International Journal of Bio-resource and Stress Management 2015, 6(6):690-694 DOI: 10.5958/0976-4038.2015.00106.2

Full Research Article

Studies on Persistence of Ready-mix Chlorpyrifos+Cypermethrin Formulation on Tomato (*Solanum lycopersicum* L.)

Tanuja Banshtu*, Surender Kumar Patyal and Rajeshwar Singh Chandel

Dept. of Entomology, Dr. Y. S. Parmar University of Horticulture and Forestry, Nauni, Solan, Himachal Pradesh (173 230), India

Article History

Manuscript No. AR1348
Received in 24th March, 2015
Received in revised form 29th November, 2015
Accepted in final form 6th December, 2015

Correspondence to

E-mail: twinkle_banshtu5@yahoo.in

Keywords

Chlorpyrifos, cypermethrin, persistence, residues, tomato

Abstract

Persistence of ready-mix and individual insecticide chlorpyrifos and cypermethrin was studied during 2009 and 2010 under field conditions. Chlorpyrifos and cypermethrin were applied at recommended rate 500 and 50 g ai ha^{-1} and at double the recommended rate on tomato crop. The fruits and soil samples were collected after second spray at different intervals. Residues were extracted with acetone and cleaned up by column chromatography. Residues of both insecticides were determined by using gas chromatograph, Agilent 6890N having electron capture detector. In fruits, the residues of chlorpyrifos and cypermethrin reached below the limit of determination in 10 and 7 days at recommended rate and in 15 and 10 days at double recommended rate, respectively. In ready-mix product, chlorpyrifos deposits reduced to half in 1.24-1.42 days and cypermethrin deposits required 1.38-1.73 days to reduce to half but when applied individually, chlorpyrifos initial deposits were reduced to their half in 1.07-1.39 days and cypermethrin deposits became half in 1.57-2.08 days. In soil, residues of chlorpyrifos persisted upto10 days in individual as well as in ready-mix insecticides. However, residues of cypermethrin were below determination limit in 10th day sampling in case of individual application of insecticides whereas, cypermethrin residues were not detected even on the 0 day sampled soil in ready-mix formulation. The study revealed that the persistence behavior in fruits were almost same when applied individually or as ready-mix.

1. Introduction

Tomato (*Solanum lycopersicum* L.) is an important vegetable crop and is grown throughout the year in the country. Tomato provides all the nutrients components, like carbohydrates, protein, fat, vitamins, minerals and water along with roughages which are the essential constituents of a balanced diet. It is a main cash crop in Himachal Pradesh as it gives good monetary returns to the farmers. However, insect pests are major limiting factor in its productivity. In order to maintain a high production, the use of pesticides is a conventional agricultural practice (Engindeniz, 2006). As insects are becoming resistant to more and more insecticides so in order to combat this menace, usage of insecticide mixtures is being advocated. In India, a large number of ready-mix insecticide formulations have been registered for use on various crops (Regupathy et al., 2004). Ready-mix insecticide formulations have been found effective against insect pests of many vegetables (Dharne and Kabre, 2009). In tomato, chlorpyrifos and cypermethrin has been reported to be highly effective for the control of major insect-pests (Sarangdevot et al., 2010a and b). Chlorpyrifos is an organophosphorus and cypermethrin is a synthetic pyrethroid, broad-spectrum and contact insecticides registered against both sucking and chewing insects. But the persistence of these combo products in/or tomato crop has not been studied under present environmental conditions. So Therefore, Cannon 55EC a ready-mix combination of chlorpyrifos 50%+cypermethrin 5% was used to know the fate of residues of these insecticides in the environment. Therefore, the present investigations were carried out to study the persistence behavior of chlorpyrifos and cypermethrin after the application of ready-mix and individual insecticide formulation.

