International Journal of Chemical Studies

P-ISSN: 2349–8528
E-ISSN: 2321–4902
IJCS 2018; 6(1): 1791-1794

Received: 11-11-2017
Accepted: 12-12-2017

Sushil
Department of Entomology CCS HAU, Hisar, Haryana, India

Reena Chauhan
Department of Entomology CCS HAU, Hisar, Haryana, India

Beena Kumari
Department of Entomology CCS HAU, Hisar, Haryana, India

RS Jaglan
Department of Entomology CCS HAU, Hisar, Haryana, India

Correspondence
Reena Chauhan
Department of Entomology CCS HAU, Hisar, Haryana, India

Studies on persistence and dissipation behavior of selected pesticides in hot pepper (*Capsicum annuum*)

Sushil, Reena Chauhan, Beena Kumari and RS Jaglan

Abstract
The crop was raised at Research Farm of the Department of Entomology, CCS Haryana Agricultural University, Hisar (India) following recommended agronomic practices. The commercial formulations of each insecticide were sprayed on hot pepper crop in a randomized block design (RBD) with three replications. The insecticide residues in fruits were estimated by gas liquid chromatography (GLC) and gas chromatography-mass spectrometry (GC-MS). Spiromesifen dissipated fast and reached below detectable level (BDL) of 0.05 mg kg^{-1} on 20th day after application. No residue was found in soil at the time of harvesting except in case of ethion (0.720 mg kg^{-1}).

Keywords: Hot pepper, Dissipation, Half-life, Soil, GC-MS

Introduction
Hot pepper [*Capsicum annuum* (L.) var. longum], a member of Solanaceae family, is one of the most valuable vegetable crops of India and chiefly popular for its green pungent fruits [1], which are used both green and ripe to impart tanginess to vegetable and non-vegetable food articles. It is indispensible to kitchen in day to day curries, pickles, salads and sauces [2]. It is a rich source of minerals like molybdenum, manganese, potassium, copper and vitamin A, B, C and E [3]. Different varieties of hot pepper have been developed for spices, condiments, sauces and pickles [4].

India is the principal producer of hot pepper but its production pattern is highly inconsistent[5] since its plant is attacked by 51 species of insects and 2 species of mites belonging to 27 families under nine orders, resulting in huge yield [4], thus, various pesticides are used for the management of pests in hot pepper [6]. Use of insecticides is necessary to avoid the loss of yield, however, the farmers are using insecticides even at picking stage, due to which, the residues of noxious insecticides are left in/on fruits, which are very hazardous to consumer health. The constant intake of these left over chemical substances, although in minute amount, can result in their deposition in the human body, causing ill effects on human health [7]. The persistence of an insecticide varies with the nature of insecticides, dosage applied, numerous applications, crop variety and agro-climatic conditions [8]. Before any pesticide is suggested for use in the field, it is obligatory to study its residues on the crop so that its efficiency against pest along with its toxicologically acceptable deposit in/on food products can be acknowledged, thus, proper assessment of pesticide residues is very important for reducing health hazard to consumers. Therefore, the present study was designed to inspect the persistence and dissipation behavior of selected of pesticides in hot pepper fruits at Hisar, Haryana and thereby to suggest half-life period.

Material and Method
Chemicals and reagents
Chlorpyriphos 20% EC, ethion 50% EC, quinalphos 25% EC and spiromesifen 22.9% SC used for application were procured from local market. Magnesium sulphate and hexane were purchased from Merck, and primary secondary amine was purchased from Agilent Technologies. Anhydrous magnesium sulphate used during residue extraction was activated at 300 °C overnight before use.

Field Trials

The research trials were conducted at Research Farm of the Department of Entomology, CCS Haryana Agricultural University, Hisar (India) following recommended agronomic practices in a randomized block design (RBD) with three replications. The commercial formulations *viz*., 20% EC chlorpyriphos 300 g a.i. ha^{-1}, 50% EC ethion 500 g a.i. ha^{-1}, 25% EC quinalphos 250 g a.i. ha^{-1} and 22.9% SC spiromesifen 96 g a.i. ha^{-1} were sprayed on hot pepper cv. Kanshi Anmol crop twice at fruiting stage at an interval of 10 days using Knapsack sprayer. Three untreated plots were used as control where only water was sprayed. The soil of crop field was light textured with low organic matter content (0.67%), phosphorus 15 kg and potassium 10.08 kg ha^{-1}, pH 7.6 and EC 2 dSm^{-1}.

Sampling Procedure

Half kg marketable size fruits of hot pepper were randomly collected from each treated plot at 0 (1 h after spray), 1, 3, 5, 7, 10, 15 and 20 days after insecticides application. The samples were brought immediately to the laboratory in the polythene bags along with control and processed on the same day.

