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Full Length Research Paper

Sorption of Cypermethrin from Alfisol and Inceptisol using acidified simulated rainwater in a soil column set-up

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Cypermethrin is a synthetic, pyrethroid insecticide and used for agricultural practices. The leaching of this pesticide through soil is of great concern because of the possibility of contaminating ground and surface water. The mobility of pesticide in soil being the main environmental reservoir varies among soil orders and the concept is still under investigation. Hence, this study was aimed at investigating the sorption capability of Alfisol and Inceptisol at different soil depth when leached with simulated rainwater of different pH values. The leachates were determined for cypermethrin concentration using a new UV/Visible spectrometry method. The CEC, organic matter content of Alfisol were 4.05±0.03 cmol/kg and 1.74±0.02%, while the corresponding characteristics of Inceptisol were 4.45±0.05 cmol/kg and 1.03±0.01%, respectively. pH of Alfisol and Inceptisol soil orders were 5.92 and 6.25, respectively. Simulated rainwater (pH 4) of 50, 100 and 150 mL leached out 37.0±0.1, 43.1±0.1 and 59.4±0.2% of cypermethrin, respectively from Alfisol at soil depth of 10 cm. At pH 6.8, the corresponding volumes of simulated rainwater leached out 31.8±0.1, 35.4±0.1 and 37.4±0.1% of cypermethrin, respectively. For each soil order, these proportions of sorbed cypermethrin decreased progressively as soil depth increased from 10-30 cm. The proportions of cypermethrin sorbed by Inceptisol were more than the corresponding proportions sorbed by Afisol. Afisol has high clay and organic contents, which might be responsible for its surpassing potential to sorb cypermethrin compared to Inceptisol.

Key words: Pyrethroid insecticide, leaching, Alfisol-Inceptisol soil orders, simulated rainwater, UV/Visible spectrometry.

INTRODUCTION

Increase in food production is a major target of all countries as the world population increased yearly (Saravi and Shokrzadeh, 2011). The demand for food by the entire world population cannot be met without improving crop production. Technological advances involving the utilization of agrochemicals have contributed considerably to increasing yields and regular crop production (Aubertot et al., 2007). The process of

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increasing crop production currently demands for the application of herbicides, insecticides, fungicides, fertilizers and soil amendments in higher quantities than in the past (Adeyinka and Mustapha, 2005). The demand for the use of pesticides is not restricted to developing countries. Crop productivity has increased dramatically in most developed countries such as United Kingdom and USA where wheat and corn yield increased (Akhtar et al., 2009). French farming has also developed production system based on the application of pesticides (Aubertot et al., 2007). The use of organochlorine pesticide has since been banned for agricultural practices in all these developed countries, but is still in use in developing countries like Nepal (Sharma et al., 2013), Egypt (Ibitayo, 2006) and Nigeria (Aiyesanmi and Idowu, 2012; Ize-Iyamu et al., 2007). As much as pesticides play a vital role in agricultural setting, adverse consequences to non target organism as well as human often occur (Vijverberg and vanden Bercken 1990).

The applied pesticide retained by soil is often released through a number of mechanisms into ground water and surface water. Weakly sorbed pesticides are lost from soil through storm run-off and percolation mechanisms (Ismail et al., 2013). The transport and fate of pesticides in soil are greatly affected by many processes such as volatilization, leaching, sorption, chemical and biological degradation (Hayward et al., 2009; Nolan et al., 2008). Of all these processes, sorption of pesticides readily occur as either rainwater or irrigation water percolates the soil column to affect the environment. Among the available pesticides, cypermethrin is one of the most stable pyrethroids whose soption potential in soil is still generating research interest. It was reported that pyrethroid is unlikely to undergo significant migration because of its strong tendency to adsorb to soils and organic matter. However, cypermethrin has been found in groundwater in France (Legrand et al., 1991) and surface water and sediment in the United Kingdom (House et al., 1991). The migration of cypermethrin to the environmental media seems to be generating public interest and concern due to its increasing use and potential effects on food crop and aquatic system. This concern necessitated further investigation to its sorption capacity in different types of soil. The sorption of pesticides is always influenced by some soil properties such as soil type, soil texture, organic matter content, soil pH and temperature. Several studies on cypermethrin have been reported, which include toxicity, occupational exposure and environmental impact studies (Abu-Zreig et al., 2000; Chauhan et al., 2012; Ismail and Kalithasan, 2004; Ismail et al., 2013; Kaufman et al., 1981; Persson et al., 2008; Rani et al., 2014). There is still dearth of data on the sorption of cypermethrin with respect to soil type and nature of the solution that leaches the pesticide. Therefore, the objective of this study was to investigate the extent to which simulated rainwater solutions of different pH values can leach cypermethrin through different soil orders such as Alfisol and Inceptisol packed at different depths in a column. In a way, the understanding of how to define such soil orders better based on the adsorption capacity to immobilize pyrethroid insecticide will be established.

