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Leaching behaviour of chlorpyriphos and cypermethrin in sandy loam soil

Mamta Rani · Sunayana Saini · Beena Kumari

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Abstract The mobility of chlorpyriphos and cyperme thrin in sandy loam soil was studied in soil columns under laboratory conditions at two application rates, 25 and 50 μg, with simulated rainfall of 300 mm. Residues of chlorpyriphos and cypermethrin in soil and leachate were estimated by gas–liquid chromatography and confirmed by gas chromatography–mass spectrometry. Though maximum concentration of both the insecticides was found in the top 10-cm layer, chlorpyriphos was found distributed in the soil up to a depth of 35 cm and cypermethrin remained up to 15 cm. Results indicated the low mobility of both the insecticides under saturated moisture condition and hence may not contaminate ground water. No residues of any insecticide were detected in the leachate fractions.

Keywords Leaching · Chlorpyriphos · Cypermethrin · Sandy loam soil · Column · Residues

Introduction

Intensive agricultural practices often include the use of pesticides to enhance crop yields. However, the improvement in yield is sometimes concomitant with the occurrence and persistence of pesticide residues in soil and water (Ware and Whitacre 2004). Soil, an important component of the environment, acts as a sink for majority of the pesticides used in agriculture. It acts as a filter and buffer and has degradation potentials with respect to storage of pollutant through soil organic carbon (Burauel and Bassmann 2005). The fate of pesticides in the soil is greatly influenced by their interaction with soil components, the environment and their transport from one environmental compartment to another (Ismail and Kalithasan 2003; Racke 1993a, b). The rate of degradation of pesticides in the soil is one of the most important criteria that determine the behaviour of pesticides in the environment (Goring and Hamakers 1975). Heavy usage of pesticides in agriculture may cause adverse effects on the environment and, consequently, on human health. The leaching of pesticides into groundwater is a major environmental concern because it affects the quality of underground water (Lehmann et al. 1993). In India, a number of ready-mix formulations containing a mixture of an organophosphate and a synthetic pyrethroid are registered for use on various crops (Regupathy et al. 2004). Two such ready-mix formulations are Roket 44EC (profenophos 40 %+cypermethrin 4 %) and Action 505EC (chlorpyriphos 50 %+cypermethrin 5 %). These insecticides, separately or in combination, have been found effective in controlling insect pests of vegetables (Tripathi et al. 2003; Mishra 2002; Rao and Satpathy 1999). In this ready-mix formulation, chlorpyriphos (O, O-diethyl-O-3,5,6-trichloro-2-pyridyl phosphorothionate) is a broad-spectrum insecticide whose mode of activity is as a cholinesterase inhibitor. It is effective against both sucking and chewing insects and has been widely used to control pests of various

M. Rani · S. Saini · B. Kumari
Department of Chemistry and Physics, CCS Haryana Agricultural University, Hisar 125 004, India

M. Rani · S. Saini · B. Kumari (✉)
Department of Entomology, CCS Haryana Agricultural University, Hisar 125 004, India
e-mail: beena@hau.ernet.in

vegetables. It has low water solubility and sorbs strongly to soil particles. It is rapidly hydrolyzed to its primary metabolite, TCP, which is moderately mobile and persistent in soil (Racke 1993a, b; Jin and Webster 1998a, b). Cypermethrin is a highly hydrophobic insecticide with low solubility of 4 μg L^{-1} in water. It has a corresponding high octanal-water partitioning coefficient (log Kow of 6.6) indicating that it has a high affinity for sorption to soil organic matter (Tomlin 1994). It acts as both, a stomach poison and a contact insecticide (Jin and Webster 1998a, b). It is relatively non-persistent in soils with the typical half-life in sandy soils of 2–4 weeks (Chapman and Harris 1981). Increased cypermethrin persistence was observed in soil with high organic matter, high clay content, reduced microbial activity and anaerobic conditions (Chapman et al. 1981). Hydrolysis and photolysis play major roles in the degradation of cypermethrin in soil (Sakata et al. 1986). Despite the extensive use of chlorpyriphos and cypermethrin in agriculture, very little is known about their leaching behaviour in Indian soil. Since ground water is the main source of drinking and irrigation water, due to leaching of these insecticides, ground water may contaminate. Thus, to know the leaching potential of both insecticides in sandy loam soil and to assess the risk of ground water contamination, an experiment was carried out under laboratory conditions.