Soil

Soil samples of 1 kg were collected from 8 to 10 sites of each treated plot at the time of harvesting with the help of a tube auger from a depth of about 0-15 cm, dried in shade, crushed in pestle and mortar and then sieved through 2 mm sieve to remove extraneous matter including pebbles.

Extraction and cleanup

Hot pepper

The samples were extracted and cleaned up by using QuEChERS technique. The entire sample of 0.5 kg was crushed thoroughly in a large volume homogenizer (Robot Coupe, Heidolph), from which, 15 g sub-sample of hot pepper was drawn in a 50 ml PTFE centrifuge tube and shaken vigorously for 1 minute after adding 30 ml of acetonitrile and centrifuged (Centrifuge, Remi, Mumbai, India) for 2 minutes at 1400-1500 rpm. Thereafter, 3 g of sodium chloride was added and mixed gently on vortex and again the sample was centrifuged for 3 minutes at 2500-3000 rpm to separate the organic layer, 18 ml of which was taken in another centrifuge tube and shaken vigorously for one minute after adding 9 g of anhydrous sodium sulphate. Eleven milliliter of the supernatant was transferred to centrifuge tube (15 ml) and shaken with 0.4 g PSA and 1.15 g magnesium sulfate. Matrix was centrifuged for 5 minutes at 3000 rpm and 6 ml of supernatant was taken in test tube, concentrated on rotary vacuum evaporator until dryness, and made 3 ml final volume in n-hexane for analysis.

Soil

Soil samples were processed by adopting method of Kumari *et al.,* (2008) [9]. Ground, sieved and dry representative soil sample (15 g) was mixed thoroughly with 0.3 g activated charcoal, 0.3 g florisil and 10 g anhydrous sodium sulphate. The mixture was packed compactly in a glass column (60 cm x 22 mm) in between two layers of anhydrous sodium sulphate. Pesticide residues were eluted with 125 ml of hexane**:** acetone (9**:**1 v/v) mixture at a flow rate of 2-3 ml^{-1}. The eluate was concentrated on rotary flash evaporator and the final volume was made to 2 ml for GC analysis.

Residue Estimation

The residues of chlorpyriphos, ethion and quinalphos were determined by gas liquid chromatography (GLC) Shimadzu Model 2010 equipped with FTD (Ni^{63}), split injection system and fused capillary column (SPB-5) 30 m x 0.32 mm i.d. and 0.25 µm film thickness (5% diphenyl and 95% dimethyl polysiloxane). GC operating conditions were carrier gas flow 60 ml min^{-1}, injector port temperature 280 °C and oven temperature programme 150 °C (5 min), increasing @ 8 °C min^{-1} up to 190 °C (2 min) and further increasing @ 15 °C min^{-1} up to 280 °C (10 min). Under these operating conditions, the retention time of chlorpyriphos, ethion and quinalphos was found 15.164, 17.872 and 16.080 minutes, respectively. The residues of spiromesifen were quantified by gas chromatograph mass detector (GC-MS), model Shimadzu GC-MS-QP 2010 Plus fitted with a 30m x 0.25 i.d. x 0.25 µm film Rxi-1ms column (Restek International, USA) and operated in full scan mode (50-500 m/z). Instrument conditions included spit less injection at 175 °C and injector at 260 °C. Helium was used as a carrier gas with flow rate of 1 ml min^{-1}. Under these conditions, the retention time of spiromesifen was found 7.631 minutes with major ions at 274, 254 and 99.

Statistical analysis

Residue half-life was calculated by determining linear regression equation between log [residues (µg ml^{-1} or mg kg^{-1}) x 10^3] and days after treatment. The days after treatment were taken on x-axis and log [residues (mg kg^{-1}) x 10^3] was taken on y-axis. The method of least square was used to find out the slope (b) of x- and y-axis [10].

Results and Discussion

To establish the reliability and validity of the analytical method and to check the efficiency of procedure used in the present research, the recovery experiments were carried out at different levels, *i.e.,* 0.05 and 0.10 mg kg^{-1}. For this purpose, the control samples of hot pepper were fortified with different insecticides at above said levels and analyzed as per the methodology described above. Percent recoveries of all the insecticides in hot pepper were found consistent and more than 85% (Table 1). Limit of quantification (LOQ) was found to be 0.05 and limit of detection was 0.01 mg kg^{-1} for hot pepper fruits.

