ISSN NO. 2320-5407

Journal homepage: http://www.journalijar.com

INTERNATIONAL JOURNAL OF ADVANCED RESEARCH

RESEARCH ARTICLE

PERSISTENCE PATTERN OF CHLORPYRIFOS, CYPERMETHIRN AND MONOCROTOPHOS IN OKRA

SUBHASH CHANDRA[1], MUKESH KUMAR[2], ANIL N. MAHINDRAKAR[1], L.P. SHINDE[1]

1. P.G. Department of Chemistry, N.E.S. Science College, Nanded-431 605, Maharashtra, India.
2. Department of Chemistry, Vardhman College, Bijnaur-246701, Uttar Pradesh, India.

Manuscript Info

Manuscript History:

Received: 19 October 2014
Final Accepted: 22 November 2014
Published Online: December 2014

Key words: -
Chlorpyrifos; Cypermethrin; Monocrotophos; Persistence; Okra; GC-MS.

Corresponding Author

SUBHASH CHANDRA

Abstract

Persistence of chlorpyrifos, cypermethrin and monocrotophos on okra was studied following application at dose of 100,200,300g a.i.h^{-1} to work out the safe preharvest waiting period. Samples of okra fruits were collected periodically days at harvest after treatment of the pesticides. A multi-residue extraction procedure was carried out using acetonitrile containing 1% acetic acid and cleaned up with PSA and magnesium sulphate extract analysed by GC-MS. The average initial residues chlorpyrifos, cypermethrin and monocrotophos were in the range of 0.389-0.874, 0.378-0.862 and 0.391-0.898mgkg^{-1}respectively. The residues of pesticides fell below detection in the 15, 17 and 19 days of chlorpyrifos, cypermethrin and monocrotophos, respectively.

Introduction

Okra Abelmoschus esculentus (L) vegetable crop is prone to attack by large number of insect pests among which okra shoot and fruit borer, cause enormous yield loss (Deen et al., 2009). From germination to harvesting the crops is attacked by different insects and pests resulting in low yield production. Intensive sprays of insecticides required to protect the crop at fruiting stage are more likely to leave toxic residues on fruits, which may be hazardous to the consumers. The consumption of pesticide treated food commodity become risky due to the residual persistence of the pesticide. So it is necessary that, pesticide should be effective against pest along with its toxicologically acceptable residue on food commodity (Singh et al., 2007). Chemical control of pest is relatively cheap and quick for controlling the pests. The dissipation of chlorpyrifos in soil and the six selected plants was different, indicating that the persistence of chlorpyrifos residues strongly depends upon leaf characteristics of the selected vegetables (Meng-Xiao Lu et al.,2014). Various pesticides have been used for management of pests in vegetables by (Aktar et al., 2008; Gupta et al., 2009; Mukherjee, 2003; Sahoo et al., 2009 and Sharma et al.,2007) .

There is currently an increasing concern and awareness the hazards of pesticides to consumers. Even with the adoption of integrated pest management, farmers believe in the control of pests using pesticide because of its quick effect. The application of pesticides pre- or post-harvest could, however, leave residues on food products which pose a potential risk to the health of consumer (Lindsay, 1997). Use of insecticides for controlling insect pest complex of vegetable should, therefore, be examined for residues. Hence an attempt has been made to estimate the quantity of residue of chlorpyrifos, cypermethrin and monocrotophos in okra at different days of pre-harvest intervals for safe consumption. The present study was designed to determine the residual persistence and dissipation behavior of pesticides in okra at experimental field at Goa, thereby to suggest waiting period between the spray of pesticides and crop harvesting.

Experimental

Chemical and reagents

Acetic acid HPLC grade, acetonitrile magnesium sulphate, hexane, sodium acetate were purchased from E Merck and primary secondary amine purchased from Agilent Technologies. Technical grade pesticide standards were used for standardizations and it were stored in a freezer. Pesticides used for supervised trial chlorpyrifos EC 20% (Chloro-20), cypermethrin 25%EC (Molthrin-25) and monocrotophos SL36% (Monophos-36) were purchased from local pesticide suppliers. Anhydrous magnesium sulphate used during residue extraction was maintained at 300^{o}C overnight and kept in air tight container, polyethylene or PFTE tube of 15ml and 50 ml capacity with screw cap.

