

Adsorption-Desorption and Mobility of Fenvalerate in Three Tropical Agricultural Soils

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Abstract: A study of the adsorption-desorption and mobility of fenvalerate [(RS) α -cyano-3-phenolxybenzyl (RS) 2-(4-chloro-phenyl)-3-methylbutyrate] was carried out on three agricultural soils under laboratory conditions. These soils have different contents of clay, minerals and organic carbon. Adsorption isotherms conformed to the Freundlich equation. Fenvalerate reached adsorption equilibrium after approximately 3 to 4 h of shaking for the 3 soil types. The K_{ads} values for the sandy clay soil, silty soil and sandy clay loam soil were 226.5, 89.4 and 62.7, respectively. The adsorption of fenvalerate correlated better with clay content than with organic carbon content. The result of the desorption study showed a significant correlation with organic carbon content. The hierarchical order of the desorption coefficient for fenvalerate was: silty soil > sandy clay > sandy clay loam soils. The leaching rate of fenvalerate in the column increased with increasing volume of simulated rain. The mobility rate through the soil column was higher in the silty soil than in the sandy clay and sandy clay loam soils. A high concentration of fenvalerate was detected in the topsoil layer of the column and the concentration decreased with depth.

Key words: Adsorption • desorption • leaching • fenvalerate

INTRODUCTION

The fate of pesticides and their behaviour in soil are influenced by several factors including sorption-desorption, movement and decomposition. A thorough understanding of sorption-desorption is paramount for the prediction of pesticide movement in soil profiles [1], which can occur by leaching, runoff and volatilization [2]. Information on movement of pesticides is useful in order to predict both the probable effectiveness of the chemicals and their influence on the quality of groundwater [3].

Synthetic pyrethroids, including fenvalerate [(RS) α -cyano-3-phenolxybenzyl (RS) 2-(4-chloro-phenyl)-3-methylbutyrate] are broadly categorized as a major class of synthetic organic insecticides. The history and progress of the development of pyrethroids as insecticides, from the discovery of the insecticidal activity of pyrethrum, through the synthesis of analogues of natural pyrethrins, to the improvement in the activity and selectivity of synthetic pyrethroids, has been comprehensively reviewed [4, 5]. The first two synthetic

pyrethroid - allethrin and cyathrin, were introduced around 1950 and in the mid-1970s, respectively. The photostable pyrethroids include deltamethrin, cypermethrin, fenprothrin and fenvalerate [6]. Pyrethroids have been used primarily for the control of household and agricultural insect pests, as well as for industrial, stored product and veterinary applications.

Fenvalerate is an effective broad-spectrum pyrethroid insecticide. In addition to its highly selective insecticidal properties, fenvalerate exhibits photolytic stability and an extended field residual activity [7]. Previous investigations have studied the effects of organic matter in the soil on fenvalerate activity and degradation [8-10]. Fenvalerate has been extensively tested on a wide spectrum of freshwater organisms [11] and plants [12].

Fenvalerate is one of the more persistent synthetic pyrethroids in soils. In agricultural soils, fenvalerate is tightly adsorbed to soil particles, does not easily move laterally or to lower soil layers with groundwater and is almost always localized at the application site because of its extremely low solubility in water [13]. Fenvalerate degradation rates from mineral surfaces are dependent

on soil type, moisture, temperature and microbial activity [8, 14]. Half-time persistence in soil usually ranges between 2 and 18 days, but 3 months has also been recorded. The primary degradation reactions of fenvalerate involve the cleavage of the ester linkage, hydration of the cyano moiety and the hydroxylation of the phenoxy moiety of the parent molecule [14].

Many of the above studies were carried out under temperate conditions, which are considerably different from tropical climatic conditions such as those in Malaysia. This report presents results of studies on the sorption-desorption and mobility of fenvalerate in three Malaysian agricultural soils, namely, silt soil, sandy clay soil and sandy clay loam soil.

