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Dissipation Pattern of Triazophos and Chlorpyriphos in Curry Leaf

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Abstract

Field experiments were conducted during *kharif* 2014 and 2015 with curry leaf variety Suwasini to study the dissipation pattern of triazophos 40 EC at 500 g a.i. ha^{-1} and chlorpyriphos 20 EC at 300 g a.i. ha^{-1} by giving two sprays first at vegetative stage and second 10 days later. The leaf samples collected at the 0, 1st, 3rd, 5th, 7th, 10th, 15th, 20th, 25th, 30th and 45th day after the second spray and soil samples at the 45th day for residue analysis showed initial deposits of triazophos 18.19 $mg{\cdot}kg^{-1}$ and chlorpyriphos 14.73 $mg{\cdot}kg^{-1}$, respectively. No residues were observed in soil samples. The residues reached to Below Determination Level (BDL) at 20 and 15 days, respectively. As there were no pesticide recommendations and MRLs fixed for any of the pesticide in curry leaf, the day at which residues reached BDL can be suggested as the safe harvest period for curry leaf.

Subject Areas

Agricultural Science, Entomology

Keywords

Dissipation Pattern, Triazophos, Chlorpyriphos, Curry Leaf

1. Introduction

Curry leaf [*Murraya koenigii* (L.) Sprengel] is a leaf spice of the citrus family Rutaceae. Curry leaves forming an integral part of spicing up dishes are not a part of mere garnishing. They are rich in medicinal, nutraceutical properties and have even cosmetic uses. In India, of late it is cultivated on commercial scale (Tamil Nadu, Karnataka, Andhra Pradesh and Telangana) and has gained importance as a major spice crop with high export potential [1]. A total of 12 insect pests belonging to 10 families of 5 orders were recorded infesting curry leaf plants [2]. As per Insecticides act 1968, there is no pesticide recommendation for spray on curry leaf as on today and hence there are no MRLs suggested by Codex Alimentarius Commission. However, farmers are using pesticides indiscriminately that are designed to control the pest even if there are no recommendations for the crop and whether the pest is present or not. Hence, residues were detected at the farm gate level for export location and led to the rejection of the consignment [3]. According to the report of the Indian delegation at the 45th session of the Codex Committee on Pesticide Residues (CCPR) held at Beijing, China (6-11 May, 2013) in agenda no. 11, India is considered for fixation of new and revised MRLs of profenophos, chlorpyriphos, cypermethrin, methyl parathion, triazophos, ethion and quinalphos in curry leaves based on Good Agricultural Practice (GAP) trials and monitoring data and should submit in the prescribed format to Joint FAO/WHO Meeting on Pesticide Residues (JMPR), as a follow-up, for evaluation in 2014 for fixation of MRL on curry leaves. By keeping in view all these most important issues of concern, the present comprehensive study, on dissipation of newer insecticides viz., triazophos and chlorpyriphos, was carried out in curry leaf.

2. Material and Methods

A field experiment was conducted during *kharif*, 2014 and 2015 at Department of Agroforestry, College of Agriculture, Professor Jayashankar Telangana State Agricultural University (PJTSAU), Rajendranagar, Hyderabad with seven treatments and three replications in Randomized Block Design (RBD) on curryleaf Variety Suwasini. The experimental site is situated in Southern Telangana Zone with semi-arid climate and between 17˚19' North latitude, 78˚23' East longitude and 542.3 m above mean sea level utilizing the insecticidal treatments *viz.,* triazophos 40 EC at 500 g a.i. ha^{-1} and chlorpyriphos 20 EC at 300 g a.i. ha^{-1} sprayed twice, first at vegetative stage and second at 10 days after first spray with hand compression knapsack sprayer and the amount of spray fluid used was 500 $l \cdot ha^{-1}$. The laboratory studies (2015-16) were carried out in the All India Network Project on Pesticide Residues, Extension Education Institute premises, Rajendra-nagar, Hyderabad. The weather parameters during the crop period are given in **Table 1**.