Material and methods

Chemicals and reagents

All the solvents used for this study were of analytical grade. Formulation Nurelle-D 505 (chlorpyriphos 50 % and cypermethrin 5 %) was procured from the local market. The analysis of the formulation in acetone extract with respect to its active ingredient of chlorpyriphos and cypermethrin was estimated using gas–liquid chromatography (GLC). The results showed that the concentrations of chlorpyriphos and cypermethrin in the formulation were correct as claimed by the manufacturer. Solvents like acetone, dichloromethane and hexane were procured from Merck, Darmstadt, Germany. Sodium chloride (ASC reagent grade ≥99.9 %) was also obtained from Merck, Darmstadt, Germany. Sodium sulphate anhydrous (AR grade) was from SD Fine Chemicals Mumbai. Activated charcoal decolorizing powder was obtained from Qualigens Fine Chemicals, Mumbai. All the common solvents were redistilled before use in glass apparatus and their suitability was ensured by running reagent blanks before actual analysis. The stock solution of ready-mix formulation was prepared at concentration of 100 μg ml^{-1}.

Preparation of standard solution

A standard stock solution of chlorpyriphos and cypermethrin having a concentration of 1 mg ml^{-1} was prepared in acetone. The standard solutions required for plotting a calibration curve (2.00, 1.50, 1.00, 0.50, 0.25 and 0.10 μg mL^{-1}) were prepared from stock solution by serial dilution using n-hexane. All standard solutions were stored at 4 °C.

Instruments

Analysis of chlorpyriphos and cypermethrin was carried out on gas chromatograph (GC) (Shimadzu Model GC-2010) equipped with ^{63}Ni electron capture detector supplied by Shimadzu, Kyoto, Japan. Confirmation of chlorpyriphos and cypermethrin was carried out on a gas chromatograph coupled with mass detector on a GC-MS/MS Model—Agilent 7890 coupled with mass detector (Mass 7000 GC/MS Triple Quadrupole).

Experiment

The leaching experiment was conducted under laboratory condition. Soil was collected from the Research Farm, CCS Haryana Agricultural University, Hisar, with no history of pesticide application. Soil was air dried in shade, ground and sieved through 2-mm sieve. Soil was sandy loam. Other relevant parameters of soil were as follows: EC 2dSm^{-1}, pH 7.6 and organic carbon 0.67 %. Commercial ready-mix formulation (Nurelle D) was used for leaching experiment. Plexiglass columns (90×5 cm internal diameter) fitted with a perforated sieve covered with filter paper (Whatman No. 1) was used. Each column was sequentially filled with soil up to the height of 60 cm to a bulk density of 1.35 g cm^{-1}. Weighed amount of soil (137 g) was poured in the column each time. The process was repeated till each column was uniformly filled to a height of 60 cm. The experiment was conducted with triplicates and a blank. Before packing, the filter paper