2. Materials and Methods

Field experiments were conducted during 2009 and 2010 in a randomized block design. Six treatments were undertaken in total and each treatment was replicated thrice. The tomato crop variety, Him Sohna was raised by following package

of practices of vegetable crops (Anonymous, 2009). Tomato crop was sprayed twice at 15 days interval starting at fruit formation stage. Chlorpyrifos and cypermethrin were applied at the recommended rate (RR) 500 and 50 g ai ha^{-1} and at double recommended rate (DRR) 1000 g and 100 g ai ha^{-1}, respectively. Control plots with only water spray were maintained simultaneously for comparison. After the second spray, fruit samples (1 kg) from each replication were collected randomly at 0 (2 hours after spray), 1, 3, 5, 7, 10 and 15 days intervals. Soil samples (1 kg) from each replication were collected on 0, 10 and 20 days after application. The tomato fruits were homogenized and analysed for respective insecticides. Soil samples were shade dried and sieved. Extraction and clean up of tomato fruit samples were undertaken according to the method of Sharma (2007) and soil samples were analyzed according to the method given by Brar (2003). The chemicals used were of analytical grade obtained from M/S Merck Specialties Private Limited, Mumbai, India. Residues were estimated by using Gas-Chromatograph (Agilent 6890N) having ECD detector and DB-5 Ultra Performance Capillary column (Cross-linked Methyl Silicon, length 30 m, 0.250 mm internal diameter with 0.25 µm film thickness). The analytical method employed to estimate chlorpyrifos residues was validated by spiking the control fruit samples at four different concentrations viz., 0.01, 0.05, 0.10 and 0.5 mg kg^{-1} whereas, soil samples were fortified at 0.05, 0.10, 0.5 and 1.0 mg kg^{-1}. Cypermethrin samples were spiked at 0.05, 0.10, 0.50 and 1.0 mg kg^{-1} concentrations. The limit of determination (LOD) of chlorpyrifos was 0.01 mg kg^{-1} in fruits while in soil, it was 0.05 mg kg^{-1} and for cypermethrin fruits and soil, LOD was 0.05 mg kg^{-1}. The residue data were subjected to statistical analysis (Hoskins, 1961).

3. Results and Discussion

Data presented in Table 1 depicts reliability of analytical method tested by spiking of untreated tomato fruits and soil samples at different concentrations. Recovery of chlorpyrifos was between 90.00-92.00% with relative standard deviation (RSD) of 0.107-1.007% in fruits and 90.00-94.00% with 0.081-0.893% RSD in soil fortified samples. Recovery of cypermethrin was between 88.00-90.00% with relative standard deviation (RSD) of 0.034-0.738% in fruits and 86.80-90.00% recovery with 0.062-0.728% RSD in soil fortified samples. The results are in agreement with Pal (2011) who has observed recovery 88.80-91.39% for malathion and 86.60-92.31% for cypermethrin in capsicum fruits. Tashiro and Kuhr (1978) reported 89.00-108.00% recovery of chlorpyrifos in sandy loam soil while Brar (2003) reported 78.60% recovery of pyrethroids in soil. The decrease in level of residues in individual and combi insecticides treatments at different intervals in fruits are presented in Table 2 and 3.

Table 1: Recovery of chlorpyrifos and cypermethrin from tomato fruits and soil samples

Insecticides	Fruits			Soil	
	Fortification level, (mg kg^{-1})	Mean recovery (%)	Relative standard deviation (% RSD)	Mean recovery (%)	Relative standard deviation (% RSD)
Chlorpyrifos	0.01	90.00	1.007	-	-
	0.05	90.00	0.934	90.00	0.893
	0.10	91.00	0.335	90.00	0.782
	0.50	92.00	0.107	92.00	0.121
	1.00	-	-	94.00	0.081
Cypermethrin	0.05	88.00	0.738	88.00	0.728
	0.10	88.00	0.286	88.00	0.301
	0.50	89.00	0.147	86.80	0.401
	1.00	90.00	0.034	90.00	0.062