Sample collection

Supervised trial was conducted on okra (Abelmoschus esculentus L), Parbhani kranti variety at the experimental field Vasco-Da-Gama, Goa, during summer season. In supervised trials, chlorpyrifos, cypermethrin and monocrotophos were applied with different concentrations (100, 200 and 300g a.i.ha^{-1}) on the okra. Each treatment was separated by a 3m buffer zone to prevent cross contamination. One control plot (unsprayed) was included for blank analysis and also for recovery experiments. Samples of okra fruits were collected on 0 (2hr), 1, 3, 5, 7, 9, 11, 13, 15, 17 and 19 days at harvest after treatment of pesticide and solvent extraction of the samples were carried out using 1% acetic acid solution of acetonitrile and the extract analysed by GC-MS.

Extraction and Cleanup

Samples of okra 2 kg quantity was taken for the extraction of pesticide residues. The samples were macerated to make paste with Philips mixer (equipped with stainless steel knives), a 15 g portion of the homogenized sample was weighed into a 50 ml polytetrafluoroethylene (PTFE) tube added 15 ml of acetonitrile containing 1% acetic acid (v/v). Then, 6 g $MgSO_4$ and 2.5 g sodium acetate trihydrate (equivalent to 1.5 g of anhydrous form) were added, and the sample was shaken forcefully for 4 min and kept in ice bath. The samples were then centrifuged at 4000 rpm for 5 min and 6 ml of the supernatant were transferred to a 15 ml PTFE tube to which 900 mg MgSO4 and 300 mg PSA were added. The extract was shaken using a vortex mixer for 20 s and centrifuged at 4000 rpm again for 5 min, approximately 2ml of the supernatant were taken in a vials. This extracts were evaporated to dryness under a stream of nitrogen and reconstituted in n-hexane in auto sampler tube for the GC-MS analysis.

Instrumentation

The analysis of pesticide was carried out by an integrated system of gas chromatography, equipped with automatic injection system and coupled to a mass spectrometric system with ion trap analyser. Varian CP-3800 GC, Saturn-2200 mass spectrometer with auto injector CP-8410 was used for analysis. The mass spectrometer was auto tuned using perfluorotributylamine (PFTBA). The separation of pesticide was done in a 30 meter length, 0.25 mm internal diameter and 0.25 µm film thickness coated with 5% phenyl-95% methylpolysiloxane Varian VF-5MS column. Helium was used as the carrier gas at 9.6 psi pressure and 1 ml min^{-1} flow. The injector was used at constant temperature 280^{0}C. The initial oven temperature was 80^{0}C (4min. isothermal) to 180^{0}C (at 20^{0}C min^{-1}) to 250^{0}C (at 2^{0}C min^{-1}) to 280^{0}C (at 10^{0}C min^{-1}) isothermal for 4 minutes. The injection volume was 1µL in splitless mode. The temperature of ion trap, manifold and transference line was 220^{0}C, 50^{0}C and 300^{0}C respectively. The mass spectrometer was used in SIM mode under electron impact at 70 eV and scan time 1 second. The computer that controlled the system also held a GC-MS library specially created for the target analytes under our experimental conditions. The mass spectrometer was calibrated weekly with perfluoro-tributylamine. Helium (99.999%) at a flow-rate of 1 ml min^{-1} was used as carrier and collision gas.