2.1. Sample Collection

The curry leaf samples were collected at 0, 1, 3, 5, 7, 10, 15, 20, 25, 30 and 45th day after second spray and soil samples at 45th day for residue analysis. The leaf samples (1 kg) were collected randomly from each treatment in polythene bags and brought to the laboratory immediately for further sample processing. Soil samples (2 kg) were collected following "Z" sampling plan, air dried, grounded, and sub-sampling was done following quartering method.

2.2. Extraction and Clean up Procedure for Leaf Samples

The leaf samples were analyzed for both triazophos and chlorpyriphos residues

Table 1. Meteorological data during the crop period.

Standard meteorological week	Date, Month & Year	Temperature (˚C)		Mean Relative Humidity		Mean Sunshine ($hrs \cdot day^{-1}$)	Mean evaporation ($mm \cdot day^{-1}$)	Rainfall (mm)	Wind speed ($km \cdot hr^{-1}$)
		Maximum	Minimum	I	II				
36	3-9 September 2014	27.5	22.6	86.0	66.4	5.1	2.6	12.2	8.2
37	10-16	31.0	22.8	87.4	62.0	5.8	3.2	14.0	5.4
38	17-23	31.1	22.2	90.0	62.7	4.2	2.9	8.0	3.8
39	24-30	32.3	22.1	86.3	50.6	6.2	3.8	15.0	2.0
40	1-7 October	34.1	21.9	80.3	44.9	7.6	5.3	40.2	1.3
41	8-14	32.4	20.3	78.0	49.0	4.3	4.5	0.8	3.9
42	15-21	32.8	19.2	85.4	46.9	8.2	5.6	6.2	2.5
43	22-28	28.3	19.0	89.0	67.6	4.0	4.0	22.0	2.0
44	29-4 November	30.4	18.4	79.9	24.3	8.3	4.8	0.0	2.3
45	5-11	30.9	16.4	76.1	42.0	6.8	5.4	0.0	2.3
46	12-18	30.0	19.7	81.1	61.1	5.5	4.5	10.6	1.8
47	19-25	30.6	16.4	87.0	42.3	7.6	4.6	0.0	1.2
48	26-2 December	30.6	12.1	72.6	25.6	8.5	4.1	0.0	1.7
49	3-9	30.5	12.0	81.3	41.6	9.1	4.1	0.0	1.6
50	10-16	28.2	15.9	88.7	68.0	3.6	2.8	0.0	1.5
51	17-23	27.1	9.3	70.7	41.1	7.7	2.8	0.0	1.8
52	24-31	27.1	11.4	69.4	46.6	8.1	2.9	0.0	1.5
1	1-7 January 2015	29.0	17.1	77.6	46.4	6.3	3.9	0.0	1.5
2	8-14	27.1	9.0	66.0	22.9	9.8	3.7	0.0	1.3
3	15-21	28.2	9.1	74.6	31.9	9.2	3.7	0.0	1.6
4	2-28	29.4	12.5	78.9	30.0	9.1	4.4	0.0	2.5
5	29-4 February	28.8	13.3	85.6	35.6	9.3	4.5	0.0	2.3
6	5-11	30.7	13.4	74.1	25.9	9.9	5.0	0.0	3.2
7	12-18	33.1	15.0	65.7	18.4	10.2	5.4	0.0	1.2

following the AOAC official method 2007, 01 (QuEChERS) after validation of the method at the laboratory. One kg of leaf samples collected from all treatments was homogenized with robot coupe blixer separately. 7.5 g sample was taken in 50 ml centrifuge tube and added with 30 ± 0.1 ml acetonitrile. The sample was homogenized at 14,000 – 15,000 rpm for 2 - 3 min using Heidolph silent crusher. The samples were then added with 3 ± 0.1 g sodium chloride and mixed by shaking gently followed by centrifugation for 3 min at 2500 - 3000 rpm to separate the organic layer with the room temperature of 22˚C ± 2˚C. The top organic layer of about 16 ml was taken into the 50 ml centrifuge tube and added with 9 ± 0.1 g anhydrous sodium sulphate to remove the moisture content. 8 ml of extract was taken into 15 ml tube, containing 0.4 ± 0.01 g PSA sorbent (for dispersive solid phase d-SPE cleanup), 1.2 ± 0.01 g anhydrous magnesium sulphate and 0.05 ± 0.01 g GCB (remove chlorophyll). The sample tube was vortexed for 30 sec, followed by centrifugation for 5 min at 2500 - 3000 rpm. The extract of 1 ml acetonitrile was transferred into 2 ml vial by filtering through 0.22 µm filter paper for the analysis on LC-MS under standard operational conditions (Table 2).