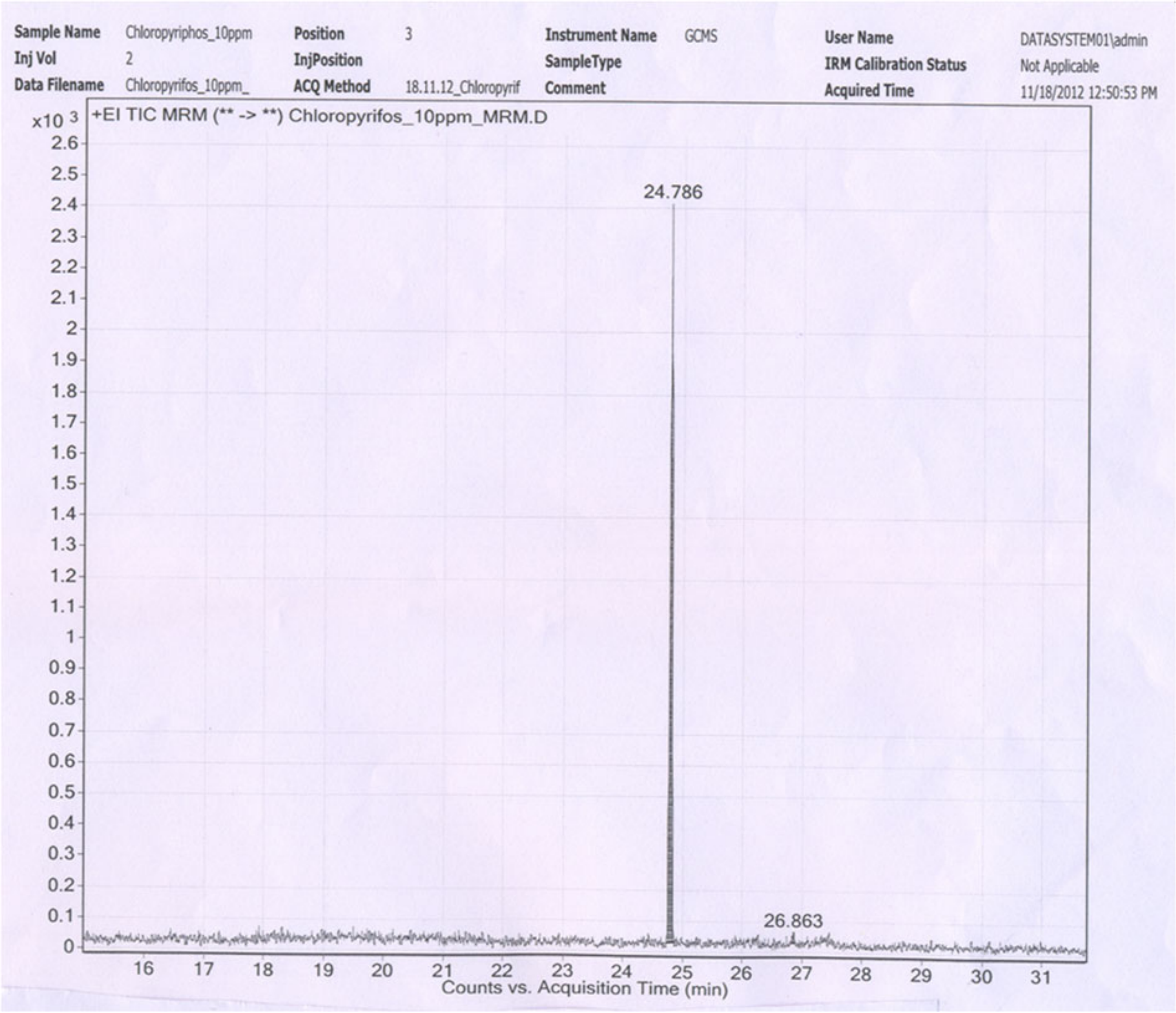

Fig. 1 Retention time (R_t) observed for chlorpyriphos in MRM mode

was kept at the perforated distal end of the column to allow only the passage of leachates. Ready-mix formulation was dissolved in deionized water and simultaneously applied to the last 5 cm of the soil in the column at the dose of 25 and 50 μg as single and double dose, respectively. After application of premix formulation, the columns were irrigated with 98 ml of water daily (equivalent to 300 mm rain) at the time interval of 24 h. After 6 days, when addition of water was completed, the soil columns were allowed to drain for 36 h. Three leachate fractions were collected from each treatment. Columns were then cut into two equal halves and the soil was sampled in 5-cm segments. The segments from the same column were pooled for use in analysing residues.

