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GAS CHROMATOGRAPHIC STUDIES OF FENPROPATHRIN ON CHILLI

Sushil, Reena Chauhan, Sushma Bisht and Beena Kumari
Department of Entomology
Chaudhary Charan Singh Haryana Agricultural University
Hisar-125004, Haryana

ABSTRACT

Persistence behaviour of fenpropathrin in chilli and soil under crop in field conditions were studied by applying fenpropathrin formulation (Danitol10 EC) @ 375 (T_1) and 750 (T_2) g a.i ha^{-1} at fifty percent fruiting stage. Samples of chilli and soil were collected periodically on 0 (1 h after spray), 1, 3, 5, 7, 15 and 30 days after applications. Residues of fenpropathrin were estimated by GC-ECD system equipped with capillary column. Initial residues of 0.413 and 0.946 mg kg^{-1} on 0 day on chilli in T_1 and T_2 dose, respectively reached to below detectable level (BDL) of 0.01mg kg^{-1} after 15 days. In soil also, residues persisted upto 15 and 30 days in respective doses. The half-life values of fenpropathrin in chilli were recorded to be 3.10 and 3.30 days and 6.95 and 7.94 days in soil at, respective doses.

Keywords Fenpropathrin. Chilli. Dissipation. Soil. Half-life. Residues. Below detectable level.

Introduction

Chilli (*Capsicum annum* L.) is most widely used and universal spice of India. It has excellent nutritive value and rich in vitamins, especially in vitamin A and C [10]. It is an essential pillar of the cuisines of India and the most important condiments having immense commercial and therapeutic value [11]. India is the world's largest producer, consumer and exporter of chilli peppers [2]. There are several factors which could be attributed for low production of chilli in the country, one of the most important factor is the damage caused by various insect pests. The crop is ravaged by a wide array of insect pests, including 51 species of insects and two species of

mites which belong to 27 families under nine orders in both the nursery as well as the main field resulting in yield losses [5].

Among the different classes of pesticides, pyrethroids are most commonly used for controlling crop pests. Now days, they are widely used because of their effectiveness against various insects, low dosage, and advantageous environmental properties such as photostability and nontoxicity to mammals [1]. Fenpropathrin (a-cyano-3-phenoxybenzyl-2, 2, 3, tetramethyl cyclopropane carboxylate), a typical pyrethroid insecticide used as an acaricide/ insecticide to control many species of mites and insects on cotton field crops, glass house crops, vegetables etc. Appreciable level of pyrethroid residues can occur in food commodities from crops, food of animal origin (eg. milk, eggs and meat), soils, sediments, and surface, ground and drinking water [9].

The presence of pesticide residues in food commodities is a matter of concern to human health due to the toxic nature of pesticides. Hence, it is imperative to study the persistence of pesticides on edible crops to ensure human safety. It is also important to ensure that the level of harvest time residues of pesticides on foodstuffs do not pose any hazard to consumers and are admissible in domestic as well as international trade. In this context, the present study was carried out to investigate the residual behavior and risk assessment of fenpropathrin on chilli fruits at different time intervals.

Materials and methods

Fenpropathrin (Danitol 10 EC) used for field application was procured from local market. Solvents and reagents like dichloromethane, acetone, sodium chloride, and anhydrous sodium sulfate all were procured from Merck (Darmstadt, Germany). Before use all the common solvents were redistilled in glass apparatus. By running reagent blanks the suitability of all the solvents was ensured before actual analysis.

Field experiment was conducted at University Research Farm, Department of Entomology, CCS Haryana Agricultural University Hisar, Haryana, India under recommended agronomical practices. Fenpropathrin formulation (Danitol 10 EC) was applied @ 375 (T_1) and 750 (T_2) g a.i ha^{-1} on the chilli crop (*Variety*: HPH-2024) with Knap Sack sprayer in plots of $25m^2$ size, along with a control plot where no insecticide was applied. The soil under crop was of light texture, other relevant properties of the soil were EC $2dSm^{-1}$; K 10.08, P_2O_5 15 kg ha^{-1} with pH 7.6 and organic carbon 0.67 percent.

About ¼ kg (250g) of green chilli fruits were collected randomly from each treatment including control at 0 (1 hr after spray), 1, 3, 5, 7, 15 and 30 days after spray, packed in polyethylene bags, and brought to the laboratory for processing. Soil samples under crop were also collected periodically with the help of a steel auger from a depth of 0-15 cm each plot in polythene bags and brought to the laboratory for further analysis. The samples were processed and analyzed at the Pesticide Residue Laboratory, Department of Entomology, CCS Haryana Agricultural University, Hisar.