Results and discussion

The study revealed that the initial deposits of chlorpyrifos, 0.389, 0.696 and 0.874mgkg^{-1} when applied 100,200 and 300ga.i.ha^{-1} on first day declined to 0.258, 0.432 and 0.525mgkg^{-1} showing 33.7, 37.9 and 39.9%

dissipation, respectively(table 1). The initial deposits of cypermethrin 0.378, 0.685 and 0.862mgkg^{-1} when applied 100,200 and 300g a.i.ha^{-1} on first day declined to 0.236, 0.424 and 0.515mgkg^{-1} showing 37.6, 38.1 and 40.2% (table 2), respectively whereas the initial deposits of monocrotophos 0.391, 0.698 and 0.898mg kg^{-1} when applied 100,200 and 300g a.i.ha^{-1} on first day declined to 0.256, 0.435 and 0.533mg kg^{-1} showing 34.5, 37.7 and 40.6% , respectively (table 3). Residues of chlorpyrifos, cypermethrin and monocrotophos reached below detection limit (BDL) showing complete dissipation of each pesticide in 15, 17 and 19 days respectively when it was applied 100, 200 and 300g a.i. h^{-1} , on okra.

Tajeda et al., (1983) reported that the disappearance of residues in and on plants is the effect of the interactions of environmental conditions such as wind, rain, sun, humidity and temperature and chemical and physical factors such as volatilization and growth of the plants. Singh and Udeaan (1989) investigated the persistence and dissipation of cypermethrin in okra fruits where 50 or 100g a.i.ha^{-1} was applied three times. After 2nd and 3rd spray, the initial residues were 0.76 and 0.65 mgkg^{-1} for 50g a.i.ha^{-1} dose, respectively and 1.53 and 1.43mgkg^{-1} for 100g a.i.ha^{-1} dose, respectively (Khan et al., 1999).The average residue level of any insecticides depends primarily on the quantity of its active ingredient. Field studies were conducted by Kumar et al., (1998) on chick pea where cypermethrin was applied either at 60 or 90g a.i.ha^{-1} (low and high dose, respectively). Initial mean residue levels on green pods were 0.42 and 0.62mg kg^{-1} at low and high doses, respectively. These dissipated by 73.81 and 70%, respectively after 15days which was also close to the residues at initial level (dry season) and degradation rate of both seasons. Residues of cypermethrin were determined by (Singh and Kalra, 1992) in the fruits and leaves of aubergines and in the soil when applied at 50 and 100g a.i.ha^{-1}. After eight applications at lower dosage, initial deposits on the fruits were 0.73mgkg^{-1} which declined to 0.08mgkg^{-1}in 10 days. Rai et al., (1986) observed the persistence of cypermethrin for 11 days which was below prescribed maximum residue limit within eight days on cauliflower which was close to the safe period for wet season. Persistence and safe period on okra fruits were investigated by Khan et al., (1999). They observed an initial concentration of 1.31 mgkg^{-1} which dissipated to a mean concentration of 0.05mgkg^{-1} after 10 days where residues existed below the maximum residue limit set in India for cypermethrin (0.2mgkg^{-1}) at 5.91 days after final application. Singh SP et al., (2004) studied dissipation and decontamination of cypermethrin (50 and 100gaiha^{-1}) and fluvalinate (40 and 80g a.i.ha^{-1}) in okra fruits. Initial deposits of 0.274 and 0.382 mg kg^{-1} of cypermethrin at 50 and 100g a.i.ha^{-1} treatments, dissipated to 0.013 and 0.020 mg kg^{-1} in 15 days after third application with respective half-life values of 3.4 and 3.5 days and waiting periods of 2 and 3 days.