Extraction and clean-up

Chlorpyriphos and cypermethrin residues from soil and leachates were processed as per method of Kumari et al. (2008). Ground, sieved and dry representative subsoil (15 g) was mixed with activated charcoal and Florisil (0.3 g each) and 10 g anhydrous sodium sulphate. The mixture was packed compactly in a glass column (60 cm×22 mm i.d.) in between two layers of anhydrous sodium sulphate. The residues were eluted with 125 ml

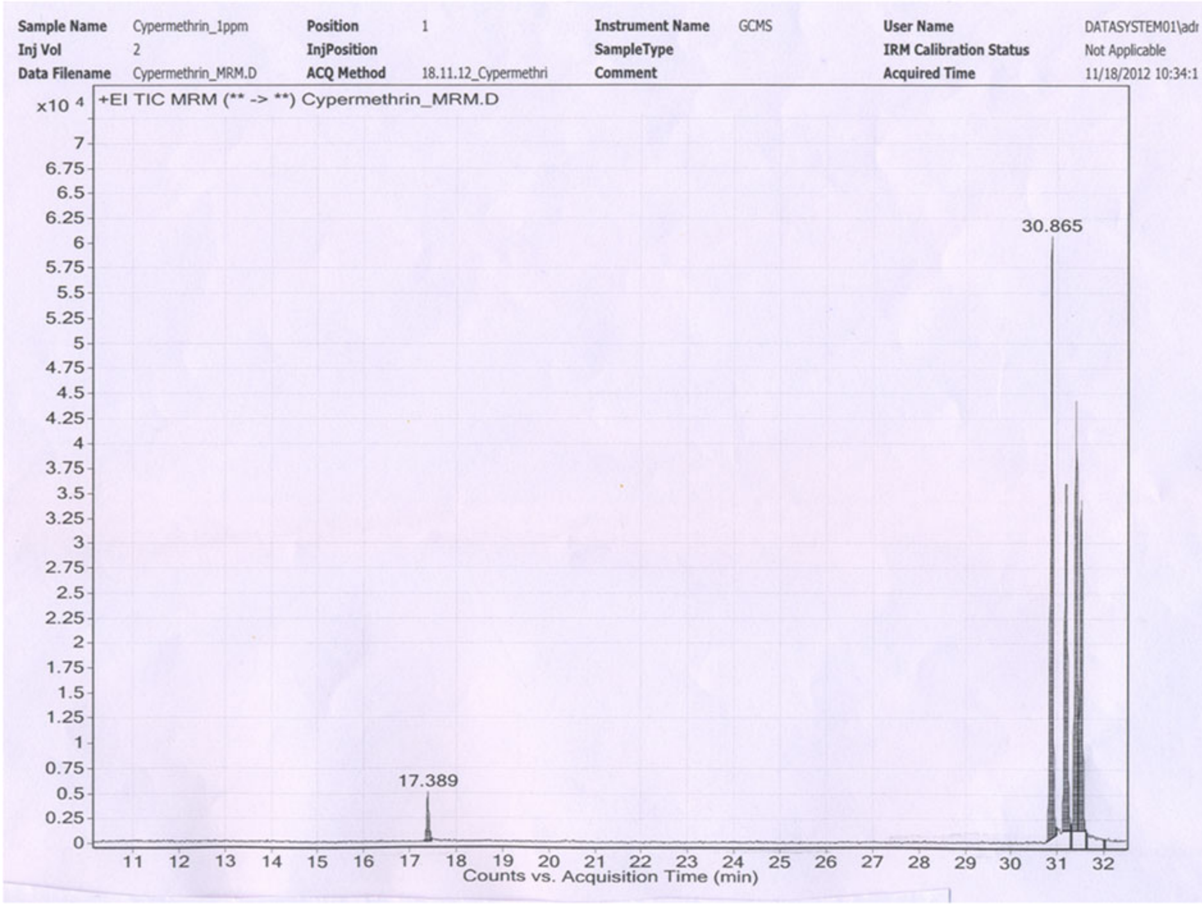

Fig. 2 Retention time (R_t) observed for cypermethrin in MRM mode

hexane: acetone (9:1 *v*/*v*) mixture. The elute was concentrated on a rotary vacuum evaporator and final volume was made to 2 ml in n-hexane. Leachate samples collected were subjected to liquid–liquid partitioning with dichloromethane: hexane (15:85 *v*/*v*) thrice after addition of 5 % NaCl solution. The organic layer was collected and concentrated on the rotary vacuum evaporator up to 10 ml.