Extraction and clean-up

Extraction and clean-up was performed as method of Bhardwaj et al. 2012 [3]. Finely chopped 25g representative sample of green chilli was macerated and shaken with acetone (100 ml) on mechanical shaker for 1 h and kept overnight in an Erlenmeyer flask. The extract was filtered in the separatory funnel, diluted with 600 mL brine solution (10% sodium chloride solution), and partitioned the contents twice (75, 75 mL) with dichloromethane. The combined organic layers were passed through anhydrous sodium sulfate. Aqueous layer was partitioned twice with hexane using 75 mL each time and collected hexane phase. Combined both, dichloromethane and hexane phases and treated with 300 mg activated charcoal powder for about 2–3 h at room temperature. When the solution became clear, it was filtered through Whatman filter paper no. 1. The clear extract so obtained was concentrated using a rotary vacuum evaporator at 50-55°C. The extract was finally made up to 2 ml and added to the liquid – solid chromatography column. The concentrated extract was transferred to the top of a glass (60cm x 22mm i.d) was packed compactly with silica gel (5g) in between two layers of anhydrous sodium sulphate and prewetted with hexane. The column was eluted with 125 ml solution of hexane: acetone (1:1v/v). Combined the organic phases and concentrated to about 5 ml on a rotary vacuum evaporator at 50-55°C. Finally, the extract was concentrated to dryness on gas manifold evaporator and final volume was made to 2ml in n-hexane and analysed by GC.

Soil

Soil samples were extracted and cleaned-up as per method of Kumari et al. 2008 [7]. The samples were air dried, ground and sieved (2 mm) before use. To the representative (15g) soil samples added 0.5 ml ammonia solution and kept for half an hour. Then added 10 g anhydrous sodium sulphate, 0.3 g Florisil and 0.3 g activated charcoal and mixed properly. Packed the homogenized sample compactly in a glass column (60 cm x 22 mm i.d.) in between two layers of

anhydrous sodium sulphate and eluted the column with 125 ml solution of hexane: acetone (9:1 v/v) at flow rate of 2–3 mL min^{-1}. Concentrated the eluate up to 5 ml on a rotary vacuum evaporator at 40°C followed by gas manifold evaporator to dryness. Final volume of the concentrated extract was reconstituted by adding n-hexane up to 2 ml and analyzed by GC.

Estimation by GLC

Gas chromatograph (Shimadzu-2010) equipped with ^{63}Ni electron capture detector (ECD) and HP-1 capillary column provide good results. Working parameters of GC were as follows: Temperature (ºC): oven: 150 (5 min^{-1}) →8 min^{-1}→190 (2 min) →15 min^{-1} →280 (10 min). Injection port, 280 ºC, detector, 300 ºC; carrier gas (N_2) flow was maintained at 60 ml min^{-1}, 2 ml min^{-1} through column with split ratio 1:10. Before use, the column was primed with several injections of a standard solution of fenpropathrin until a consistent response was obtained. Under these operating conditions, the retention time of fenpropathrin was found to be 18.265 min. The residues of fenpropathrin in samples were identified and quantified by comparing retention time and area of sample chromatograms with that of standards run under identical conditions.

Chilli and soil samples were spiked with fenpropathrin at two concentration levels (0.010 and 0.025 mg kg^{-1}) processed and analyzed as per the methodology described above to check the validity of the method. Percent recoveries in chilli were 92.10 and 94.36 while in soil were 94.70 and 96.56 at two fortification levels, respectively. As the percent recovery obtained were more than 90%, therefore, the results have been presented as such without applying any correction factor. Limit of detection (LOD) was 0.003 mg kg^{-1} and limit of determination/quantification (LODe /LOQ) was calculated as 0.01 mg kg^{-1}.

Result and discussion

Residue data and percent dissipation of fenpropathrin at single and double dose in chilli are presented in Table 1 (Fig. 1). The average initial deposits in chilli were found to be 0.413 and 0.946 mg kg^{-1} on 0 (1h after spray) day after application, respectively. These residues level dissipated to an extent of 0.327, 0.275, 0.135 and 0.760, 0.639, 0.330 mg kg^{-1} on 1, 3 and 5th day after application at single and double dose, respectively. The per cent dissipation observed on 7th day was 76.99 and 75.88. On 15th day 96.85 and 97.78 percent dissipation was observed in, respective doses and thereafter reached below detectable level (BDL) of 0.01mg kg^{-1} in the marketable fruits in both the doses. Residue data were subjected to statistical analysis for computation of regression equations, half-life ($t_{1/2}$) values and per cent degradation. The residues

dissipated with half-life 3.10 days at single dose (T_1) and 3.30 days at double dose (T_2) following first order kinetics. Jyot et al. 2013 [5] reported that the residues of cypermethrin in red chilli collected after 15 days of the last spray were found to be below its determination limit of 0.01 mg kg^{-1} at both the dosages. Similarly, the residues of endosulfan, dicofol, dimethoate, and λ-cyhalothrin in harvested red chillies were below the detectable levels in all the treatments [9]. Pandher et al. 2012 [8] reported that the residues of deltamethrin declined to below determination limit of 0.01 mg kg^{-1} after 5, 7, 10 and 15 days, respectively, at four different locations in India. The dissipation behaviour of pesticide in/on crops depend on the climatic conditions, type of application, plant species, dosages, the interval between application and harvest [6]. Galera et al. 1997 [4] reported that the half-life value of fenpropathrin was 3.4 to 4.2 days in the tomatoes and 4.0 to 4.5 days in the green beans. In another study on chilli [13] when different insecticides i.e., chlorpyriphos (32 g a.i ha^{-1}), endosulphan (14 g a.i ha^{-1}), dimethoate (6 g a.i ha^{-1}) and malathion (31.68 g a.i ha^{-1}) applied, it was found that half-life periods were 3.22d for chlorpyriphos,4.99 for endosuphan, 4.7 d for dimethoate, and 5.49 for malathion. Thus earlier reports corroborate the present findings.