MATERIALS AND METHODS

Fenvalerate: The commercial grade of fenvalerate (Sumicidin® 30% g a.i/l) was obtained from ACM (Agricultural Chemical (M) Sdn. Bhd.). Stock solution was prepared at 100 µg ml⁻¹ by diluting the commercial grade fenvalerate with distilled water. For the calibration curve, the analytical grade of fenvalerate (PESTANAL®) 99.9% purity was obtained from Riedel-de Haën. Working standard solutions containing 2.0-10.0 µg ml⁻¹ were prepared by appropriate dilution of the standard stock solution of 100 µg ml⁻¹ with hexane (HPLC grade).

Soil collection and analysis: Three different soil types were sampled from three different locations. The silt soil samples were collected from vegetable growing areas in Sepang, Selangor; the sandy clay loam soil was from an experimental plot located near the Department of Agriculture, Serdang, Selangor and the sandy clay soil was from an experimental plot at the Universiti Kebangsaan Malaysia (UKM) in Bangi, Selangor. The soil samples were analyzed and classified at the Soil Testing Laboratory of the Department of Geology, UKM. The physico-chemical properties of each soil are given in Table 1. All the samples were collected from the 0-10 cm depth, air-dried and sieved through a mesh (2 mm). The samples were placed in labelled black polyethylene bags and stored at -4°C.

Recovery study: From each sample of air-dried soil (50% moisture), each 25 g portion was weighed into a 250 ml conical flask separately prior to fortification with 10 ml of 50 mg kg⁻¹ of analytical grade fenvalerate. The soil sample was mixed thoroughly and 10 ml distilled water and 50 ml acetonitrile were added after 1 h, followed by shaking on an orbital shaker (250 rpm)

for 1 h. The experiment was replicated thrice. The sample was set aside for about 1 h and then transferred into the separatory funnel, where 50 ml hexane was added. The sample was shaken for approximately 15 min, then 50 ml of 2% NaCl was added to the extract. The hexane layer was filtered through 40 g of NaSO₄ in a glass column. A sample of the supernatant was collected and filtered through a RC membrane (pore size 0.45 µm) to remove particulates. Finally the extract was evaporated to dryness under a stream of nitrogen gas and reconstituted in 1 ml of hexane prior to GC analysis.

Adsorption-desorption study: The adsorption and desorption study conducted was similar to those described by other researchers [2, 15]. Each 5 g sample of each soil type was weighed into a centrifugal tube. Then 10 ml of one of the various concentrations (50, 75, 100, 125 or 150 µg ml⁻¹) of fenvalerate were added. The experiment was replicated thrice. The preliminary kinetic studies have shown that adsorption had reached pseudo-equilibrium at 4 h for silt and sandy clay loam soil and 3 h for sandy clay, after shaking at 150 rpm. After shaking, the suspensions were centrifuged (Model IECHN-SII) at 4,500 rpm for 15 min.

The supernatant (10 ml) was transferred into the separatory funnel before adding 10 ml hexane and 10 ml acetonitrile. The sample was shaken for 15 min on an orbital shaker. Then, 10 ml of 2% NaCl was added to the extract. The hexane layer was filtered through 40 g of NaSO₄ in a glass column. The sample of the supernatant was collected and filtered through a RC membrane (pore size 0.45 µm) to remove particulates. Finally, the extract was evaporated to dryness under a stream of nitrogen gas and reconstituted in 1 ml of *n*-hexane prior to GC analysis.

Desorption was determined on the same soil samples which had been used for the adsorption study. After the supernatant obtained by centrifugation for adsorption had been removed, 10 ml of distilled water was added into each centrifuged flask. The mixture was then shaken for 15 min and centrifuged at 4,500 rpm for 15 min as described above. A 10 ml aliquot was removed from each vial. The process was repeated four times. The supernatants were cleaned up as before prior to GC analysis.