MATERIALS AND METHODS

Chemicals and standard solution preparation

Commercial grade of cypermethrin (10% Emulsifiable Concentrate) were obtained from Jubaili-Agrotec, Beirut Lebanon. Appropriate dilutions of the 10% emulsifiable concentrate of cypermethrin were done with ethanol and used for the experiments. The analytical grade of cypermethin (100 µg/mL) was obtained from Sigma Aldrich, Germany. For the calibration curve, working standard solution of 1.0 – 6.0 µg/mL were prepared by appropriate dilution of the standard stock solution with ethanol. Alfisol and Inceptisol which are cypermethrin-free soil classes were collected from Forestry Research Institute of Nigeria.

Soil sampling, preparation and characterization

The soil samples were collected in an aluminium foil and air-dried. The air-dried samples were manually ground to a fine powder mortal and passed through a 2 mm mesh. The physicochemical properties of the soil as shown in Table 1 were determined using the standard methods of analysis. The pH of soil samples was determined in a soil to water (1:1) suspension using a glass electrode. Organic matter contents of the soil samples were determined using the Walkley-Black method (Nelson and Sommers, 1982). The soil texture analysis was carried out using hydrometer method. Cation exchange capacity (CEC) of the soils were analysed by the sodium acetate method. The physicochemical analyses of the soil order were replicated five times.

Procedure for soil column set up

Three glass columns of 2.5 cm internal diameter each were used in the leaching experiments. The air-dried sieved soils were uniformly packed in each column to depths of 10, 20 and 30 cm, respectively. Another set of glass column was set up for control experiment Soil columns were tapped uniformly to ensure compact packing of the soil in the columns to the required depth. Each of the packed columns was clamped and supported by a retort stand.

Each column was packed with Alfisol and soaked with de-ionized water above soil level. The de-ionized water was then allowed to drain completely. Each column was spike with 5 mL of 10 mg/L cypermethrin. After 1 h, the three columns were eluted with varying volume of rainwater of pH 4.0 and 6.8 separately. The rainwater was collected without passing through roof material over some days and the pH was adjusted to 4.0 and 6.8 using 0.1 M HNO_3 to simulate the common pH range of rainwater acidity data. Clean rainwater has a pH value of 5.0-5.5 but can become much more acidic when combine with oxides of sulphur and nitrogen to give pH value of 4.0. The understanding of the acidification phenomenon of rainwater as available in the literature necessitated the choice of the pH values (Esmen and Fergus, 1976). Cypermethrin was leached down the Afisol with 50, 150 and 150 mL of simulated rainwater. The leachates were collected in a glass flask and cypermethrin concentrations were determined by UV/Visible Spectrometry (Spectro UV/Vis spectrophotometric version 3.5 Labomed Inc.). This procedure was replicated five times for Alfisol and repeated

Table 1. Physicochemical properties of Alfisols and Incetptisol.