Chlorpyrifos initial deposits on tomato fruits from mixture (Cannon 55EC) and individual insecticide formulation (Lethal 20EC) were 1.633-1.708 mg kg^{-1} which dissipated to 0.036-0.044 mg kg^{-1} and 1.098-1.185 mg kg^{-1} which dissipated to 0.010-0.019 mg kg^{-1} on 7^{th} day, respectively at recommended rate. In double the recommended rate, initial deposits of chlorpyrifos from mixture were 3.367-3.487 mg kg^{-1} which dissipated to 0.012-0.025 mg kg^{-1} and deposits 2.000-2.129 mg kg^{-1} from individual chlorpyrifos dissipated to 0.014 mg kg^{-1} in 10 days. Two years persistence data showed that they followed almost the same dissipation pattern in the same day whether applied individually or as ready-mix formulation. Our findings are in agreement with Reddy and Reddy (2011), who observed 2.75 mg kg^{-1} initial deposits of chlorpyrifos on cabbage at 0.05% spray concentration. Peter et al. (2001) also reported the initial deposits of chlorpyrifos 3.01 mg kg^{-1} in tomato.

Initial deposits of cypermethrin on tomato fruits from mixture with chlorpyrifos applied @ 50 g ai ha^{-1} were 0.608-0.694 mg kg^{-1} whereas at double recommended rate, the initial deposits were 1.007-1.085 mg kg^{-1}. When applied individually, cypermethrin initial deposits at recommended rate were 0.291-0.488 mg kg^{-1} and at double the recommended rate cypermethrin deposits were 0.994-1.074 mg kg^{-1}. Rai et al. (1986) observed 0.46 mg kg^{-1} initial deposits of cypermethrin on cauliflower at 0.0075% spray concentration. Bhupinder and Udeaan (1989) reported 0.65 mg kg^{-1} and 1.43 mg kg^{-1} initial deposits at 50 g ai ha^{-1} and 100 g ai ha^{-1} doses of cypermethrin, respectively in okra fruits.

Data contained in Table 4 revealed that there is decline in residues with the time lapse at both the level of application. The

Table 2: Persistence of chlorpyrifos (500 g ai ha^{-1}) and cypermethrin (50 g ai ha^{-1}) in tomato fruits

Interval (Days)	2009				2010			
	Combination		Individual		Combination		Individual	
	Chlorpyrifos	Cypermethrin	Chlorpyrifos	Cypermethrin	Chlorpyrifos	Cypermethrin	Chlorpyrifos	Cypermethrin
	Residues±SD (mg kg^{-1})	Residues±SD (mg kg^{-1})	Residues±SD (mg kg^{-1})	Residues±SD (mg kg^{-1})	Residues±SD (mg kg^{-1})	Residues±SD (mg kg^{-1})	Residues±SD (mg kg^{-1})	Residues±SD (mg kg^{-1})
0	1.708±0.258	0.608±0.002	1.098±0.008	0.291±0.004	1.633±0.007	0.694±0.005	1.185±0.004	0.488±0.006
1	1.266±0.171	0.347±0.047	0.805±0.076	0.236±0.004	1.305±0.008	0.386±0.005	0.811±0.069	0.398±0.002
3	0.783±0.135	0.172±0.002	0.401±0.040	0.178±0.005	0.824±0.013	0.182±0.005	0.408±0.038	0.245±0.011
5	0.313±0.002	0.051±0.001	0.096±0.005	0.051±0.001	0.351±0.002	0.052±0.004	0.099±0.002	0.050±0.009
7	0.044±0.003	BDL	0.010±0.003	BDL	0.036±0.007	BDL	0.019±0.008	BDL
10	BDL		BDL		BDL		BDL	

BDL: Below determination limit; SD: Standard deviation

Table 3: Persistence of chlorpyrifos (1000 g ai ha^{-1}) and cypermethrin (100 g ai ha^{-1}) in tomato fruits

