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Dissipation Kinetics of Trifloxystrobin and Tebuconazole on Chili and Soil

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Abstract Dissipation of trifloxystrobin and tebuconazole were studied following two applications of a combination formulation of Nativo 75 WG (trifloxystrobin 25% + tebuconazole 50%) @ 250 and 500 g ha^{-1} at 10 days interval. Samples of chili were collected at 0, 1, 3, 5, 7, 10 and 15 days after the last application. Red chili and soil samples were collected after 20 days of last application. Half-life period for trifloxystrobin were found to be 1.81 and 1.58 days and for tebuconazole these values were observed to be 1.37 and 1.41 days, respectively, at single and double the application rates. Trifloxystrobin residues dissipated below its limit of quantification (LOQ) of 0.01 mg kg^{-1} after 5 and 7 days, respectively, at single and double the application dosages whereas tebuconazole residues took 7 and 10 days, respectively. Red chili & soil samples collected after 20 days did not reveal the presence of trifloxystrobin and tebuconazole at their determination limit of 0.01 mg kg^{-1}.

Keywords Trifloxystrobin · Tebuconazole · Residues · Dissipation · Half-life

Chili (*Capsicum annuum* L.; *Capsicum frutescene* L.), also called red pepper', is an important cash crop in India and is grown for its pungent fruits, which are used both green and ripe (the latter in the dried form) to impart pungency to the food. As a condiment, it has become indispensable in every Indian home. It is also used medicinally, and in chutnies and pickles. The pungency is due to the active principle 'capsicin' contained in the skin and the septa of the fruit. The world consumption of chilies and paprika is going up due to the increasing popularity of ethnic foods. The increased availability of oleoresins and spice oils of chili has also enhanced its consumption in various food preparations. India is the largest producer of chilies in the world but its production pattern is highly erratic (Thamburaj and Singh 2005).

Nativo 75WG is a water dispersible granular formulation containing 25% w/w trifloxystrobin and 50% w/w tebuconazole (Fig. 1). It is a broad spectrum systemic fungicides with protectant and curative properties for use on brussels sprouts, cabbage, broccoli, cauliflower, carrots and leeks for the control of dark leaf spot, light leafy spot, powdery mildews, phoma leaf spot, whit blisters, purple blotch etc. (http://www.bayercropscience.com, 2009). The presence of residues on crops is a matter of serious concern; therefore, it becomes mandatory to assess the impact of use of this fungicide from residues point of view for the safety of the consumers. However, no information is available on persistence of trifloxystrobin and tebuconazole on chili under subtropical condition. Therefore, the present study was carried out to investigate the dissipation kinetics of trifloxystrobin and tebuconazole residues in samples of chili and soil.

Materials and Methods

The working standards of trifloxystrobin and tebuconazole (purity 98.5%) were supplied by M/s Bayer Crop Science Limited, Mumbai. All the solvents used were of laboratory grade. These were redistilled in all glass apparatus and

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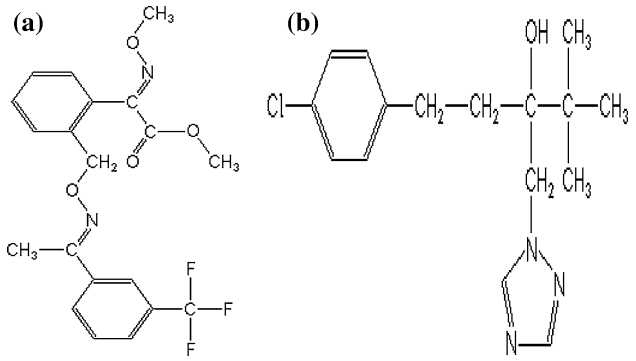

Fig. 1 Chemical structure of **a** Trifloxystrobin **b** Tebuconazole

suitability of solvents was ensured by running reagent blank along with actual analysis. The stock solutions of trifloxystrobin and tebuconazole were prepared at 1,000 μg mL^{-1} in distilled acetone. These solutions were diluted to obtain concentrations of 100.0, 10.0, 1.0, 0.1, 0.01 μg mL^{-1}.

Chili (var. CH-1) was raised and transplanted during summer according to recommended agronomic practices at Entomological Research Farm, Punjab Agricultural University, Ludhiana, India using randomized block design (RBD). The first application of Nativo 75WG @ 187.5 and 375 g a.i. ha^{-1} was made at fruit development stage using Aspee Knapsack sprayer fitted with hollow cone nozzle. Subsequently the 2nd application was made at 10 days interval. Each treatment was replicated thrice and size of each plot was 50 m^2. In control plots, only water was sprayed.