2.3. Extraction and Clean up Procedure for Soil Samples

The soil samples were analyzed for both triazophos and chlorpyriphos residues following the QuEChERS method after validation of the method in the laboratory. Two kg of soil was collected from each plot in Polythene bags. The soil samples were pooled treatment wise, mixed well and about 200 g of the representative sample was drawn by quartering method. The soil samples were dried at room temperature under shade, ground, passed through 2 mm sieve and a representative 10 g sample was taken into 50 ml centrifuge tube. The sample tube is then added with 20 ± 0.1 ml acetonitrile. The sample is then added with 1 ± 0.1 g sodium chloride and 4 ± 0.1 g Magnesium sulphate mixed by shaking gently followed by centrifugation for 3 min at 3300 rpm to separate the organic layer. The top organic layer of about 10 ml was taken into the 15 ml centrifuge tube containing 1.5 ± 0.1 g magnesium sulphate and 0.25 g PSA and sonicated for 1 min to remove air bubbles and centrifuged for 10 min at 3000 rpm. The extract of about 1 ml (0.5 g sample) was transferred into vials for LCMS/MS analysis under standard operational conditions (Table 2). The final extract of the sample *i.e.*, 1 ml which is equal to 0.5 g sample of both curry leaf and soil were directly injected in LCMS/MS and the residues of pesticides recovered from fortified samples were calculated using the following formula.

$$\text{Residues}\left(\text{mg}\cdot\text{kg}^{-1}\right)=\frac{a\times b\times c\times d}{e\times f\times g}$$

where *a*: sample peak area

Table 2. LCMS operating parameters for analysis.

LC-MS/MS	SHIMADZU LC-MS/MS 8040
Detector	Mass Spectrophotometer
Column	KINETEX, 2.6 µ, C18 Column, 100 × 3.0
Column Oven Temperature	40˚C
Retention Time (RT)	Triazophos - 13.29 min Chlorpyriphos - 3.79 min
Nebulizing gas	Nitrogen
Nebulizing flow gas	2.0 litres/min
Pump Mode/flow	Gradient/0.4ml/min
LC Programme	A: Ammonium formate in water (10 Mm) - 65% B: Ammonium formate in methanol (10 Mm) - 35%
Total Time of Programme	24 min

b: concentration of standard (ppm)

c: μl standard injected

d: final volume of the sample

e: standard peak area

f: weight of sample analyzed

g: μl of sample injected

$$\text{Weight of the sample analyzed} = \frac{\text{Sample weight}\ (7.5\ \text{g}) \times \text{aliquot taken}}{\text{Volume of acetonitrile}\ (30\ \text{ml})}$$

The recovery percentage and recovery factors were calculated using the following formula.

$$\text{Per cent recovery} = \frac{\text{Residue quantified in fortified sample}}{\text{Fortified level}} \times 100$$

$$\text{Recovery factor} = \frac{100}{\text{Per cent recovery}}$$

2.4. Fortification and Recovery Studies

The untreated control leaf and soil samples were fortified with required quantity of triazophos and chlorpyriphos to obtain 0.5, 0.25 and 0.05 mg·kg^{-1} fortification levels and the samples were extracted and cleaned up as per QuEChERS method to validate the suitability of method.

The recovery of triazophos is 85.49, 115.7 and 88.62 per cent from the curry leaf fortified at 0.5, 0.25 and 0.05 mg·kg^{-1}, while chlorpyriphos fortified at 0.5, 0.25 and 0.05 mg·kg^{-1} has shown the recovery of 91.68, 115.07 and 90.37 per cent. Hence, the limit of quantification (LOQ) is 0.05 mg·kg^{-1} in curry leaf for both triazophos and chlorpyriphos.