Interval (Days)	2009				2010			
	Combination		Individual		Combination		Individual	
	Chlorpyrifos	Cypermethrin	Chlorpyrifos	Cypermethrin	Chlorpyrifos	Cypermethrin	Chlorpyrifos	Cypermethrin
	Residues±SD (mg kg^{-1})	Residues±SD (mg kg^{-1})	Residues±SD (mg kg^{-1})	Residues±SD (mg kg^{-1})	Residues±SD (mg kg^{-1})	Residues±SD (mg kg^{-1})	Residues±SD (mg kg^{-1})	Residues±SD (mg kg^{-1})
0	3.367±0.546	1.007±0.004	2.000±0.006	0.994±0.004	3.487±0.007	1.085±0.003	2.129±0.006	1.074±0.005
1	2.176±0.055	0.711±0.005	1.268±0.056	0.635±0.041	2.189±0.005	0.783±0.014	1.307±0.002	0.750±0.015
3	1.036±0.062	0.425±0.035	0.735±0.034	0.383±0.054	1.047±0.053	0.485±0.003	0.775±0.012	0.431±0.034
5	0.408±0.002	0.227±0.026	0.293±0.018	0.212±0.010	0.468±0.010	0.263±0.006	0.295±0.005	0.229±0.016
7	0.103±0.004	0.050±0.003	0.073±0.060	0.051±0.001	0.143±0.003	0.052±0.044	0.079±0.007	0.052±0.019
10	0.012±0.002	BDL	0.014±0.005	BDL	0.025±0.002	BDL	0.014±0.006	BDL
15	BDL		BDL		BDL		BDL	

BDL: Below determination limit; SD: Standard deviation

Table 4: Degradation kinetics of chlorpyrifos and cypermethrin on tomato fruits

Years, Insecticides	Application rate	Chlorpyrifos			Cypermethrin		
		Regression equation (y=---)	r	RL50	Regression equation (y=---)	r	RL50
2009, Combination	RR	0.358-0.214X	-0.956	1.40	-0.215-0.208X	-0.994	1.44
	DRR	0.642-0.241X	-0.897	1.24	0.064-0.174X	-0.971	1.73
Individual	RR	0.209-0.281X	-0.969	1.07	-0.477-0.144X	-0.943	2.08
	DRR	0.391-0.215X	-0.991	1.39	0.030-0.171X	-0.976	1.76
2010, Combination	RR	0.373-0.220X	-0.938	1.37	0.159-0.218X	-0.994	1.38
	DRR	0.604-0.212X	-0.995	1.42	0.110-0.175X	-0.963	1.70
Individual	RR	0.183-0.252X	-0.984	1.19	-0.224-0.192X	-0.952	1.57
	DRR	0.414-0.217X	-0.991	1.38	0.088-0.177X	-0.917	1.72

RR: Recommended rate; DRR: Double recommended rate; r: Correlation coefficient; RL50: Residue half-life

persistence of insecticides is generally expressed in terms of RL50 i.e. time for disappearance of insecticide initial deposits to 50%. The RL50 values are often obtained by fitting first-order kinetics to observed degradation pattern. The half-life of chlorpyrifos was 1.07-1.42 days and for cypermethrin 1.38-1.76 days. The half life values in the present study was in conformity with Raina and Raina (2008) who reported that the half life values of chlorpyrifos ranged from 1.4-1.5 days when chlorpyrifos was sprayed at 500 g ai ha^{-1} in cauliflower.

Studies suggested safe waiting period of 2 days for chlorpyrifos and 3 days for cypermethrin at recommended rate on tomato whether applied individually or in ready-mix formulation on the basis of MRLs as per Codex Alimentarius Commission: 0.5 mg kg^{-1} for chlorpyrifos and cypermethrin on tomato for safe consumption.

Chlorpyrifos residues 0.231-0.269 mg kg^{-1} and 0.391-0.421 mg kg^{-1} were detected in soil at the recommended and double the recommended rate, respectively in ready-mix formulation which became non-detectable on 20th day at both the doses (Table 5). When chlorpyrifos applied individually on the crop then residues in soil also became non-detectable on 20 days sampled soil at both rates. Whereas, Gupta et al. (2011) observed no chlorpyrifos residues in soil on the day of application at single dose and detected residues (0.012 mg kg^{-1}) at double dose which became below detection level after 3 days of Action 55EC (chlorpyrifos 50%+cypermethrin 5%) @ 0.8 and 1.6 L ha^{-1} on tomato crop.