The dissipation pattern of different pesticide residues with time in hot pepper has been shown in Table 2. The percent dissipation of spiromesifen as shown by extractable residues was highest and that of ethion was lowest in hot pepper. The residues of pesticide dissipated continuously with the passage of time. After 1 h (i.e. 0 d) of spraying chilly, showed the deposit of chlorpyrifos to be 1.191 mg kg^{-1}, ethion as 7.650 mg kg^{-1}, quinalphos as 1.988 mg kg^{-1} and spiromesifen as 1.982. The values reached to a level of 0.141, 1.920, 0.195 and 0.055 mg kg^{-1} on 15^{th} day after application in chlorpyrifos, ethion, quinalphos and spiromesifen respectively. In case of spiromesifen residues reached below detectable level (BDL) of 0.05 mg kg^{-1} on 20^{th} day while residues reached below detectable level on 25^{th} day in chlorpyriphos, ethion and quinalphos. The half-life ($t_{½}$) period of 4.93, 8.85, 4.42, 3.20 days for chlorpyrifos, ethion, quinalphos and spiromesifen respectively. Soil samples were collected at the time of harvesting. No residue was detected in any of the samples except ethion (0.720 mg kg^{-1}). Hence, the residues reached below detectable level (BDL) of 0.05 mg kg^{-1}.

Similar results were reported by Waghulde *et al.,* (2011) [5] in hot pepper and okra when chlorpyriphos (Hilban 20 EC) was applied @ 32 g a.i. ha^{-1}. The residues on 21st day after application dissipated up to 0.09 mg kg^{-1} with half-life 3.22 days. Kumari & Chauhan, 2015[11] studied the dissipation behavior of chlorpyriphos (160 and 320 g a.i.ha^{-1}) in hot pepper. In starting, the residues dissipated slowly and then reached below detectable levels (0.010 mg kg^{-1}) on 15th and 30th days of treatment in single and double dose, showing dissipation of 97.48 and 98.14% with half-life value of 6.02 and 5.67 days at respective doses, respectively. In soil, the dissipation on 30th day was observed 91.57% for single and 90.25% for double dose. Sharma & Parihar, 2013 [12] reported that when ethion 50 EC was applied @ 500 and 1000 g a.i. ha^{-1}, the initial deposits were 2.4 and 4.84 mg kg^{-1} with half-life value of 1.81 and 2.32 days, respectively. The ethion residues on 15th and 20th day of its application reached below detection limit (0.01 mg kg^{-1}). Priyadarshini *et al.,* 2017 [13] reported that when ethion 50 EC was applied @ 500 g a.i. ha^{-1} on curry leaves, the initial deposit was 21.04 mg kg^{-1}, which dissipated to a level below determination (< 0.05 mg kg^{-1}) on 25th day with half-life value 3.14 days, respectively. Soil samples collected after harvesting (45th day) were free from the residues. Chandel *et al.,* (2011) [14] studied the dissipation pattern of quinalphos (500 and 1000 g a.i. ha^{-1}) in cabbage, cauliflower and potato and found that the residues reached below detectable on 7th day in cabbage and cauliflower at both the doses, while potato had no residue even on 0 day, however, its soil contained detectable residues. Results of the present study corroborate the findings of Varghese, 2011 [15] when spiromesifen 240 SC was applied @ 96 g a.i. ha^{-1} on hot pepper. The residue persisted up to 5 days with half-life value 2.62 days. George *et al.,* (2014) [16] applied spiromesifen twice @ 150 and 300 g a.i. ha^{-1} at 7 days interval on tomato fruits and observed residues below determination level (0.05 mg kg^{-1}) after 5th and 7th day with a half-life 2.05 and 2.29 days, respectively and no residue in soil collected at harvesting time.

Table 1: Average recoveries of chlorpyriphos, ethion, quinalphos and spiromesifen in hot pepper fruits

Fortification level (mg/kg)	Average*±SD			
	Chlorpyriphos	Ethion	Quinalphos	Spiromesifen
0.05	88.30±2.17	85.67± 2.77	90.35± 2.60	90.40± 2.30
0.10	91.27± 3.01	88.84±1.15	93.09±2.95	92.35±3.89

Table 2: Dissipation pattern of different insecticides (mg kg^{-1}) on hot pepper at different time intervals

Days after treatment	Chlorpyriphos (300 g a. i. ha^{-1})	Ethion (500 g a. i. ha^{-1})	Quinalphos (250 g a. i. ha^{-1})	Spiromesifen (96 g a. i. ha^{-1})
	Average Residues ±SD	Average Residues ±SD	Average Residues ±SD	Average Residues ±SD
0	1.191±0.052	7.650±0.008	1.988±0.050	1.982±0.027
1	1.142±0.104 (4.11%)	4.290±0.671 (43.92%)	1.267±0.414 (36.26%)	1.094±0.357 (44.80%)
3	0.881±0.056 (26.03%)	3.380±0.069 (55.81%)	0.929±0.300 (53.26%)	0.587±0.185 (70.38%)
5	0.617±0.027 (48.19%)	2.570±0.365 (66.40%)	0.834±0.007 (58.04%)	0.474±0.136 (76.08%)
7	0.333±0.009 (72.04%)	2.430±0.521 (68.23%)	0.735±0.027 (63.02%)	0.361±0.044 (81.78%)
10	0.322±0.044 (72.96%)	2.130±0.098 (72.15%)	0.433±0.109 (78.21%)	0.198±0.008 (90.01%)
15	0.141±0.005 (88.16%)	1.920±0.162 (74.90%0	0.195±0.008 (90.19%)	0.055±0.004 (97.22%)
20	0.075±0.008 (93.70%)	1.010±0.209 (86.79%)	0.061±0.009 (96.93%)	BDL
25	BDL	BDL	BDL	BDL
Soil (Harvest time)	BDL	0.720±0.160	BDL	BDL
Regression Equation	y = -0.151x+2.984; R^2= 0.992	y= - 0.034x + 3.686; R^2 = 0.848	y= - 0.068x + 3.252; R^2 = 0.974	y= - 0.094x + 3.177; R^2 = 0.974
Half life	4.93 days	8.85 days	4.42days	3.20days