Parameter	Alfisol	Inceptisol
pH	5.92 ± 0.02	6.25 ± 0.03
Cation exchange capacity (cmol/kg)	4.05 ± 0.03	4.45 ± 0.05
Organic matter (%)	1.74 ± 0.02	1.03 ± 0.01
Total organic carbon (%)	1.00 ± 0.01	0.60 ± 0.01
Sand (%)	19.2 ± 0.2	88.0 ± 0.3
Silt (%)	61.6 ± 0.4	4.8 ± 0.1
Clay (%)	19.2 ± 0.2	7.2 ± 0.1
Classification of soil	Sandy-loam	Sandy

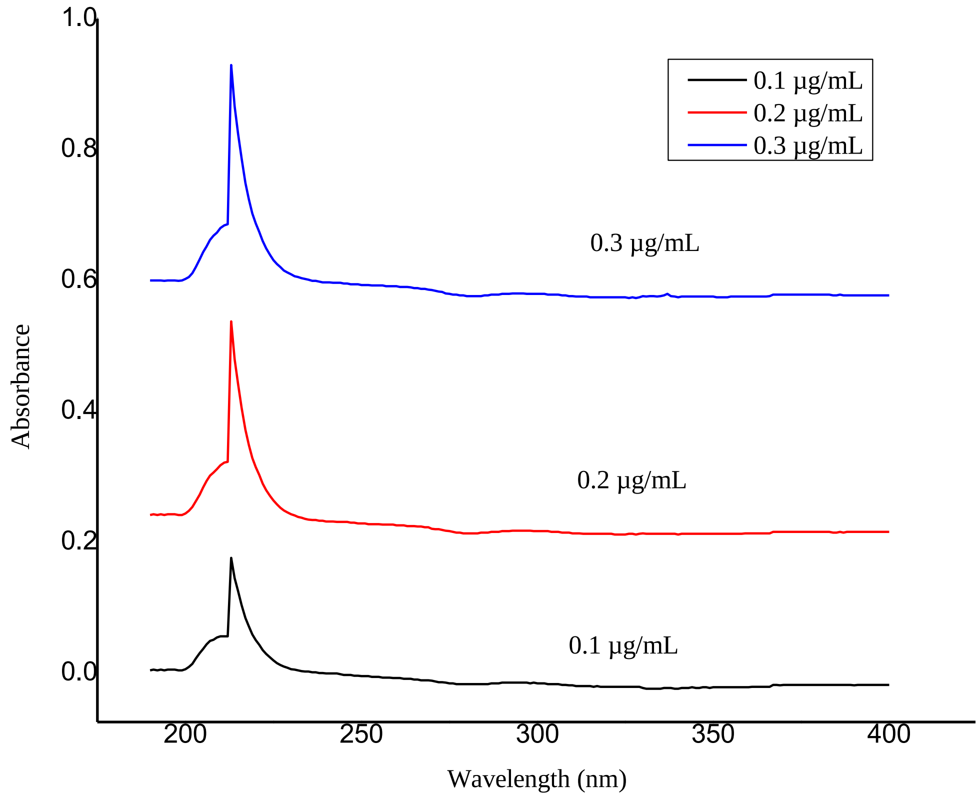

Figure 1. UV/Visible scanned spectrum of cypermethrin standards of different concentrations.

for Inceptisol. The columns for the control experiment at various soil depths were run with rainwater without spiking with cypermethrin.

Instrumental analysis

A sensitive spectrophotometric method was employed to determine the concentration of cypermethrin (Janghel et al., 2007). The wavelength for the UV/Visible spectrometric determination of cypermethrin was determined by scanning the absorbance of 0.1, 0.2 and 0.3 µg/mL of cypermethrin standard solutions. The solutions were prepared by adding 1 mL of 20% NaOH to little volume of each standard solution in a 25 mL volumetric. The solutions were kept for 10 min at room temperature for complete hydrolysis of cypermethrin. 1 mL of 0.1% potassium iodide in acidic medium was added followed by 1 mL leuco crystal violet indicator. The librated iodine selectively oxidizes the leuco base dye to liberate iodine. The solutions were kept for 15 min for full colour development and made up to the mark with ethanol. The absorbance values of the solutions were scanned through the wavelength range of 190 to 800 nm (Figure 1). The reagent blank had negligible absorbance at this wavelength. This procedure was followed for standard working solutions prepared for the calibration curve. Calibration curve was prepared using working standard solutions of 1.0 – 6.0 µg/mL prepared by appropriate dilution of cypermethrin standard stock solution of 100 µg/mL with ethanol. Ethanol was used because of the low solubility of cypermethrin in water. The absorbance values of the solutions were measured at

Table 2. Proportion (%) of cypermethrin leached by simulated rainwater of pH 4.0 from Alfisol and Inceptisol at various soil depths.