The equilibrium adsorption coefficient (K_{ad}) was calculated from the Freundlich equation as the ratio of adsorbed concentration to aqueous concentration. Differences between the amounts of fenvalerate in the initial concentrations and the amounts in the supernatant of the samples were considered to be the amounts

adsorbed. The herbicide sorption isotherm was calculated using the Freundlich equation as follows:

$$\begin{aligned} x/m &= K C_e^{1/n} \\ \ln x/m &= \ln K + 1/n \ln C_e \end{aligned} \quad (1)$$

where;

K = adsorption /desorption coefficient,

x/m = the adsorbed amount ($\mu\text{g g}^{-1}$),

C_e = solution concentration (mg l^{-1}) after adsorption equilibrium,

1/n = constants (slope)

The relationship between organic matter (OM) content and the adsorption percentage was determined according to the following equation:

$$K_{oc} = \frac{K \times 100}{\% \text{ OM}} \quad (2)$$

where; K_{oc} = the Freundlich OM distribution coefficient,
% OM = % organic matter

The logarithmic form of the above equation was fitted by the least square method to the set of experimental data. The K_d and n constants were calculated and a linear regression analysis was performed to determine the degree of fit between observed data and the Freundlich constants.

Mobility study: PVC tubes, 2.5 cm diameter, were cut into 5 cm lengths and reassembled into one tube of 25 cm. Each column was packed with soil from a single soil type to a depth of 25 cm. The process was repeated three times for each soil type. Once the soil column had settled, a 5 cm thick layer of soil treated with 45 $\mu\text{g g}^{-1}$ of fenvalerate was placed on top of each soil column. The concentration used was the same as the suggested field application. The soil surface in each column was covered with one sheet of Whatman No. 3 filter paper. After 1 h, the soil column was watered with 400 ml water (equivalent to 426 mm of rainfall), 200 ml water (equivalent to 197 mm of rainfall) and 100 ml water (equivalent to 99.8 mm of rainfall). A flask was placed at the bottom of each column to collect the leachate. The experiment was replicated thrice.

The columns were arranged randomly in the greenhouse. After 24 h, each column was separated into 4 segments (0-5, 5-10, 10-15 and 15-20 cm) and the leachate was collected. A 25 g soil sample from each segment was placed in a 250 ml conical flask and extraction with

50 ml of hexane and acetonitrile was carried out. Then 50 ml of 2% NaCl was added to the extract. The flasks were sealed with aluminum foil and shaken on an orbital shaker at 240 rpm for 1 h. The samples were then centrifuged at 4,500 rpm for 15 min. Five ml each of the supernatant and of the leachate were cleaned-up as described for GC determination of the fenvalerate residue.

Extracts obtained from adsorption, desorption and mobility experiments were concentrated to dryness, the residues dissolved in *n*-hexane and analyzed by GC. Fenvalerate residues were estimated using a Hewlett Packard 6890N Series II Gas Chromatograph equipped with μ -electron capture detector (μ -ECD), manual injector and HP-5 Crosslinked 5% Phenyl Methyl Siloxane column (30.0 m x 0.32 μm id, 0.25 μm film thickness). The operating temperatures were: detector 300°C, injector port 280°C, with the oven programmed initially to 205°C for 2 min and then increased to 300°C at the rate of 30°C/min and maintained for 4 min. The carrier gas was nitrogen (N₂, 99%) with flow rate of 1 ml min⁻¹. The volume of injection was 1 μml . There were three replicates and each solution was injected twice. Under these conditions the retention time of fenvalerate was 8.187 min (isomer I) and 8.390 min (isomer II).

External standards of the fenvalerate were used to identify the peaks in three agricultural soils. The detection limit was set at three times the height of the noise peaks (that appeared where the pesticides peaks would appear if the pesticide concerned existed) in the blank sample. The detection limit of the silt soil was 0.011 $\mu\text{g g}^{-1}$, sandy clay soil 0.002 $\mu\text{g g}^{-1}$ and sandy clay loam soil 0.003 $\mu\text{g g}^{-1}$.

RESULTS AND DISCUSSION

Recovery study: The percentage recovery of fenvalerate from the three soil samples was >80% (Table 1). The highest recovery was obtained from the silty soil (88.30%), perhaps due to the high content of organic matter. In contrast, the recovery from the sandy clay soil was the lowest (83.12%) and the recovery from sandy clay loam soil was 84.69%.