Table 1 Recovery studies of chlorpyriphos and cypermethrin in soil

Substrate	Level of fortification (mg kg^{-1})	Chlorpyriphos % recovery* ± SD	Cypermethrin % recovery* ± SD
Soil	0.01	86.35±4.03	85.42±2.25
	0.10	88.05±2.95	91.22±3.46
	0.25	89.60±1.90	93.05±3.92
Water	0.01	93.06±2.60	92.50±2.66
	0.10	94.60±3.40	93.60±4.20
	0.25	97.80±5.10	95.10±4.60

*Average of three replicates

Estimation by GLC

Residues of chlorpyriphos and cypermethrin were quantified on a GC (Shimadzu Model GC-2010) equipped with capillary column HP-1 (30 m×0.32 mm i.d×0.25-μm film thickness of 5 % diphenyl/95 % dimethyl polysiloxane). Other GC parameters were as follows: temperature (in degrees Celsius): column: 150 (5 min^{-1})→8 min^{-1}→190 (2 min)→15 min^{-1}→280 (10 min). Injection port, 280 °C, Detector, 300 °C; carrier gas (N_2) flow was maintained at 30 and 2 ml min^{-1} through column with split ratio 1:10. Retention time (*Rt*) observed for chlorpyriphos was 13.924 and for cypermethrin were 20.723, 20.844 and 20.978 min.

Table 2 Leaching behaviour of chlorpyriphos in sandy loam soil

Depth (cm)	Residues (μg)*		Mean
	T_1 (25 μg) Average ± SD	T_2 (50 μg) Average ± SD	
0–5	7.50±0.031 (34.09)	15.02±0.052 (33.67)	11.260
5–10	5.25±0.002 (23.86)	10.50±0.029 (23.54)	7.875
10–15	3.80±0.015 (17.27)	8.20±0.003 (18.38)	6.000
15–20	2.05±0.067 (9.31)	4.65±0.019 (10.42)	3.350
20–25	1.20±0.001 (5.45)	3.50±0.005 (7.84)	2.350
25–30	0.80±0.003 (3.63)	1.12±0.002 (2.51)	0.960
30–35	0.40±0.007 (1.81)	1.05±0.001 (2.35)	0.725
Mean	3.000	6.291	

No residues were detected in leachate

CD ($p \geq 0.05$): treatment=0.017, depth=0.031, treatment×depth=0.044

*Average residues of three replicates; Figs. in parentheses are % retention of residues

Confirmation by GC-MS

Confirmation of chlorpyriphos and cypermethrin was achieved by gas chromatography mass spectrometer (GC-MS) in single ion monitoring mode. A capillary column (30 m×250 μm×0.25-μm film thickness) was used for confirmation of these residues. The GC-MS operating conditions were: Oven (programme) initial temperature was 70 °C and held for 2-min ramped 25 °C min^{-1} to 150 °C which was held for 0 min, then ramped 3 °C min^{-1} to 200 and held for 0 min then again ramped 8 °C min^{-1} to 280 °C and held for 1 min; injector temperature 280 °C. Helium was used as a carrier gas with a flow rate of 1 ml min^{-1}. Injection volume was 2 μl with a split ratio of 1:10. On the basis of the above information, a programme was developed in product ion monitoring mode with molecular mass 350.6 in chlorpyriphos at four different collision energies of 5, 10, 15, and 20 and MS_1 range starting from 250 and MS_2 range ending at 350. The *Rt* in multiple reaction monitoring (MRM) mode for chlorpyriphos was observed to be 24.786 min (Fig. 1) and for cypermethrin as 30.865 min. (Fig. 2).