* Average of three replicates

* Average of three replicates; Below determination level (BDL)**:** 0.05 mg kg^{-1}

Conclusion

In conclusion, selected pesticides can be recommended for use on hot pepper, as at recommended dose, they did not leave any harmful residues on the hot pepper fruits and are safe to consumers, in addition to this, no accumulation of pesticides in soil was found except ethion.

Acknowledgments

The authors wish to express their gratitude to the Head, Department of Entomology for providing research facilities.

References

1. Pariari A, Khan S. Integrated nutrient management of hot pepper (*Capsicum annuum* L.) in Gangetic alluvial plains. Journal of Crop Weed. 2013; 9:128-130.
2. Singh Yadwinder, Mandal Kousik, Singh B. Persistence and risk assessment of cypermethrin residues on chilli (*Capsicum annuum* L.). Environmental Monitoring and Assessment. 2015; 187(120):1-10.

3. Thamaraikannan M, Palaniappan G, Sengottuvel C. Time to step up hot pepper exports. Facts for you Market survey 2011, 30-35.
4. Jyot Gagan, Mandal Kousik, Battu RS, Singh B. Estimation of chlorpyriphos and cypermethrin residues in hot pepper (*Capsicum annuum* L.) by gas–liquid chromatography. Environmental Monitoring and Assessment. 2013; 185:5703-5714.
5. Thamburaj S, Singh N. Textbook of vegetables, tuber crops and spices Published by Directorate of Information and Publication of Agriculture; ICAR New Delhi 2005, 468.
6. Waghulde PN, Khatik MK, Patil VT, Patil PR. Persistence and dissipation of pesticides in chilly and Okra at North Maharashtra Region. Pesticide Research Journal. 2011; 23:23-26.
7. Sharma KK, Mukherjee Irani, Singh Balwinder, Sahoo SK, Mandal Kousik, Mohapatra Soudamini *et al*. Dissipation pattern and risk assessment of flubendiamide on chili at different agro-climatic conditions in India. Environmental Monitoring and Assessment 2015; 187:245-254.
8. Sahoo SK, Mandal K, Kaur R, Battu RS, Singh B. Persistence of thiacloprid residues on brinjal (Solanum melongena L.). Environmental Monitoring and Assessment. 2013; 185:7935-7943.
9. Kumari B, Madan VK, Kathpal TS. Status of insecticide contamination of soil and water in Haryana, India. Environmental Monitoring and Assessment. 2008; 136:239-244.
10. Regupathy A, Dhamu KP. Insecticide decay curve. In: Statistics Work Book for Insecticide Toxicology, Suriya Desktop Publishers, 1990, 76-84.
11. Kumari B, Chauhan Reena. Persistence and Effect of Processing on Reduction of Chlorpyriphos in Chilli. Journal Food Processing and Technology. 2015; 6(10):1-4.
12. Sharma BN, Parihar NS. Dissipation and persistence of dimethoate and ethion residues in/on chilli, *Capsicum annuum* (L.) Pesticide Research Journal. 2013; 25(1):80-82.
13. Priyadarshini G, Vemuri Shashi, Reddy CN, Swarupa S. Dissipation pattern of ethion and profenophos in curry leaf. Journal of Global Bioscience. 2017; 6(1):4661-4665.
14. Chandel RS, Sharma ID, Patyal SK. Persistence and risk assessment of quinalphos in some vegetables. Pesticide Research Journal. 2011; 23(2):194-199.
15. Varghese Thania, Biju MT, Sara G Thomas, Naseema Beevi S, George Xavier. Dissipation of propargite and spiromesifen in/on hot pepper Fruits. Pesticide Research Journal. 2011; 23(2):135-139.
16. George Thomas, Beevi SN, Mathew TB, Paul Ambily, Xavier George, Prathibha Ravi K. Dissipation and safety of spiromesifen (Oberon 240SC) on Tomato. Pesticide Research Journal. 2014; 26(2):160-163.