Adsorption study: The adsorption of fenvalerate to the three soil types fit the Freundlich adsorption isotherm as indicated by the coefficient of correlation ($r^2 > 0.9$) (Table 2). The 1/n values, which are the values for the slope of the line, were obtained using a least square fit (Fig. 1) of the adsorption isotherms and the values are shown in Table 2. The adsorption coefficient of

Table 1: Physico-chemical properties of three Malaysian tropical soil types

| Physico-chemical properties | Silty soil | Sandy clay soil | Sandy clay loam soil |
|-----------------------------|------------|-----------------|----------------------|
| pH | 4.38 | 5.16 | 6.61 |
| % Organic matter | 82.82 | 12.67 | 3.56 |
| % Organic carbon | 34.84 | 0.93 | 1.02 |
| CEC (meq/100 g) | 33.18 | 11.56 | 8.64 |
| Sand (%) | 2.90 | 52.25 | 50.70 |
| Silt (%) | 1.20 | 9.60 | 26.90 |
| Clay (%) | 95.90 | 38.15 | 22.40 |

Table 2: Adsorption, desorption and organic carbon distribution coefficients of fenvalerat

| Parameter | Silty soil | Sandy clay soil | Sandy clay loam soil |
|-------------------|------------|-----------------|----------------------|
| Adsorption | | | |
| K_{ads} | 89.4000 | 226.5.000 | 62.7000 |
| 1/n | 0.2544 | 0.2573 | 0.4158 |
| K_{oc} | 111.0000 | 1784.0000 | 1742.0000 |
| r^2 | 0.9258 | 0.9506 | 0.9647 |
| Desorption | | | |
| K_{des} | 152.4000 | 120.7000 | 58.0000 |
| 1/n | 0.4696 | 0.2050 | 0.5041 |
| K_{oc} | 190.2000 | 952.6000 | 1629.2000 |
| r^2 | 0.9349 | 0.9943 | 0.948 |

fenvalerate was significantly different for the soil types studied. The highest adsorption was in the sandy clay soil ($K_{ads} = 226.5$), followed by the silty soil ($K_{ads} = 89.4$) and the sandy clay loam soil ($K_{ads} = 62.7$). The K_{oc} values in the sandy clay soil, sandy clay loam soil and silty soil were 1784, 1742 and 111, respectively. The high K_{oc} value for the sandy clay soil suggests a high adsorption of fenvalerate onto the soil particles. The low K_{oc} value for silty soil suggests a lower adsorption of fenvalerate to silty soil. The K_{ads} value, which is considerably lower, confirms that fenvalerate is less adsorbed onto silty soil.

Desorption study: The desorption isotherm also conformed well to the Freundlich equation (Table 2). The 1/n of the Freundlich desorption equilibrium for all the soil types was greater than 1, which indicated that the desorption percentages were positively correlated with the total insecticide adsorbed (Fig. 2). The K_{des} value was highest in the silty soil (152.4), followed by sandy clay soil (120.7) and lowest in the sandy clay loam soil (58.0). This shows weaker binding of fenvalerate to the silty soil and easier release into soil water than to the other two soils. Similarly, the K_{oc} value was highest in the sandy clay loam soil (1629.2), followed by the sandy clay soil (952.6) and lowest in the silty soil (190.2).

Mobility study: The results of the column leaching study are presented in Fig. 3. The leaching rate of fenvalerate in the column increased with increasing rate of simulated rain. These results are congruent with the findings of other researchers, who have demonstrated that simulated rain was positively correlated with the leaching rate of pesticides [3, 16, 17]. The rate of mobility through the soil column was highest in silt soil, followed by sandy clay and sandy clay loam soils. High mobility of fenvalerate in silt soil is correlated with high K_{des} (152.4), which is higher than those of the other two soils but lower in terms of K_{oc} (111). More residue of fenvalerate was available in soil water and large quantities of fenvalerate were found in the leachate of the silt soil, irrespective of the simulated rainfall. It is not surprising that fenvalerate residue was detected in the leachate of the silty soil column, even at 100 ml of simulated rain. However, in the sandy clay and sandy clay loam soil columns, no residues of fenvalerate were present in the leachate with 100 ml of simulated rain. Most of the fenvalerate residues in the column of sandy clay and sandy clay loam soils were detected in the topsoil layer and decreased with depth. The weak binding of fenvalerate to soil indicated by its significant desorption from the soil contributed to its high mobility in the soil column, especially in silt soil.