In soil samples, the recovery of triazophos is 118.65, 90.52 and 87.32 per cent at 0.5, 0.25 and 0.05 mg·kg^{-1} level of fortification, while the chlorpyriphos fortified at 0.5, 0.25 and 0.05 mg·kg^{-1} have shown the recovery of 126.97, 90.85 and 90.63 per cent. Hence, the limit of quantification (LOQ) is 0.05 mg·kg^{-1} in soil for both triazophos and chlorpyriphos.

3. Results and Discussion

The initial deposits of triazophos 40 EC @ 500 g a.i. ha^{-1} and chlorpyriphos 20 EC @ 300 g a.i. ha^{-1} were 18.19 and 14.73 mg·kg^{-1}, respectively which dissipated to below determination levels (<0.05 mg·kg^{-1}) at 20 and 15 days, respectively. The half-life values were 2.08 and 1.43 days, respectively. As there were no MRLs fixed, the day at which residues reached to BDL was suggested as safe harvest *i.e.*, 20 and 15 days, respectively. Soil samples collected at harvest (45th day) were free from the residues of both pesticides (**Table 3**, **Table 4**, **Figure 1** and **Figure 2**). The initial deposits of 1.10 mg·kg^{-1} of triazophos detected in fruit samples of tomato, dissipated to BDL by the 7th day [4]. [5] reported initial deposits of 2.13 mg·kg^{-1} reached BDL on the 10th day with half-life of 1.78 days in capsicum. The variation of results pertaining to the initial deposits (18.19

Table 3. Dissipation of triazophos in curry leaf.

Days after last spray	Residues of triazophos (mg·kg⁻¹)				Dissipation (%)
	R_1	R_2	R_3	Average	
0	18.04	17.99	18.54	18.19	0.00
1	15.29	15.84	14.59	15.24	16.22
3	10.98	9.87	10.03	10.29	43.43
5	6.92	5.9	6.77	6.53	64.10
7	3.88	3.56	3.99	3.81	79.05
10	1.09	1.12	1.01	1.07	94.12
15	0.07	0.17	0.11	0.12	99.34
20	BDL	BDL	BDL	BDL	100.00
Soil (45th day)	BDL	BDL	BDL	BDL	-
Regression equation	Y = 4.412 + (−0.144)X				
R^2	0.968				
Half-life (Days)	2.08				

BDL: Below Determination Level (<0.05 mg·kg^{-1})

Table 4. Dissipation of chlorpyriphos in curry leaf.

Days after last spray	Residues of chlorpyriphos (mg·kg⁻¹)				Dissipation (%)
	R_1	R_2	R_3	Average	
0	14.63	13.54	16.02	14.73	0.00
1	13.08	12.99	12.58	12.88	12.56
3	8.92	9.05	9.23	9.07	38.42
5	4.22	4.63	3.58	4.14	71.89
7	1.97	2.02	1.58	1.86	87.37
10	0.09	0.04	0.12	0.08	99.46
15	BDL	BDL	BDL	BDL	100.00
Soil (45th day)	BDL	BDL	BDL	BDL	-
Regression equation	Y = 4.419 + (−0.210) X				
R^2	0.882				
Half-life (Days)	1.43				

BDL: Below Determination Level (<0.05 mg·kg^{-1})