Soil depth (cm)	Alfisol			Inceptisol		
	50 mL	100 mL	150 mL	50 mL	100 mL	150 mL
10	37.0 ± 0.1[a]	43.1 ± 0.1[b]	59.4 ± 0.2[c]	39.5 ± 0.2[b]	46.6 ± 0.1[b]	66.6 ± 0.1[b]
20	35.4 ± 0.2[a]	36.5 ± 0.1[a]	40.1 ± 0.1[b]	37.0 ± 0.2[a]	43.5 ± 0.1[b]	63.2 ± 0.2[a]
30	32.1 ± 0.2[a]	35.7 ± 0.1[a]	37.7 ± 0.1[a]	35.2 ± 0.1[a]	38.1 ± 0.1[a]	62.6 ± 0.1[a]

Mean values along the column with different supercript (a,b,c) are significantly different.

213 nm against a reagent blank. The corresponding concentrations of cypermethrin were determined from the calibration curve whose R^2 value was 0.9847.

Procedure for cypermethrin analysis in leachates

1 mL of 20% sodium hydroxide was added to a 25 mL volumetric flask containing 1 mL of the leachate. After 10 min, 1 mL of 0.1% potassium iodide was added in acidic medium followed by 1 mL leuco crystal violet. The solution was shaken and allowed to stand for 15 min for full colour development. A light crystal violet solution obtained was made up to the mark with ethanol and the absorbance was measured at 213 nm against a reagent blank. The cypermethrin concentrations in the leachates were deduced from the calibration curve.

RESULTS AND DISCUSSION

Physicochemical characteristics of soil

Sorption behavior of pesticide is influenced by soil properties and pesticide characteristics, which are equally essential for the assessment of environmental fate of pesticide Both Alfisol and Inceptisol were acidic in nature, with pH of 5.92±0.06 and 6.25±0.03, respectively. Based on the soil texture composition, Alfisol was classified as sandy loam while Inceptisol as sandy. This implies that cypermethrin can permeate Inceptisol more than Alfisol due to its larger pores, thus allowing cypermethrin to move through rapidly. The higher permeability of Inceptisol over Alfisol can make it more sensitive than Alfisol that has low leaching potential. The clay content of Alfisol was observed to be almost thrice the content found in Inceptisol. Surface inorganic and organic functional groups in soil that play significant role in sorption process are associated with clay. Such functional groups include phenolic, carbonyl, and aluminol which are chemically reactive molecular units that have potential of binding unto pesticides such as cypermethrin. The fact that Inceptisol permits more pesticide movement rapidly is corroborated by its low organic matter content of 1.03±0.01% compared with Alfisol that has organic matter content of 1.74±0.02%. Organic matter improves soil water holding capacity and its high content for Alfisol compared to contents found in Inceptisol may be responsible for Afisol surpassing ability over Inceptisol to sorb cypermethrin. This suggests that Inceptisol was more sensitive to ground water contamination.

Impacts of simulated rainwater on the mobility of cypermethrin

The amount of rainfall is an essential factor in determining how far a pesticide can migrate down the soil. Simulated rainwater leached out appreciable proportion of cypermethrin from Alfisol and Inceptisol packed at various depths. The proportions of cypermethrin leached out with rainwater of pH 4 from Alfisol of depth 10 cm were 37.0±0.1, 43.1±0.1 and 59.4±0.2%, respectively. This proportion decreased as soil depth increased from 10 to 30 cm (Table 2). The corresponding proportions at soil depth of 30 cm were 32.1±0.2, 35.7±0.1 and 37.7±0.1%, respectively. For Inceptisol, rainwater of pH 4 leached out 39.5±0.2, 46.6±0.1 and 66.6±0.1% of cypermethrin for soil depth of 10 cm. These proportions of cypermethrin leached out for soil depth of 10 cm were significantly higher than ($P < 0.05$) the corresponding proportions for soil depth of 30 cm.