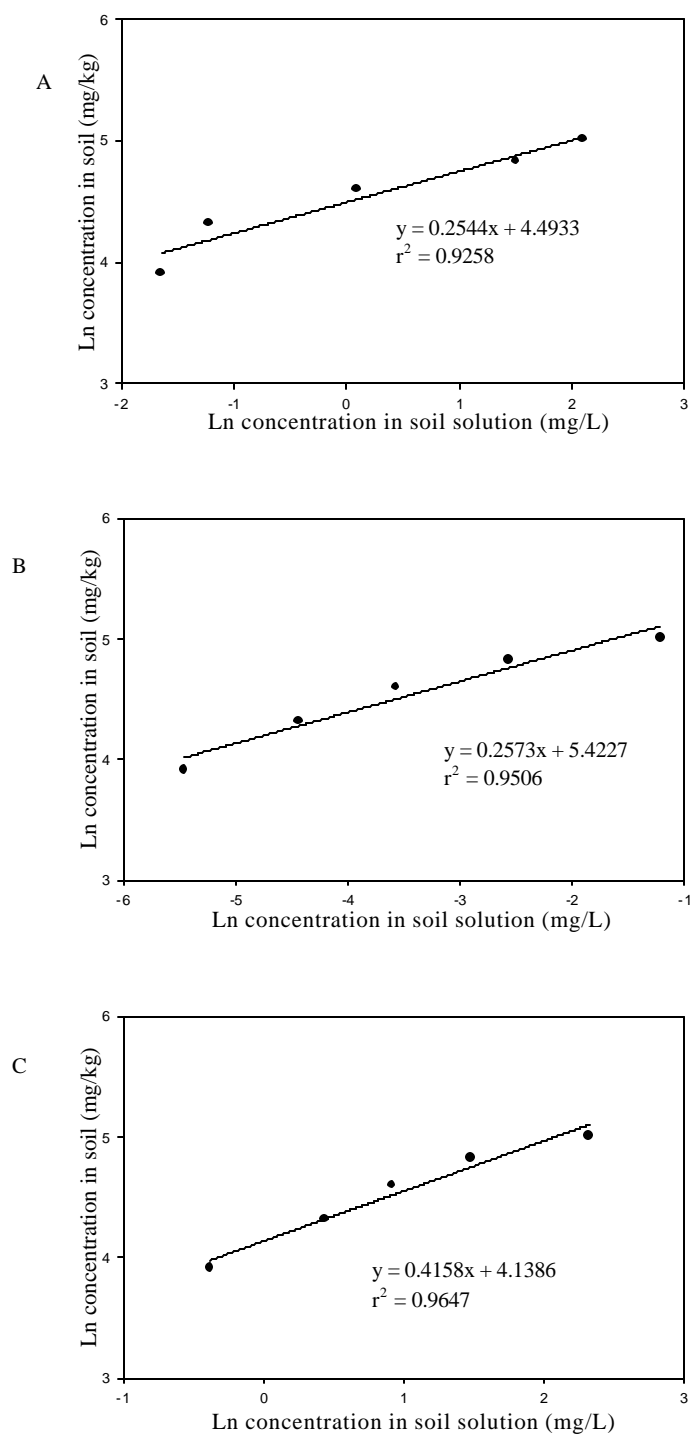


Fig. 1: Adsorption isotherm of fenvalerate in A) silty soil, B) sandy clay soil, C) sandy clay loam soil

