

**RESEARCH ARTICLE****STUDIES ON PERSISTENCE PATTERN OF PESTICIDES ON BRINJAL****SUBHASH CHANDRA, ANIL N. MAHINDRAKAR, M.K. FUGARE*, L.P. SHINDE**

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*Department of Physics N.E.S. Science College, Nanded-431 605, Maharashtra,
India.Corresponding Author: dr.chandra37@gmail.com**Abstract**

A study was conducted to investigate persistence pattern of chlorpyrifos, cypermethrin and monocrotophos pesticide on brinjal. The pesticides were applied at dose of 100,200,300g a.i.h⁻¹ on brinjal. Samples of brinjal fruits were collected on 0, 1, 3, 5, 7, 9, 11, 13, 15 and 17 days at harvest after treatment of pesticide and extraction of the samples were 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 were in the range of 0.362-0.876, 0.340-0.858 and 0.388-0.891mgkg⁻¹ of chlorpyrifos, cypermethrin and monocrotophos, respectively. The residues pesticides fell below detection in the 13-17, 11-15 and 13-17 days of chlorpyrifos, cypermethrin and monocrotophos, respectively.

Keywords: Chlorpyrifos; Cypermethrin; Monocrotophos; Persistence; Brinjal; GC-MS.**Introduction**

Vegetables, an essential component of the human diet, have taken third place along with fruit crops in taking over the pesticide load next to cotton and rice¹. Pesticides are human-made and naturally occurring chemicals that control insects² weeds, fungi and other pests that destroy crops. The prudent use of pesticides is considered to be indispensable for the control of insect-borne diseases in order to enhance food supply for an increasing world population. Pesticide application is still the most effective and accepted means for the protection of plants from pests, and has contributed significantly to enhance agricultural productivity and crop yield^{3,4}. The problem of contamination of food sources, especially vegetables by pesticide residues constitutes one of the most serious challenges to public health. The hazards of toxic residues can be considerably reduced if pesticides are used in accordance with "good agricultural practice". The total dietary intake of pesticide

residues that remain on agricultural commodities are known as toxins and therefore, it is desirable to reduce these residues.

It has been estimated that 85-90% of pesticides in human bodies are received through foods vegetables are of direct concern with respect to the buildup of pesticides residues from point of hazards to consumers, as they are consumed afresh immediately after field harvest without giving much time for dissipation of residues. With the growth of pesticide use in developing countries, the number of accidents, cases of poisoning and occurrence of environmental hazards are also likely to increase. In most countries, governments are endeavoring to regulate pesticide usage and increase farmer's awareness of hazards, while at the same time trying to promote the use of environmental friendly alternatives such as integrated pest management⁵. It was showed that the residues of imidacloprid in

tomato leaves were persisted up to 30 days after the seed treatment @ 10g/kg⁶. Residues of lambda-cyhalothrin @ 15g ha⁻¹ and 30 g ha⁻¹ in/on acid lime were persisted for 20 days by imparting 3.4 and 8.0 days as half life and waiting period, respectively⁷. The present study aimed to investigate persistence pattern of residues of some commonly used pesticides on brinjal grown under local agroclimatic conditions.

Experimental

Chemical and reagents

The organic solvent acetic acid, acetonitrile HPLC grade, magnesium sulphate, hexane, sodium acetate AR grade purchased from E Merck and primary secondary amine purchased from Agilent Technologies. The 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) purchased from local pesticide suppliers. Anhydrous magnesium sulphate used during residue extraction was maintained at 300°C overnight and kept in air tight container. Polyethylene or PTFE 15ml and 50 ml with screw cap tubes.

Sample collection

Supervised trial was conducted on brinjal (Agassim variety) at the farmer orchard 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 brinjal. 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 brinjal fruits were collected on 0 (2hr), 1, 3, 5, 7, 9, 11, 13, 15 and 17 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 brinjal 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 MgSO₄ 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°C. The initial oven temperature was 80°C (4min. isothermal) to 180°C (at 20°C min⁻¹) to 250°C (at 2°C min⁻¹) to 280°C (at 10°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°C, 50°C and 300°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 under laboratory conditions the initial deposits of chlorpyrifos, 0.362, 0.679 and