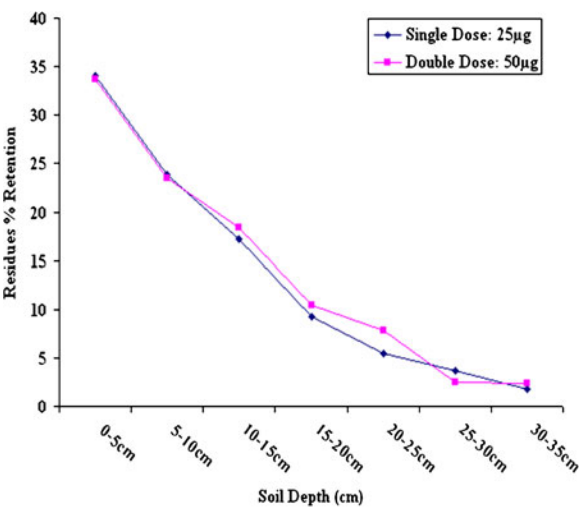

Fig. 3 Percent retention of chlorpyriphos at 0–35 cm soil depths

Result and discussion

Efficiency of the method

In the present investigation, recovery experiments were carried out at different levels to establish the reliability and validity of analytical method and to know the efficiency of extraction and clean-up procedures for soil and water. The control samples of soil and water were spiked at 0.01, 0.10 and 0.25 mg kg^{-1}, respectively, and processed by following the methodology as described above. Mean recoveries of chlorpyriphos and cypermethrin in soil were found to range from 85.42 to 93.05 % and in water ranged from 92.50 to 97.80 % (Table 1). The average recovery values from the fortified samples were found to be more than 85 %. Therefore, the results have been presented as such without applying any correction factor. The parameters like limit of detection (LOD), limit of quantification (LOQ), precision and accuracy were derived keeping in view the guidelines as mentioned by Thompson et al.

Table 3 Leaching behaviour of cypermethrin in sandy loam soil

Depth (cm)	Residues (μg)*		Mean
	T_1 (25 μg) Average ± SD	T_2 (50 μg) Average ± SD	
0–5	20.05±0.005 (87.93)	39.80±0.003 (85.59)	29. 925
5–10	2.60±0.002 (11.40)	4.10±0.001(8.81)	3. 350
10–15	BDL	2.05±0.002 (4.40)	1. 025
15–20		BDL	
Mean	7.550	15.317	

No residues were detected in leachate

CD ($p \geq 0.05$): treatment=0.001, depth=0.001, treatment×depth=0.001

*Average residues of three replicates; Figs. in parentheses are % retention of residues

(2002). Accordingly, the LOQ was found to be 0.01 mg kg^{-1} and LOD being 0.003 mg kg^{-1}.

The results of chlorpyriphos at different soil depths are presented in Table 2. The results showed that chlorpyriphos leached up to the depth of 35 cm at 300 mm rainfall condition. The maximum concentration was found at 0–5 cm soil depth. In T_1, it was 7.50 and 15.02 μg for T_2 dose. Percent distribution of chlorpyriphos in different soil cores (0–5, 5–10, 10–15, 15–20, 20–25, 25–30 and 30–35 cm) was 34.09, 23.86, 17.27, 9.31, 5.45, 3.63 and 1.81, respectively, at single dose. In case of double dose, percent distribution of chlorpyriphos was 33.67, 23.54, 18.38, 10.42, 7.84, 2.51 and 2.35 % at 0–5, 5–10, 10–15, 15–20, 20–25, 25–30 and 30–35 cm depth, respectively. Percent retention of chlorpyriphos to the depth of 0–35 cm in sandy loam soil is presented in Fig. 3. Thus total chlorpyriphos was retained between 57.95 and 57.21 % at single and double doses, respectively.

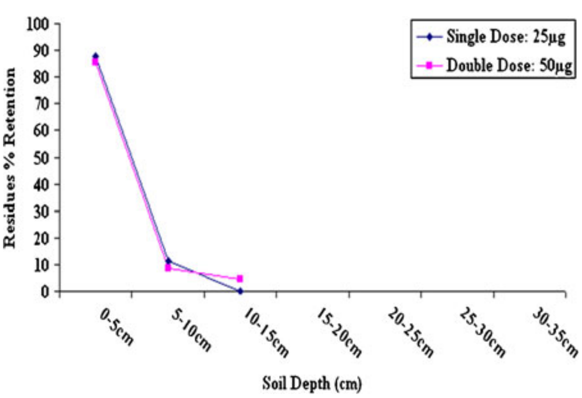

Fig. 4 Percent retention of cypermethrin at 0–20 cm soil depths at two application rates

None of the leachate fractions from both the treatments showed the presence of chlorpyriphos residues.