Cypermethrin residues in soil were below determination limit in 0 day at recommended rate (50 g ai ha^{-1}). Whereas, at double the recommended rate, 0.095-0.099 mg kg^{-1} cypermethrin residues were detected in tomato cropped soil (Table 6). However, in individually applied cypermethrin, its residues were detected in soil on 0 day and became below the determination limit in 10 days. Present findings are in accordance with findings of Gupta et al. (2011) who observed cypermethrin residues below detection limit in soil samples after the application of Roket 44EC @ 1 L ha^{-1} on tomato crop. Studies revealed that when individual insecticides were applied alone on tomato crop then higher residues were detected in soil in comparison to their application in ready-mix formulation. The present findings are in agreement with the findings of Swarcewicz and Gregorczyk (2011) who observed higher residues of pendimethalin alone in comparison to pendimethalin+metribuzin mixture in clay loam soil.

Table 5: Residues of chlorpyrifos (500 g ai ha^{-1}) and cypermethrin (50 g ai ha^{-1}) in tomato cropped soil

Interval (Days)	2009				2010			
	Combination		Individual		Combination		Individual	
	Chlorpyrifos	Cypermethrin	Chlorpyrifos	Cypermethrin	Chlorpyrifos	Cypermethrin	Chlorpyrifos	Cypermethrin
	Residues±SD (mg kg^{-1})	Residues±SD (mg kg^{-1})	Residues±SD (mg kg^{-1})	Residues±SD (mg kg^{-1})	Residues±SD (mg kg^{-1})	Residues±SD (mg kg^{-1})	Residues±SD (mg kg^{-1})	Residues±SD (mg kg^{-1})
0	0.231±0.008	BDL	0.420±0.003	0.081±0.002	0.269±0.009	BDL	0.488±0.007	0.089±0.001
10	0.052±0.003		0.197±0.002	BDL	0.053±0.002		0.238±0.007	BDL
20	BDL		BDL		BDL		BDL	

BDL: Below determination limit; SD: Standard deviation

Table 6: Residues of chlorpyrifos (1000 g ai ha^{-1}) and cypermethrin (100 g ai ha^{-1}) in tomato cropped soil

Interval (Days)	2009				2010			
	Combination		Individual		Combination		Individual	
	Chlorpyrifos	Cypermethrin	Chlorpyrifos	Cypermethrin	Chlorpyrifos	Cypermethrin	Chlorpyrifos	Cypermethrin
	Residues±SD (mg kg^{-1})	Residues±SD (mg kg^{-1})	Residues±SD (mg kg^{-1})	Residues±SD (mg kg^{-1})	Residues±SD (mg kg^{-1})	Residues±SD (mg kg^{-1})	Residues±SD (mg kg^{-1})	Residues±SD (mg kg^{-1})
0	0.391±0.004	0.095±0.002	0.817±0.004	0.108±0.003	0.421±0.001	0.099±0.001	0.848±0.005	0.131±0.004
10	0.066±0.005		0.237±0.003	BDL	0.071±0.002		0.276±0.003	BDL
20	BDL		BDL		BDL		BDL	

BDL: Below determination limit; SD: Standard deviation

4. Conclusion

The chlorpyrifos and cypermethrin persistence behavior in fruits was almost same whether applied individually or as ready-mix formulation. The initial deposits of chlorpyrifos and cypermethrin on tomato fruits from ready-mix formulation were found to be 1.708 and 0.608 mg kg^{-1}, whereas initial deposits from individual formulations were found to be 1.098 and 0.291 mg kg^{-1}, respectively.The safe waiting period of 3 days is recommended for the ready-mix formulation and the safe waiting period for individual insecticides i.e. chlorpyrifos and cypermethrin is recommended to be 2 and 3 days respectively, on tomato fruits.