With the increasing volume of rainwater, the proportion of cypermethrin leached out increased for all the soil depths. This implies that more of cypermethrin applied on a farmland can be leached down soil depth by heavy downpour on the farmland compare to when the rain is not heavy. This seems to be different from the report that cypermethrin would remain mostly in top (0-10 cm) layer of Malaysian soils and that only small concentration (0.5 mg/kg) could be detected at 50 cm soil depth (Chai et al., 2012). Figures 2 and 3 show the concentrations of cypermethrin sorbed by the soil orders with soil depth. There was a progressive increase in the concentration of cypermethrin sorbed by both Alfisol and Inceptisol as soil depth increased.

Effects of pH on the mobility of cypermethrin in soil

Cypermethrin of 32.1 – 59.4% and 35.2 – 66.6% were leached from soil depth of 10 -30 cm containing Alfisol and Inceptisol respectively when eluted with the simulated rainfall of pH 4.0 (Table 2). In comparison, less proportions of cypermethrin was leached in Alfisol(26.2 - 37.4%) and Inceptisol (28.7 - 40.1%) when eluted with

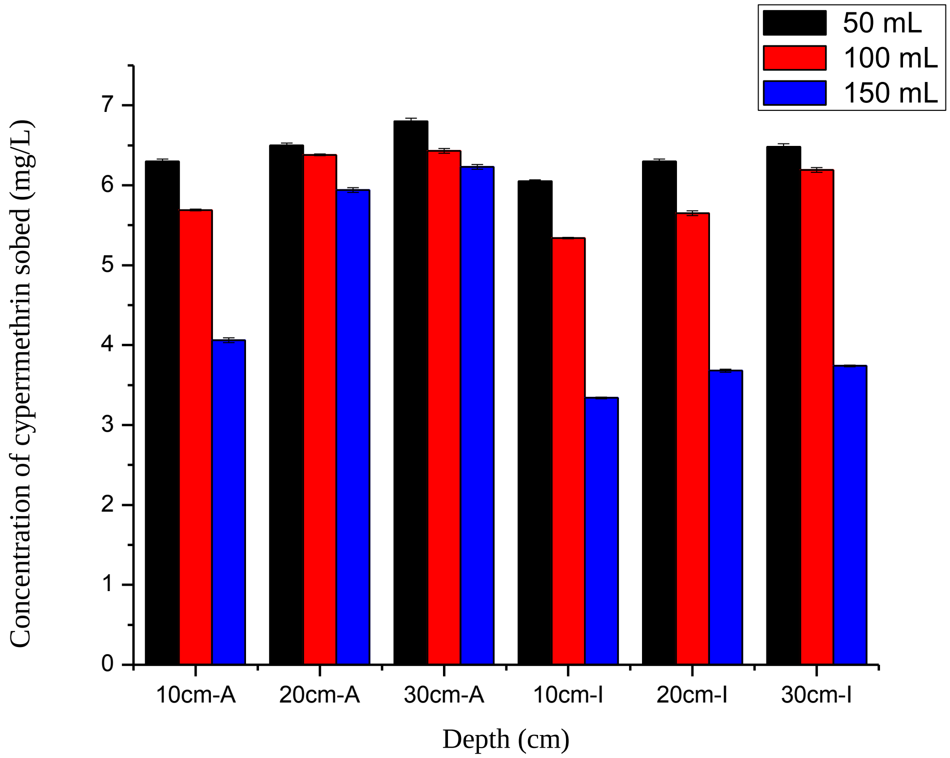

Figure 2: Variation of concentrations of cypermethrin retained by Alfisol (A) and Inceptisol (I) for rainwater of pH4