Parmar et al., (2012), studied dissipation and decontamination of deltamethrin, alphamethrin, deltamethrin (in combination), triazophos, ethion, cypermethrin and profenophos residues in/on okra fruits at middle Gujarat region, India. The samples were procured up to 7 d after application the average initial deposit of deltamethrin, alphamethrin, deltamethrin in combination, triazophos, ethion, cypermethrin and profenophos was 0.152, 0.136, 0.025, 0.543, 0.254, 0.172 and 4.519mgkg^{-1}, respectively which dissipated to 0.025 (83.55%), 0.023 (83.09%), 0.010 (60.00%), 0.015 (0.015%), 0.013 (94.88%), 0.020 (88.37%) and 0.508 (88.76%) mg kg^{-1} on 5th and 7th d. Deen et al.,(2009) studied on three pesticides viz cypermethrin, λ-cyhalothrin and endosulfan @60, 15 and 300g a.i.ha^{-1}, respectively, were applied on okra crop and the residues were determined in fruits at different time intervals. The initial deposits were 0.53 µg g^{-1} for cypermethrin @ 60 g ai ha^{-1}, 0.64µgg^{-1} for λ-cyhalothrin @15g a.i.ha^{-1} and 9.25 µgg^{-1} for endosulfan at 300g a.i.ha^{-1}. The half-life periods calculated were 3.3, 5.2 and 3.8 days and safe waiting periods were 4.7, 8.6 and 8.3 days for cypermethrin, λ-cyhalothrin and endosulfan, respectively. Residue levels reached below MRL value of each pesticide in 9 days. Washing reduced the residues of cypermethrin, λ-cyhalothrin and endosulfan maximum up to 37.4, 35.6 and 23.8%, respectively.

Nath et al., (2005) described dissipation behaviour of ready mix polytrin C 44EC (profenophos 40% + cypermethrin 4%) and spark 36EC (triazophos 35% + deltamethrin 1%) applied at 1 Lha^{-1} in okra crop during Kharif in year 2000 was studied at 0, 1, 3, 5 and 7 days after treatment. Dissipation on 7th day was found to be maximum (98.4%) for profenophos followed by triazophos (86.2%), cypermethrin (73.5%) and deltamethrin (55.7%). Half life (t1/2) values for the above insecticides were 1.35, 2.55, 4.11 and 7.60 days, respectively. All the insecticides followed a first order kinetics. Profenophos and triazophos followed a biphasic dissipation pattern with faster dissipation in phase I (0-1 days) and manifesting slower rate of dissipation in phase II (1-7 days). Samriti et al., (2011) determined residue levels of chlorpyriphos in unprocessed and processed okra fruits to evaluate the effect of different processes (washing and washing followed by boiling/cooking) on reduction of residues of this pesticide in okra. The study was carried out on okra crop (Variety, Varsha Uphar) with application of chlorpyriphos (Radar 20 EC) at 200 g a.i.ha^{-1} and 400g a.i.ha^{-1} (Single Dose, T(1)) and 400 g a.i.ha^{-1} (Double Dose, T(2)). Samples of okra fruits were collected on 0, 1, 3, 5, 7, 10, 15 days and at harvest after treatment. Residues were estimated by GC-ECD system and reached BDL of 0.010mgkg^{-1} on 7th and 15th day in case of single and double dose, respectively. The residues dissipated with half-life period of 3.15 days at lower dose and 3.46 days at higher dose following biphasic first order kinetics.

Jyot et al., (2013) studied dissipation of chlorpyriphos and cypermethrin in chilli following three applications of a combination formulation of Nurelle-D 505 (chlorpyriphos 50% + cypermethrin 5%) at 1 and 2 L ha(-1) at an interval of 15 days. Residues of chlorpyriphos dissipated to more than 80% after 10 days at both the dosages. However, residues of cypermethrin dissipated to the extent of more than 70% in 7 days. These results are almost close to the present study therefore the present results are in consistent with the earlier investigations.

Table: 1 Persistence of chlorpyrifos residues at different intervals from the day of application on okra crop collected from supervised field sprayed with 100, 200 and 300g a.i. ha^{-1}.

Days after treatment	Residue mgkg^{-1} (% of Dissipation)					
	dose (100 g a.i. ha^{-1})	Dissipation%	dose (200 g a.i. ha^{-1})	Dissipation%	dose (300 g a.i. ha^{-1})	Dissipation%
0 (2hr)	0.389	-	0.696	-	0.874	-
1	0.258	33.7	0.432	37.9	0.525	39.9
3	0.155	60.2	0.275	60.5	0.299	65.8
5	0.078	79.9	0.129	81.5	0.156	82.1
7	0.062	84.1	0.075	89.2	0.074	91.5
9	0.025	93.6	0.036	94.8	0.044	94.9
11	0.016	95.9	0.025	96.4	0.035	96.0
13	0.006	98.5	0.016	97.7	0.024	97.2
15	BDL	-	0.009	98.7	0.011	98.7
17	-	-	BDL	-	0.008	99.1
19	-	-	-	-	BDL	-

Table: 2 Persistence of cypermethrin residues at different intervals from the day of application on okra crop collected from supervised field sprayed with 100, 200 and 300g a.i. ha^{-1}.