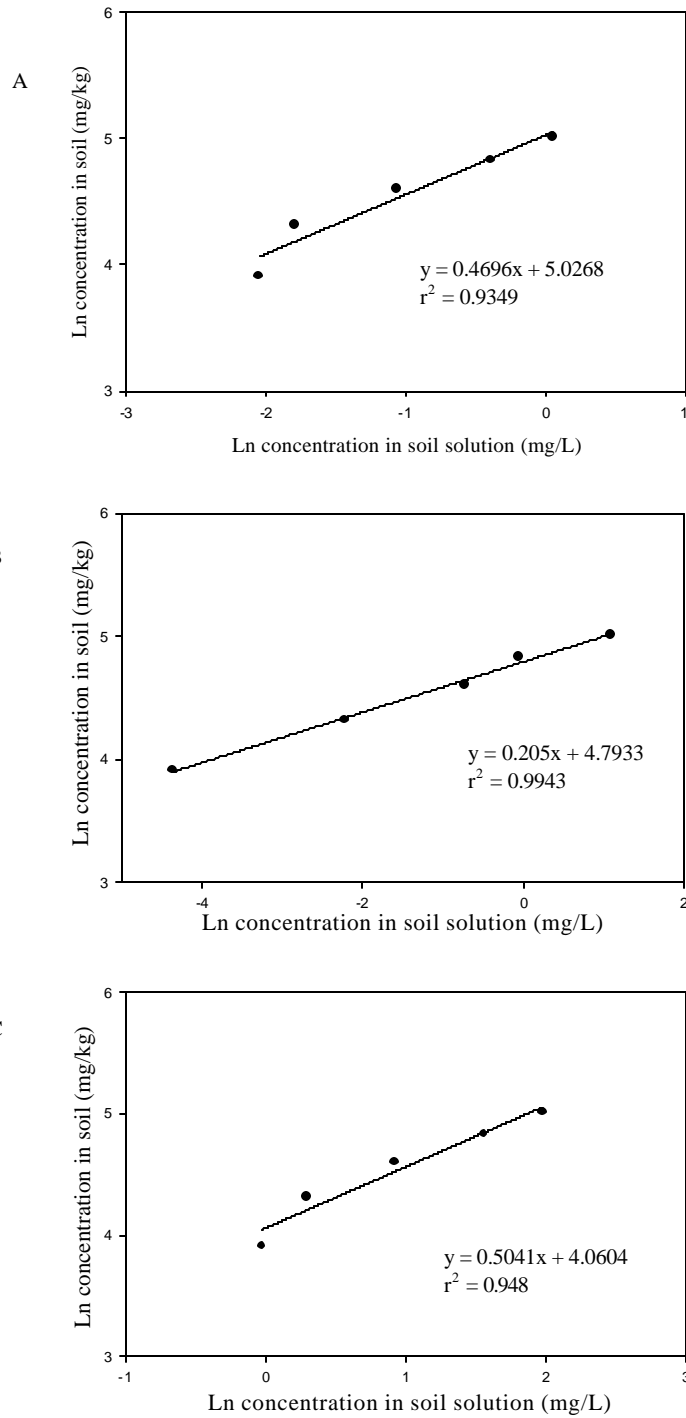


Fig. 2: Desorption isotherm of fenvalerate in A) silty soil, B) sandy clay soil, C) sandy clay loam soil