5. References

Anonymous, 2009. Package and Practices for Vegetable Crops. Directorate of Extension Education, Dr. Y.S Parmar University of Horticulture and Forestry, Solan, 294.

Bhupinder, S., Udeaan, A.S., 1989. Estimation of cypermethrin residues in the fruits of okra, *Abelmoschus esculentus* (Linn.) Moench. Journal of Insect Science 2(1), 49-52.

Brar, S.S., 2003. Monitoring of pesticide residues in soils of Himachal Pradesh. M.Sc. Thesis. Dr. Y.S Parmar University of Horticulture and Forestry, Solan, 64.

Dharne, P.K., Kabre, G.B., 2009. Bioefficacy of ready mixture of indoxacarb 14.5+acetamiprid 7.7 SC (RIL-042 222SC) against sucking pests and fruit borer on chilli. Karnataka Journal of Agriculture Science 22(3), 585-587.

Engindeniz, S., 2006. Economic analysis of pesticide use on processing tomato growing. A case study for Turkey. Crop Protection 25, 534-541.

Gupta, S., Vijay, T.G., Sharma, R.K., Gupta, R.K., 2011. Dissipation of cypermethrin, chlorpyriphos and profenofos in tomato fruits and soil following application of pre-mix formulations. Environmental Monitoring and Assessment 174(1-4), 337-45.

Hoskins, W.M., 1961. Mathematical treatment of the rate of loss of pesticide residues. FAO and Plant Protection Bulletin, FAO 9(9), 163-168.

Pal, V.K., 2011. Bio-efficacy and residues behavior of some insecticides on capsium grown under protected conditions. M.Sc. Thesis. Dr. Y.S. Parmar University of Horticulture and Forestry, Solan, 87.

Peter, A.J., Srinivasan, K., Chellaiah, S., 2001. Dissipation of chlorpyrifos 1.5% dust in/on brinjal and tomato fruits. Journal of Research ANGRAU 29(1), 62-65.

Rai, S., Agnihotri, N.P., Jain, H.K., 1986. Persistence of residues of synthetic pyrethroids on cauliflower and their residual toxicity against aphids. Indian Journal of Agricultural Sciences 56(9), 667-70.

Raina, A.K., Raina, M., 2008. Dissipation of chlorpyriphos on cauliflower (*Brassica oleracea* L. var. *botrytis*). Pesticide Research Journal 20(2), 263-265.

Reddy, C.N., Reddy, D.J., 2011. Persistence of chlorpyrifos and deltamethrin residues in cabbage. International Journal of Bio-resource and Stress Management 2(3), 338-340.

Regupathy, A., Ramasubramanian, T., Ayyasamy, R., 2004. Rationale behind the use of insecticide mixtures for the management of insecticide resistance in India. International Journal of Food, Agriculture and Environment 2(2), 278-284.

Sarangdevot, S.S., Kumar, S., Naruka, P.S., Pachauri, C., 2010a. Extent of Roket 44% EC (profenofos 40%+cypermethrin 4%) residues in/on tomato *Lycopersicum esculentum* Mill fruit. Pestology 34(7), 49-50.

Sarangdevot, S.S., Naruka, P.S., Kumar, S., Pachauri, C., 2010b. Extent of profenofos 50% EC residues in/on tomato fruit. Pestology 34(3), 42-43.

Sharma, K.K., 2007. Pesticide Residue Analysis Manual. Directorate of Information and Publications of Agriculture, Indian Council of Agricultural Research, Krishi Anusandhan Bhavan, Pusa, New Delhi, 294.

Swarcewicz, M.K., Gregorczyk, A., 2011. The effects of pesticide mixtures on degradation of pendimethalin in soils. Environmental Monitoring and Assessment. DOI 10.1007/s10661-011-2172-x.

Tashiro, H., Kuhr, R.J., 1978. Some factors influencing the toxicity of soil applications of chlorpyrifos and diazinon to European chofer grubs. Journal of Economic Entomology 71, 903-907.