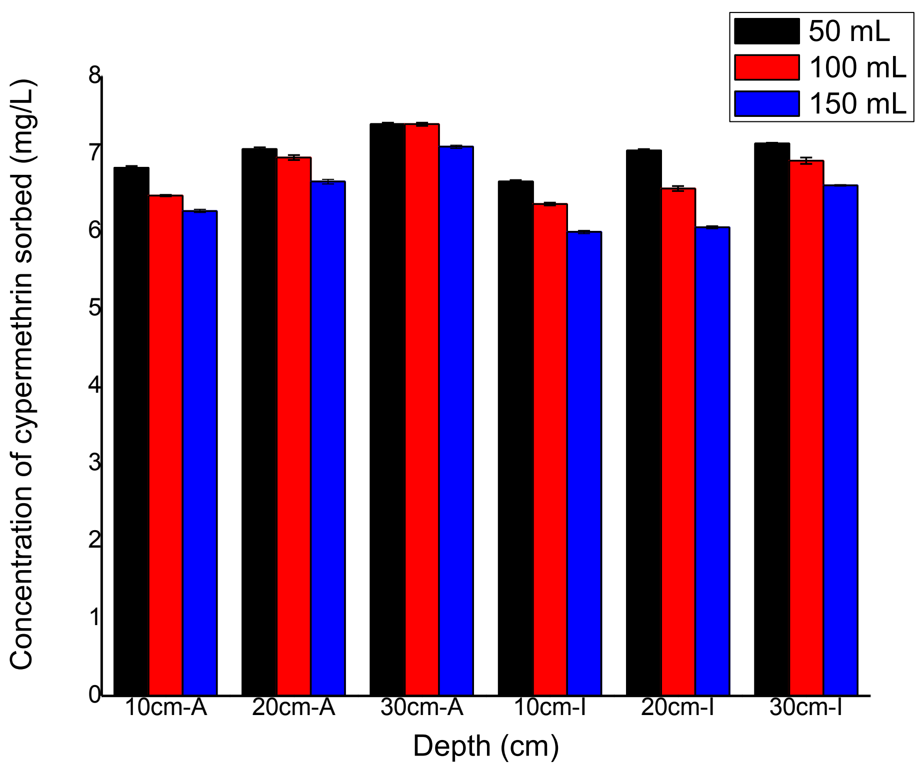

Figure 3. Variation of concentrations of cypermethrin retained by Alfisol (A) and Inceptisol (I) for rainwater of pH 6.8.

Table 3. Proportion (%) of cypermethrin leached by simulated rainwater of pH 6.8 from Alfisol and Inceptisol at various soil depths.

Soil depth (cm)	Alfisol			Inceptisol		
	50 mL	100 mL	150 mL	50 mL	100 mL	150 mL
10	31.8 ± 0.1[b]	35.4 ± 0.1[c]	37.4 ± 0.1[b]	33.6 ± 0.1[b]	36.5 ± 0.1[b]	40.1 ± 0.2[b]
20	29.4 ± 0.2[a]	30.5 ± 0.1[b]	33.6 ± 0.1[b]	29.6 ± 0.2[a]	34.5 ± 0.2[b]	39.5 ± 0.1[b]
30	26.2 ± 0.1[a]	26.9 ± 0.2[a]	29.1 ± 0.1[a]	28.7 ± 0.1[a]	30.9 ± 0.1[a]	34.1 ± 0.1[a]

Mean values along the row with different supercript (a,b,c) are significantly different.

simulated rainfall of pH 6.8 (Table 3). The proportion of cypermethrin leached from both soil orders at pH of 4.0 were much higher than the corresponding proportions leached at higher pH of 6.8. It can be deduced that more of cypermethrin is expected to be leached at lower pH than at neutral pH of the rainwater. This conforms to the observation on degradation of cypermethrin, malathion and dichlorovos in water and in tea leaves (Lin et al., 2012). In the study, more proportion of cypermethrin was leached from tea leaves when distilled water of pH 3.5 was used than when pH 6.8 was used for elution. Hydrolysis of cypermethrin by photolysis to either ester or nitrile acid metabolites occurs at higher pH particularly in alkaline condition. The photoproducts exert more toxic effect on beneficial and target insects (Al-Mughrabi et al., 1992).

Conclusion

Inceptisol has high leaching potential compared with Alfisol. Retention of cypermethrin in Alfisol cores was comparatively more than the retention found in Inceptisol. The surpassing ability of Inceptisol over Alfisol for leaching process of cypermethrin is attributable to its low clay and soil organic matter contents. There is likelihood that cypermethrin moves feely in Inceptisol because of its sandy nature to contaminate nearby groundwater and surface water. Sorption of pesticide by Alfisol and Inceptisol are pH dependent. More of the insecticide leached in both soils at lower pH than at neutral pH of rainwater. The texture of both Alfisol and Inceptisol played a crucial role in the mobility of cypermethrin through the soil.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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