Days after treatment	Residue mgkg^{-1} (% of Dissipation)					
	dose (100 g a.i. ha^{-1})	Dissipation%	dose (200 g a.i. ha^{-1})	Dissipation%	dose (300 g a.i. ha^{-1})	Dissipation%
0 (2hr)	0.378	-	0.685	-	0.862	-
1	0.236	37.6	0.424	38.1	0.515	40.2
3	0.143	62.2	0.260	62.0	0.290	66.9
5	0.065	82.8	0.120	82.5	0.146	83.1
7	0.050	85.7	0.064	90.7	0.065	92.4
9	0.024	86.8	0.025	96.4	0.032	96.3
11	0.008	97.9	0.018	97.4	0.025	97.1
13	0.004	98.9	0.010	98.5	0.016	98.1
15	BDL	-	0.004	99.4	0.008	99.1
17	-	-	BDL	-	0.005	99.4
19	-	-	-	-	BDL	-

Table: 3 Persistence of monocrotophos residues at different intervals from the day of application on okra crop collected from supervised field sprayed with 100, 200 and 300g a.i. ha^{-1}.

Days after treatment	Residue $mgkg^{-1}$ (% of Dissipation)					
	dose (100 a.i. ha^{-1})	Dissipation%	dose (200 a.i. ha^{-1})	Dissipation%	dose (300 a.i. ha^{-1})	Dissipation%
0 (2hr)	0.391	-	0.698	-	0.898	-
1	0.256	34.5	0.435	37.7	0.533	40.6
3	0.150	61.6	0.270	61.3	0.318	64.6
5	0.081	79.3	0.131	81.2	0.156	82.6
7	0.049	87.5	0.073	89.5	0.086	90.4
9	0.039	90.0	0.045	93.6	0.056	93.8
11	0.019	95.4	0.034	95.1	0.040	95.5
13	0.007	98.2	0.018	97.4	0.028	96.9
15	BDL	-	0.007	99.0	0.014	98.4
17	-	-	BDL	-	0.004	99.5
19	-	-			BDL	

BDL =Below Detection Limit

Conclusion

The dissipation of residue level chlorpyriphos, cypermethrin and monocrotophos below detection level on 15^{th}, 17^{th} and 19^{th} day at 100,200 and 300gm a.i. ha^{-1} dose, respectively. Hence applied doses were safe if the okra fruits harvested after 15^{th}, 17^{th} and 19^{th} days of application of pesticides. Moreover, a good agricultural practice is an important and effective tool in minimizing pesticide residues in food commodities. Therefore this study will provide adequate information to the farmers for safe harvesting period of the vegetables growing under agroclimatic conditions.

References

1. Deen MK, Kumari B and Sharma SS (2009). Dissipation and decontamination of residues of three pesticides in okra fruits. Pestic Res J,21,1**:**80-82.

2. Singh G, Singh B, Battu R, Jyot G, Singh B and Joia B (2007).Persistence of ethion residues on cucumber, cucumis sativus (Linn.) using gas chromatography with Nitrogen Phosphorus Detector. Bull Environ Contam Toxicol,79**:**437-439.

3. Meng-Xiao Lu1,WayneW. Jiang, Jia-Lei Wang, Qiu Jian, Yan Shen, Xian-Jin Liu, Xiang-Yang Yu1 (2014).Persistence and Dissipation of Chlorpyrifos in Brassica Chinensis, Lettuce, Celery, Asparagus Lettuce, Eggplant, and Pepper in a Greenhouse, PLoS ONE 9(6): e100556. doi:10.1371/journal.pone.0100556.