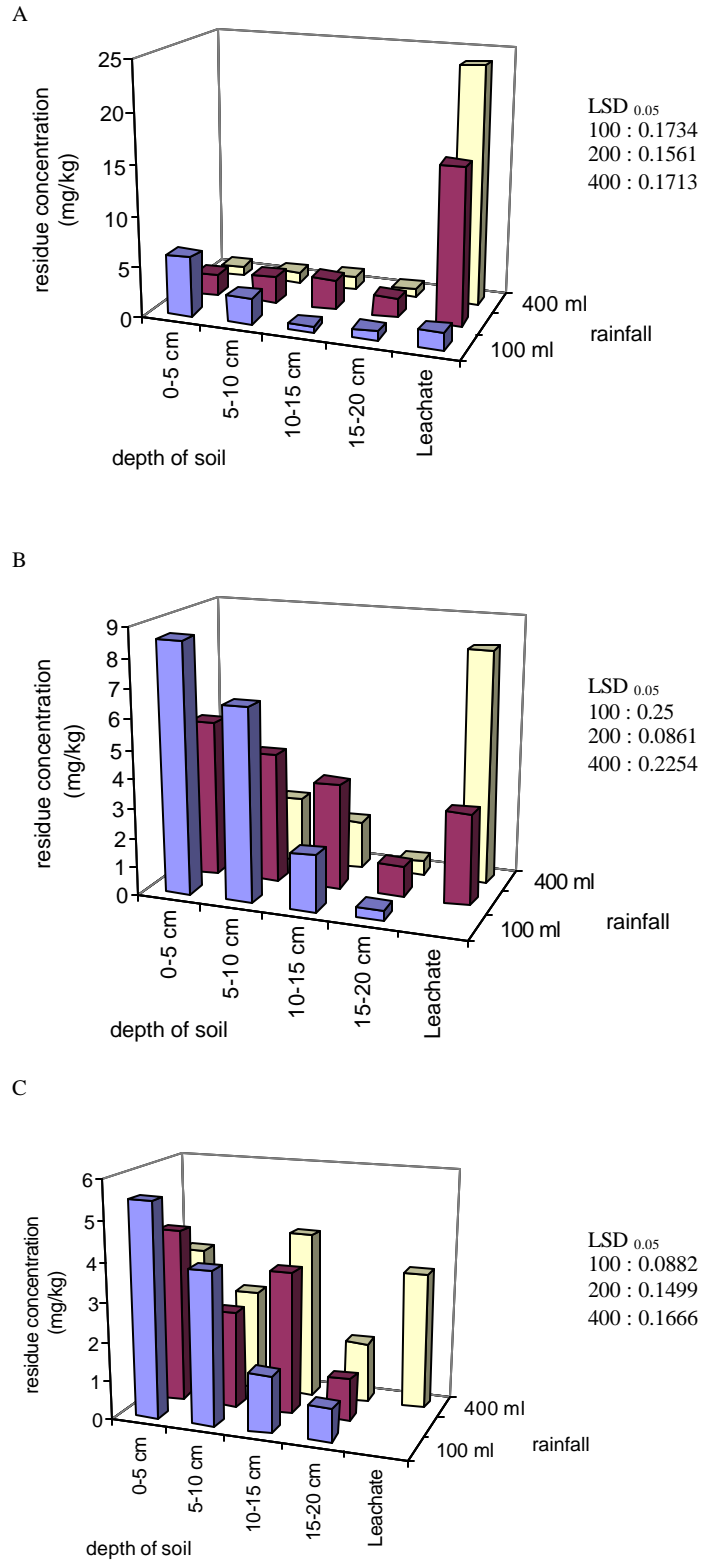


Fig. 3 : Mobility of fenvalerate in A) silty soil, B) sandy clay soil, C) sandy clay loam soil

It appears that the structure of the soil and the total organic matter content influences the mobility of fenvalerate in the soil column. Leaching of fenvalerate was faster in silty soil than in sandy clay and sandy clay loam, which is explained in terms of macropore flow. The downward mobility of the residue in a column may have been enhanced by the looser texture of the repacked soil, especially in silt soil, than the natural state of the soils in the field. A more effective macropore flow was also suggested to be the main reason why more fenvalerate leached in silt soil treated with less water input. This result is consistent with that of other researchers [18, 19], who showed that looser structure of the soil increased downward flow of the compound. Dissipation of fenvalerate residue in soil maybe attributed to the leaching process.

CONCLUSIONS

These adsorption-desorption studies demonstrate that fenvalerate possesses a stronger affinity to sandy clay soil than to silty soil and sandy clay loam soil. Fenvalerate is more mobile in silty soils than in sandy clay and sandy clay loam soils. However, other factors such as site hydrology, rates and frequency of pesticide application and persistence under local soil and environmental conditions are important considerations. Direct comparison in adsorption/desorption and mobility of fenvalerate in other soils and from other regions is difficult due to limited reports on this compound and the variety of different environmental conditions and soil types used in previous studies. Therefore, although this study has contributed to our knowledge about the behavior and fate of fenvalerate in a small array of tropical soils, further studies under field conditions need to be carried out to determine its potential to contaminate underground water in specific locations.

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