About 500 g samples of chili was collected from each treated and control plots at 0 (2 h), 1, 3, 5, 7, 10 and 15 days after the last application of the insecticide. Red chili and soil samples were collected after 20 days of the last application. Samples were extracted immediately after sampling.

The extraction and cleanup of chili and soil samples for residues of trifloxystrobin and tebuconazole were carried out as per procedure reported by Jyot et al. (2010). Samples of chili fruits were chopped and finely blended and a representative 50 g sample was placed overnight into 100 mL acetone in an erlenmayer flask. The extract was filtered into 1 L separatory funnel was diluted with 600 mL brine solution and partitioned the contents two times into 75 and 75 mL dichloromethane and two times into 75 and 75 mL ethyl acetate. Both dichloromethane and ethyl acetate fractions were combined, dried over anhydrous sodium sulphate and treated with 500 mg activated charcoal powder for about 2–3 h at room temperature. The clear extract so obtained was filtered through Whatman filter paper No.1, concentrated to near dryness and again added about 20 mL of acetone and concentrated using rotary evaporator at 30°C. Repeated the process to completely evaporate dichloromethane and ethyl acetate and the final volume was reconstituted to about 5 mL using distilled acetone. Soil samples were dried, grounded and sieved. A representative sample of 50 g was extracted as per the procedure mentioned for chili fruits.

The residues of trifloxystrobin and its metabolite CGA321113 and tebuconazole were estimated on GC equipped with Flame Thermoionic Detector (FTD). The operating conditions were; Injector temperature (°C): 300, nitrogen flow rate: 30.0 mL/min, hydrogen flow rate: 3.0 mL/min, Air: 145 mL/min. Under these operating conditions the retention time of metabolite CGA321113, trifloxystrobin and tebuconazole were found to be 3.27, 4.69, and 5.45 min, respectively. Residues were estimated by comparison of peak height/peak area of the standards with that of the unknown or spiked samples run under identical conditions. Half- scale deflection was obtained for 5 ng trifloxystrobin, CGA321113 and tebuconazole and limit of quantification (LOQ) was found to be 0.01 mg/kg for each.

Chili and soil samples were spiked with trifloxystrobin & its metabolite CGA321113 and tebuconazole at different levels and analysed as per the methodology described above. Per cent recovery were found to be consistent and more than 80%. (Table 1).

The persistence of trifloxystrobin and tebuconazole has generally been expressed in terms of DT_{50} i.e. time for disappearance of pesticide to 50% of its initial concentration. The DT_{50} of trifloxystrobin and tebuconazole were calculated using Hoskins (1961) formula.

Results and Discussion

The results of dissipation of trifloxystrobin on chili and soil are presented in Table 2. Average initial deposits of trifloxystrobin on chili were found to be 0.31 and 0.59 mg kg^{-1}, respectively, following two applications of Nativo 75 WG @ 250 & 500 g ha^{-1} at 10 days interval. Residues of trifloxystrobin dissipated below LOQ of 0.01 mg kg^{-1} in 5 and 7 days at single and double dosages, respectively. The DT_{50} trifloxystrobin was found to be 1.81 and 1.58 days at single and double dosages, respectively. CGA321113, metabolite of trifloxystrobin was not detected at 0.01 mg kg^{-1} level in chili samples collected at different time intervals. Red chili and soil samples collected at 20 days after last spray also did not reveal the presence of trifloxystrobin and its metabolite.

The average initial deposits of tebuconazole on chili were found to be 0.95 and 1.88 mg/kg respectively, following two applications at 10 days interval of a Nativo 75 WG (trifloxystrobin 25% + tebuconazole 50%) @ 187.5

Table 1 Per cent recovery of trifloxystrobin, CGA321113 and tebuconazole on chili and soil

Substrate	Fortification level	Recovery (%)		
		Trifloxystrobin	CGA321113	Tebuconazole
Chili	0.01	[a]85.15 ± 5.05	85.80 ± 3.60	82.30 ± 4.50
	0.05	86.00 ± 4.56	88.00 ± 4.00	86.90 ± 4.50
	0.20	88.33 ± 7.64	84.67 ± 4.16	89.33 ± 5.03
Soil	0.01	85.00 ± 4.03	88.00 ± 5.03	86.50 ± 2.00
	0.05	90.00 ± 3.80	91.00 ± 2.50	92.00 ± 1.08
	0.20	88.33 ± 5.77	94.33 ± 4.04	85.33 ± 1.53