4. Aktar Wasim, Sengupta D and Chowdhury A (2008). Degradation dynamics and persistence of quinolphos and methomyl in/on okra (Ablemoschus esculentus) fruits and cropped soil. Bull Environ Contam Toxicol,80**:**74-77.

5. Gupta S, Sharma RK, Gupta RK, Sinha SR, Singh R and Gajbhiye VT (2009). Persistence of new insecticides and their efficacy against insect pests of okra. Bull Environ Contam Toxicol, 82**:**243-247.

6. Mukherjee I (2003). Pesticides residues in vegetables in and around Delhi. Environ Monit Assess, 86**:**265-271.

7. Sahoo S, Sharma R, Battu R. and Singh B (2009). Dissipation Kinetics of Flubendiamide on chili and soil. Bull EnvironContam Toxicol,83**:**384-387.

8. Sharma K, Rao SC, Dubey J, Patyal S, Parihar N, Battu R, Sharma V, Gupta P, Anoop Kumar, Kalpana, Maisnam J, Singh BD, Sharma I, Amit Nath and Gour T (2007). Persistence and dissipation kinetics of spiromesifen in chili and cotton. Environ Monit Assess,132**:** 25–31.

9. Lindsay,D. G.(1997).Pesticide residue in food: the need for fairer cost-benefit analysis. Pesticide Outlook, 8:6-10.

10. Tejada, A. W., E. D. Magallona, and E. B. Lakan-Ilaw (1983). Insecticide residues in vegetables:application of the modified approach to organophosphate insecticide residues in string bean (Vigna sesquipedalis Fruw.).The Philippine Agriculturist,66:405-416.

11. Singh, B. and A. S. Udeaan (1989). Estimation of cypermethrin residues in the fruits of okra, Abelmoschus esculentus (Linn.). Moench. J. Insect Science,2,1:49-52.

12. Kumar, P., S. P. Singh, R. S. Tanwar, and P. Kumar (1998). Dissipation of cypermethrin residue on chickpea. Pesticide Research Journal,10,2:242-245.

13. Singh, I. P. and R. L. Kalra (1992). Determination of residues of cypermethrin in brinjal fruits, leaves and soils. Indian J. Entomology,54,2:207-216.

14. Rai, S., N. P. Agnihotri, and H. K. Jain (1986). Persistence of residues of synthetic pyrethroids on cauliflower and their residual toxicity against aphids. Indian J. Agricultural Science 59, 9:667-670.

15. Khan, M. A. M., D. J. Reddy, and S. V. Rao (1999). Dissipation of cypermethrin residue in okra fruits. Pesticide Research Journal,11,1:84-85.

16. Singh SP, Kiran, Kumar Sanjay and Tanwar RS (2004). Dissipation and decontamination of cypermethrin and fluvalinate residues in okra, Pesticide Research Journal,16, 2:65- 67.

17. Parmar KD, Korat DM, Shah PG and Singh Susheel (2012). Dissipation and decontamination of some pesticides in/on okra. Pesticide Research Journal:24,1:42-46.

18. Deen, M. K.; Beena Kumari and Sharma, S. S. (2009). Dissipation and decontamination of residues of three pesticides in okra fruits. Pesticide Research Journal,21,1:80-82.

19. Nath P, Kumari B, Yadav PR and Kathpal TS. (2005). Persistence and dissipation of readymix formulations of insecticides in/on okra fruits. Environ Monit Assess. 107(1-3):173-9.

20**.** Samriti, Chauhan R. and Kumari B. (2011). Persistence and effect of processing on reduction of chlorpyriphos residues in okra fruits. Bull Environ Contam Toxicol. , 87(2):198-201.

21. Jyot G, Mandal K, Battu RS and Singh B (2013). Estimation of chlorpyriphos and cypermethrin residues in chilli (Capsicum annuum L.) by gas-liquid chromatography. Environ Monit Assess. 185,7:5703-14.