0.876mgkg⁻¹ when applied 100,200 and 300g a.i.h⁻¹ on first day declined to 0.229, 0.409 and 0.501mgkg⁻¹ showing 36.7, 39.7 and 41.9% dissipation, respectively (table 1). The initial deposits of cypermethrin 0.340, 0.661 and 0.858mgkg⁻¹ when applied 100,200 and 300g a.i.h⁻¹ on first day declined to 0.207, 0.382 and 0.488mgkg⁻¹ showing 39.1, 42.2 and 43.1% (table 2), respectively whereas the initial deposits of monocrotophos 0.388, 0.689 and 0.891mgkg⁻¹ when applied 100,200 and 300g a.i.h⁻¹ on first day declined to 0.236, 0.419 and 0.521mgkg⁻¹ showing 39.2, 39.2 and 43.1% , respectively (table 3). Residues of chlorpyrifos, cypermethrin and monocrotophos reached below detection limit (BDL) showing complete dissipation on 11, 13, 15 days, 11, 13, 15 days and 13, 15, 17 days respectively when it was applied 100, 200 and 300 a.i.h⁻¹, on brinjal.

The dissipation of pesticide residues in/on crops depends on the climatic conditions, type of application, plant species, dosage, the interval

between application and harvest⁸. The persistence of chlorpyrifos till 9 days in cauliflower has been reported by ⁹ and persistence of quinalphos in cabbage up to 9 days has been reported in which residues dissipated completely within 10 days¹⁰. It was investigated the persistence and dissipation of cypermethrin in okra fruits where 50 or 100 g ai/ha were applied three times. After 2nd and 3rd spray, the initial residues were 0.76 and 0.65 mg/kg for 50 g ai/ha dose, respectively and 1.53 and 1.43 mg/kg for 100g ai/ha dose, respectively ¹¹. 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 season¹². Persistence and safe period on okra fruits were investigated that the initial concentration of 1.31 mg/kg which dissipated to a mean concentration of 0.05 mg/kg after 10 days where residues existed below the maximum residue limit set in India for cypermethrin (0.2 mg/kg) at 5.91 days after final application¹³. These results are comparable to the present investigation.

Table: 1 Persistence of chlorpyrifos residues at different intervals from the day of application in brinjal samples 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)	% of Dissipation	dose (200 g a.i. ha ⁻¹)	% of Dissipation	dose (300 g a.i. ha ⁻¹)	% of Dissipation
0 (2hr)	0.362	-	0.679	-	0.876	-
1	0.229	36.7	0.409	39.7	0.509	41.9
3	0.129	64.3	0.240	64.5	0.288	67.1
5	0.051	85.9	0.104	84.7	0.139	84.1
7	0.035	90.3	0.047	93.1	0.059	93.3
9	0.009	97.5	0.018	97.3	0.026	97.0
11	0.002	99.4	0.010	98.5	0.012	98.6
13	BDL	-	0.002	99.7	0.007	99.2
15	-	-	BDL	-	0.004	99.5
17	-	-	-	-	BDL	-

Table: 2 Persistence of cypermethrin residues at different intervals from the day of application in brinjal samples 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)	% of Dissipation	dose (200 g a.i. ha ⁻¹)	% of Dissipation	dose (300 g a.i. ha ⁻¹)	% of Dissipation
0 (2hr)	0.340	-	0.661	-	0.858	-
1	0.207	39.1	0.382	42.2	0.488	43.1
3	0.106	68.8	0.224	66.1	0.266	68.9
5	0.029	91.5	0.078	88.2	0.111	87.5
7	0.015	95.6	0.030	95.5	0.038	95.6
9	0.005	98.5	0.013	98.0	0.023	97.3
11	BDL	-	0.004	99.4	0.011	98.7
13	-	-	BDL	-	0.004	99.5
15	-	-	-	-	BDL	-
17	-	-	-	-	-	-

Table: 3 Persistence of monocrotophos residues at different intervals from the day of application in brinjal samples 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)	% of Dissipation	dose (200 a.i. ha ⁻¹)	% of Dissipation	dose (300 a.i. ha ⁻¹)	% of Dissipation
0 (2hr)	0.388	-	0.690	-	0.891	-
1	0.236	39.2	0.417	39.6	0.521	41.5
3	0.148	61.8	0.261	62.2	0.297	66.7
5	0.073	81.2	0.128	81.4	0.149	83.3
7	0.038	90.2	0.058	91.6	0.068	92.4
9	0.024	93.8	0.039	94.3	0.032	96.4
11	0.006	98.5	0.009	98.7	0.018	98.0
13	BDL	-	0.004	99.4	0.008	99.1
15	-	-	BDL	-	0.004	99.5
17	-	-	-	-	BDL	-

Conclusion

Pesticide residues in food pose a significant health effect on human and animals. To provide adequate food for growing population, the usage of pesticide is necessary but dissemination of information regarding food safety, pesticide handling and good agricultural practices (GAP) among farmers is also a dire need. Moreover, good agricultural practices and is the important and effective tools 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.

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