[a] Mean ± SD of three replicates determination

Table 2 Residues of trifloxystrobin (mg kg^{-1}) found in chili and soil at different times after the application of Nativo 75WG @ 187.5 and 375 g a.i.ha^{-1}

Days after application	62.5 g a.i./ha			125 g a.i./ha		
	Replicates	Mean ± SD	% dissipation	Replicates	Mean ± SD	% dissipation
Before application	BDL	[a]BDL	–	BDL	BDL	–
	BDL			BDL		
	BDL			BDL		
0	0.28	0.31 ± 0.02	–	0.68	0.59 ± 0.08	
	0.33			0.53		
	0.32			0.56		
1	0.16	0.18 ± 0.02	41.93	0.38	0.31 ± 0.06	47.45
	0.17			0.30		
	0.20			0.26		
3	0.09	0.10 ± 0.01	67.74	0.13	0.15 ± 0.02	74.58
	0.09			0.17		
	0.11			0.14		
5	BDL	BDL	–	0.12	0.09 ± 0.03	84.74
	BDL			0.09		
	BDL			0.05		
7	BDL	BDL	–	BDL	BDL	–
	BDL			BDL		
	BDL			BDL		
Red Chili samples after 20 days	BDL	BDL	–	BDL	BDL	–
	BDL			BDL		
	BDL			BDL		
Soil samples after 20 days	BDL	BDL	–	BDL	BDL	–
	BDL			BDL		
	BDL			BDL		
[b]$T_{½}$ (days)	1.81			1.58		

[a] BDL = Below determination limit of 0.01 mg kg^{-1}

[b] $T_{1/2}$ = Half-life time

Residues in the samples from untreated control were detected as BDL of 0.01 mg kg^{-1}

CGA321113 was not detected at 0.01 mg kg^{-1} level in chili samples collected at different time intervals and was not detected in soil

and 375 g a.i. ha^{-1}. Residues of tebuconabzole dissipated below detectable level of 0.01 mg kg^{-1} after 7 and 10 days at single and double dosages, respectively. Half-life of tebuconazole on chili was observed to be 1.37 and 1.41 days at single and double dosages, respectively. Red chili and soil samples collected after 20 days did not reveal the presence of tebuconazole at the determination limit of 0.01 mg kg^{-1} (Table 3). However, Garland et al. (1999) had reported the residues level of tebuconazole in peppermint crops following three applications of tebuconazole @125 and 250 g a.i. ha^{-1} at 0.26 and 0.80 mg kg^{-1} after 64 days of the last application.

Table 3 Residues of tebuconazloe (mg kg^{-1}) found in chili and soil at different times after the application of Nativo 75WG @ 187.5 and 375 g a.i.ha^{-1}

Days after application	125 g a.i./ha			250 g a.i./ha		
	Replicates	Mean ± SD	% dissipation	Replicates	Mean ± SD	% dissipation
Before application	BDL	[a]BDL	–	BDL	BDL	–
	BDL			BDL		
	BDL			BDL		
0	1.10	0.95 ± 0.13	–	1.99	1.88 ± 0.10	
	0.88			1.84		
	0.87			1.80		
1	0.59	0.59 ± 0.01	37.89	0.75	0.90 ± 0.17	52.13
	0.61			1.09		
	0.58			0.85		
3	0.28	0.29 ± 0.01	69.47	0.70	0.67 ± 0.03	64.36
	0.31			0.67		
	0.29			0.64		
5	0.11	0.12 ± 0.01	87.37	0.27	0.30 ± 0.06	84.04
	0.14			0.37		
	0.12			0.27		
7	BDL	BDL	–	0.06	0.09 ± 0.03	95.21
	BDL			0.09		
	BDL			0.13		
10	BDL	BDL	–	BDL	BDL	–
	BDL			BDL		
	BDL			BDL		
Red Chili samples after 20 days	BDL	BDL	–	BDL	BDL	–
	BDL			BDL		
	BDL			BDL		
Soil samples after 20 days	BDL	BDL	–	BDL	BDL	–
	BDL			BDL		
	BDL			BDL		
[b]$T_{½}$ (days)	1.37			1.41		

[a] BDL = Below determination limit of 0.01 mg kg^{-1}

[b] $T_{1/2}$ = Half-life time

The dissipation of tebuconazole in peppers was evaluated by Fenoll et al. (2009).The pepper samples were collected during 6 week period in which two successive applications of tebuconazole were performed. At harvest time residues levels were below detectibility limit.

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