cm of soil had 10.518 ng/l, followed by 5.894 ng/l and 0.354 ng/l. There was no deltamethrin in 30 cm and 60 cm soil samples. Table 5 shows results.

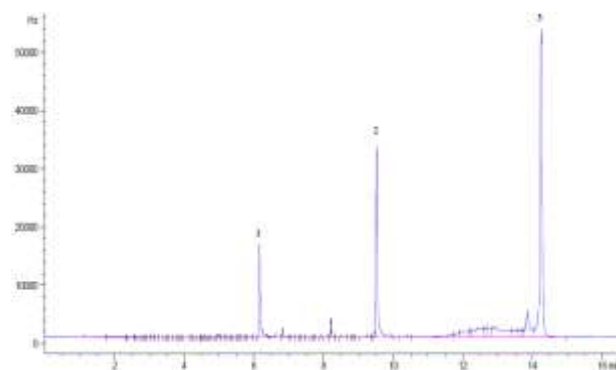


Figure 4: Chromatogram showing deltamethrin and its metabolites in soil. Peak 1. Deltamethrin, 2. PBacid, 3. Br<sub>2</sub>Ca at retention times (tR) of 6.213, 9.568 and 14.242 minutes respectively.

Table 5: Deltamethrin residue in okra field soil.

Soil depth (cm)	Deltamethrin concentration found (ng µl <sup>-1</sup> )	% of Deltamethrin in each layer
Soil- 0-10	10.518±0.08	62.734±0.09
Soil 11-20	5.894±0.09	35.154±0.35
Soil 21-30	0.354±0.07	2.111±0.04
Soil 31-60	0	0

## CONCLUSIONS

As a result of this work, it has been concluded that deltamethrin adsorption is kinetic and that the rate limiting step may be chemical adsorption whereas equilibrium adsorption takes place according to the Freundlich isotherm. Deltamethrin's soil leaching and adsorption capacities are dependent on soil physicochemical characteristics, according to studies conducted in the lab and out in the field. Because of the poor organic matter, sandy texture, alkaline pH, and limited cation exchange capacity of our soil, deltamethrin insecticide has leached to a depth of 30 centimetres.

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