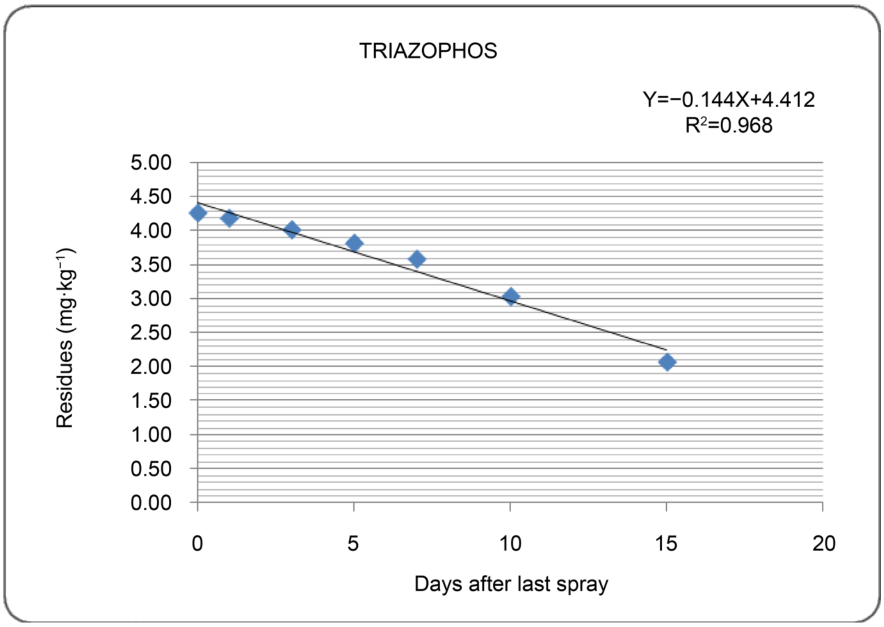

Figure 1. Dissipation of triazophos in curry leaf.

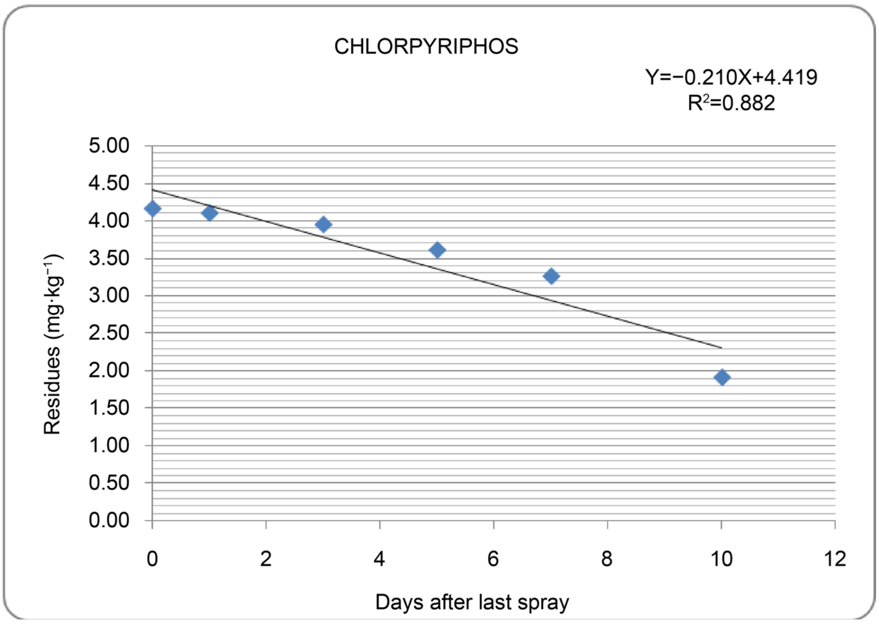

Figure 2. Dissipation of chlorpyriphos in curry leaf.

mg·kg^{-1}) may be due to variation in dosages of application, change in matrix and climatic conditions. Results were in agreement with the work done by [6], who reported the initial deposit of 15.40 mg·kg^{-1} of chlorpyriphos in curry leaf which reached BDL by the 15th day with half-life of 1.5 days and safe waiting period of 14.08 days. Similar results were obtained by [7] on curry leaf with different pesticides. The insecticide dose used with a spray interval of 10 days to protect leaves can lead to residues being detected at the farm gate level or export location and rejection of the consignment. Curry leaves from India are contaminated with insecticides, with 40% containing residues exceeding maximum residue limits of chlorpyriphos, triazophos [8]. Inappropriate insecticide use among curry leaf farmers makes it necessary to evaluate plant products, horticultural mineral oils and green-labeled insecticides against major pests of curry leaf to reduce hazards of insecticides residues. Information on use of insecticides that are safer to natural enemies, utilization of plant products and bio-agents for pest management and knowledge on pesticides dosage, application intervals and insecticide residues are needed so that internal use and export of the commodity are safe. The crops affected by some pests and diseases, trigger off major losses of quality crops and initiate the use of more pesticides. Therefore, an effective way of educating the farmers via training and electronic media is advised particularly in view of the export potential of the crop to reduce the risk of rejection at export level.

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