In soil, initial deposit of fenpropathrin on 0 (1h after treatment) day at single dose was 0.141 $mgkg^{-1}$ and 0.273 $mgkg^{-1}$ at double dose Table 2 (Fig.2). The residue dissipated with the advancement of time. In case of single dose the residue dissipated to an extent of 0.090, 0.062, 0.032 and 0.012 showing percent dissipation of 36.17, 56.02, 77.30 and 76.99 on 3, 5 ,7 and 15 day after application. At the double dose residues were detected in soil on 3,5 ,7 and 15 day were 0.176, 0.122, 0.066 and 0.029 showing percent dissipation were 36.53, 55.31, 75.82 and 89.37. Under study period of 30 days, residues reached below detectable level in single dose whereas 0.019 mg kg^{-1} at double dose. The dissipation after 30 days was observed to be 95.03 per cent for single dose and 93.04 per cent for double dose. Half-life periods in T1 and T2 doses were calculated to be 6.95 and 7.94 days respectively following pseudo first order kinetics. Residues of fenpropathrin did not follow the first order kinetics because the (R^2) were 0.887 and 0.853 for T1 and T2 doses, respectively.

Conclusion

Residues of fenpropathrin dissipated with half-life values of 3.10 and 3.30 days following first order kinetics for T_1 and T_2 doses, respectively. Therefore, application of the fenpropathrin at the recommended dose on chilli seems to be safe from crop protection and environmental

contamination points of view. In soil, half life period for respective doses was observed to be 6.95 and 7.94 days.

Acknowledegments

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References

1. Albadri AE, Abdalla AE, Hassan EA, Ibrahim AMM, Hassan YA (2012) Gas chromatographic method with electron-capture detector (gc-ecd) for simultaneous determination of fenpropathrin, λ- cyhalothrin, and deltamethrin residues in tomato and its applications to kinetic studies after field treatment. Food Anal Meth 26 February, pp. 1-7
2. Anonymous (2013) "Indian Chilli Exporters, Indian Red Dry Chilli".
3. Bhardwaj U, Kumar R, Kaur S, Sahoo SK, Mandal K, Battu RS, Singh B (2012) Persistence of fipronil and its risk assessment on cabbage, Brassica oleracea var. capitata L. Ecotoxico Environ Safety 79: 310-308
4. Galera MM, Vidal MJ, Egea FJ, Gil MD (1997) A Study of fenpropathrin residues in tomatoes and green beans grown in greenhouses in Spain. Pestic Sci 50: 127-134
5. Jyot Gagan, Mandal Kousik, Battu RS, Singh Balwinder (2013) Estimation of chlorpyriphos and cypermethrin residues in chilli (*Capsicum annuum* L.) by gas–liquid chromatography. Environ Monit Assess 185: 5703–5714
6. Khay S, Choi JH, Abd El-Aty MA (2008) Dissipation behavior of lufenuron, benzoylphenylurea insecticide, in/on Chinese cabbage applied by foliar spraying under greenhouse conditions. Bull Environ Contam Toxicol 81: 369–372
7. Kumari B, Madan VK, Kathpal TS (2008) Status of insecticide contamination of soil and water in Haryana, India. Environ Monit Assess 136: 239–244
8. Pandher Suneet , Sahoo S K, Battu RS, Singh Balwinder, Saiyad MS, Patel AR, Shah PG , Reddy NC, Reddy JD, Reddy NK, Rao Sreenivasa Ch., Banerjee T, Banerjee D, Hudait R, Banerjee H, Tripathy Vandana, Sharma KK (2012) Persistence and

dissipation kinetics of deltamethrin on chili in different agro-climatic zones of India. Bull Environ Contam Toxicol 88: 764–768

9. Priya B, Ksubrahmanyam P, Dakshayani K, Chiranjeevi P (2007) Spectrophotometric determination of fenpropathrin in its formulations and water samples. E-J Chem 4: 480-486

10. Raju KV, Luckose CK (1991) Trends in area production and exports of chillies from India. Agric Sit India 45: 767-772

11. Reddy KD, Reddy KN, Mahalingappa PB (2007) Dissipation of fipronil and profenofos residues in chillies (*Capsicum annum* L.). Pestic Res J19: 106–107

12. Reddy KN, Satyanarayana S, Reddy KD (2007a) Persistence of some insecticides in chillies. Pestic Res J19: 234–236

13. Waghulde PN, Khatik MK, Patil VT, Patil PR (2011) Persistence and dissipation of pesticides in chilly and okra at North Maharashtra Region. Pestic Res J 23 (1), 23–26