The data on leaching potential of cypermethrin in sandy loam soil revealed (Table 3) that the total amount of cypermethrin recovered out of 25 and 50 μg were 98 and 91 % from single and double dose, respectively. Percent distribution of cypermethrin in different soil cores (0–5 and 5–10 cm) was 87.93 and 11.40 %, respectively, at single dose. In case of double dose, percent distribution of cypermethrin was 85.59, 8.81 and 4.40 % at 0–5, 5–10 and 10–15 cm depth, respectively. Beyond the depth of 15 cm of soil, the amount of cypermethrin could not be detected in any of the doses. None of the leachate fractions from both the treatments showed the presence of cypermethrin residues. Percent retention of cypermethrin to the depth of 0–15 cm in sandy loam soil is presented in Fig. 4.

The recovered amount of chlorpyriphos and cypermethrin residues at various soil depths were analysed statistically at 0.05 probability level. Significant differences on the recovered amount of chlorpyriphos and cypermethrin at various depths were observed at both application rates. Irrespective of soil depth, residue levels were significantly low in single dose compared to double dose. Chlorpyriphos was retained between 57.95 and 57.21 % at single and double dose, respectively. Whereas cypermethrin was retained between 99.33 and 94.50 % in 0–10 cm core of soil in single and double dose showing very low mobility of this insecticide in soil. Retention of cypermethrin in soil cores was comparatively more than chlorpyriphos in both the doses. None of the leachate fractions contained residues of any insecticides in both the doses. Hence, both the insecticides seem to be safe for ground water.

Several factors such as adsorption of the pesticide by the soil particles, water solubility of the pesticide, volume of leachate, pH and soil texture can influence the leaching of the pesticide through the soil (Kidd and James 1991; Crisanto et al. 2000; Halimah et al. 2004). The present results are in agreement with earlier reports. Halimah et al. (2011) reported that the residues of chlorpyriphos remained within depth (0–45 cm), no residues were detected onwards (0–45 cm) soil core after 7 days of application. Ismail et al. (2004) studied the mobility of chlorpyriphos in sandy loam and reported that chlorpyriphos residue was detected at a depth of 0–50 cm 1 day after application. The mobility of the pesticide was greater in the sandy loam because of its lower adsorption. Other researchers (Walker et al. 1989; Walker and Exposito 1998) proved that organic matter had an influence on the adsorption of pesticides in the soil, and leaching potential of pesticides in the soil is influenced by the soil's physico-chemical properties as its organic matter content and the solubility of the compound. Muhamad et al. (2010) studied the leaching of chlorpyriphos in an oil palm plantation in Sepang in which chlorpyriphos residue was detected at 0–10 and 10–20-cm depths when applied at the recommended and double the recommended dosages, respectively. Chia and Zaidel (2011) studied the sorption, degradation and leaching of cypermethrin in three types of soils, and found that cypermethrin remains in the top 0–10 cm layer of the three soils. Manoj and Gajbhiye (2007) also reported similar results where mobility of bifenthrin in soil was low. Its residues remained within the top 15 cm and more than 99 % of residues were recovered from the top 0–10 cm layer. Tariq et al. (2006) observed the highest concentrations of λ-cyhalothrin in the top 0–10 cm layer. Gupta and Gajbhiye (2002) reported that the residue of β-cyfluthrin recovered was more than 99 % from 0–5 cm depth. The possibility of its leaching to ground water is negligible because of its immobility. No leaching was found by Sakata et al. (1986) in case of cypermethrin in three types of soils. Kotoula-Syka et al. (1993) reported that more leaching occurred at higher concentrations of the insecticides. Oppong and Sagar (1992) found that most pesticides persist longer in soils with high organic matter content. Hence, the results of the present studies have been well corroborated by the findings of other researchers.

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