Bull Environ Contam Toxicol (2010) 84:225–229
DOI 10.1007/s00128-009-9903-5

Dissipation Kinetics of β-Cyfluthrin and Imidacloprid in Brinjal and Soil Under Subtropical Conditions of Punjab, India

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Received: 12 May 2009 / Accepted: 29 October 2009 / Published online: 24 November 2009

Abstract Dissipation of β-cyfluthrin and imidacloprid was studied following three applications of a combination formulation of Solomon 300 OD (β-cyfluthrin 9% + imidacloprid 21%) @ 60 and 120 g a.i. ha^{-1} at 7 days interval. Samples of brinjal were collected at 0, 1, 3, 5, 7, 10 and 15 days after the last application and residues of β-cyfluthrin and imidacloprid were estimated on gas liquid chromatography (GLC) and high performance liquid chromatography (HPLC), respectively. Half-life periods for β-cyfluthrin were found to be 1.74 and 1.39 days and for imidacloprid these values were observed to be 2.31 and 2.18 days, respectively, at single and double the application rate. β-Cyfluthrin residues dissipated below the limit of quantification (LOQ) of 0.01 mg kg^{-1} after 5 and 7 days, respectively, at single and double the application dosages whereas imidacloprid residues took 10 days for both the dosages. Soil samples collected after 15 days after the last application did not show the presence of β-cyfluthrin and imidacloprid at their detection limit of 0.01 mg kg^{-1}.

Keywords β-Cyfluthrin · Dissipation · Imidacloprid · Residues · Waiting period

Brinjal (*Solanum melongena* L.) is one of the most common and popular solanaceous vegetable grown in India, occupies an area of 2.79 thousand hectares in Punjab with an annual production of 41.25 thousand tonnes per annum (Anonymous 2007). The crop is subjected to high degree of instability in production from year to year, mainly because of the losses caused by insect pests, of which brinjal fruit and shoot borer, *Leucinodes orbonalis* (Linnaeus) and jassid *Amrasca biguttula* (Ishida) are the most serious. Several insecticides are recommended for the control of these pests. Recently, β-cyfluthrin in combination with imidacloprid has been found to be very effective for the control of *Amrasca biguttula* (Ishida) and *Leucinodes orbonalis* (Bhargava et al. 2003). β-Cyfluthrin, cyano(4-fluoro-3-phenoxyphenyl)methyl 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate belonging to pyrethroid group, acts as a contact and stomach poison. Imidacloprid, *N*-[1-[(6-chloro-3-pyridyl)methyl]-4,5-dihydroimidazol-2-yl]nitramide is a broad spectrum systemic insecticide effective against wide range of pests. However, considerable concern is being expressed over the magnitude of pest control chemicals left in food stuffs following their use on crops. It is important to ensure that the levels of harvest time residues of pesticides on food stuffs do not pose any hazard to consumers and are admissible in domestic as well as international trade. Therefore, the present studies were undertaken to know the persistence of β-cyfluthrin and imidacloprid on brinjal under sub-tropical conditions of Punjab, India.

Materials and Methods

The analytical standards of β-cyfluthrin (purity 99.0%) and imidacloprid (purity 98.6%) were supplied by M/s Bayer Crop Science India Ltd., Mumbai. All the solvents used were of laboratory grade. These were redistilled in all glass apparatus and the suitability of solvents was ensured by running reagent blanks along with actual analysis. The stock solution of β-cyfluthrin was prepared at 1,000 μg mL^{-1} in

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distilled acetone whereas imidacloprid was prepared in acetonitrile of high performance liquid chromatography (HPLC) grade. These solutions were further diluted to obtain concentrations of 100.0, 10.0, 1.0, 0.1, 0.01 μg mL^{-1}.

Brinjal (var. Punjab Jamuni Gola) was raised during Rabi 2008, at Entomological Research Farm, Punjab Agricultural University, Ludhiana following the recommended agronomic practices (Anonymous 2007). The first application of Solomon 300 OD (β-cyfluthrin 9% + imidacloprid 21%) @ 60 and 120 g a.i. ha^{-1} was made at fruit initiation stage followed by another two applications at 7 days interval. Each treatment was replicated thrice and size of each plot was 50 m^2. In control plots, only water was sprayed.

Marketable size brinjal fruits were collected from each treatment at 0 (after 2 h), 1, 3, 5, 7, 10 and 15 days after last application and soil samples were collected 15 days after application. Samples were extracted immediately after sampling.

The extraction and cleanup of brinjal and soil samples for residues of β-cyfluthrin were carried out as per procedure reported by Luke et al. (1975) with slight modifications. A representative 50 g sample of chopped and macerated brinjal fruits were dipped for overnight into 100 mL acetone in an erlenmayer flask. The extract was filtered through glass wool plugged in filtering funnel into one litre separatory funnel. The residual material was rinsed with acetone and transferred to the same separatory funnel. The contents of separatory funnel were diluted with 600 mL brine solution and partitioned into 100 and 50 mL dichloromethane and once into 100 and 50 mL hexane. The combined organic layers were collected into 500 mL beaker and dried over anhydrous sodium sulfate and treated with 500 mg activated charcoal for about 2–3 h to remove coloured impurities. The clear solution was filtered through Whatman filter paper No. 1 and concentrated to near dryness on a rotary evaporator under *vacuum* and transferred to 5 mL of hexane for further analysis. Analysis of the β-cyfluthrin residues was carried out on a gas liquid chromatography (GLC) (Shimadzu Model GC-2010) equipped with electron capture detector (ECD) ^{63}Ni. A capillary column DB-1 (30 m × 0.25 mm i.d. × 0.25 μm film thickness) with split ratio 1:10 was used for estimation of β-cyfluthrin residues. GC operating parameters were as follows: Carrier gas flow rate: 30 mL min^{-1}; temperature: injection port: 290°C, detector: 300°C, column temperature: 270°C. Under these operating conditions the retention time of β-cyfluthrin were found to be 6.64, 6.79 and 6.99 min. Soil samples were collected at 15 days after spraying and processed by following the methodology as described above.

The extraction and cleanup of brinjal and soil samples for residues of imidacloprid was carried out as per procedure reported by Arora et al. (2009). A representative 50 g sample of chopped and macerated brinjal fruits was placed overnight into 100 mL acetonitrile in an erlenmayer flask. The extract was filtered through glass wool plugged in filtering funnel into one litre separatory funnel. The residual material was rinsed with acetonitrile and transferred to the same separatory funnel. The contents of separatory funnel were diluted with 600 mL brine solution and partitioned thrice into 50 and 50 mL hexane: ethyl acetate (98:2, v/v) and the organic layer (hexane: ethyl acetate) was discarded. The aqueous layer was again partitioned thrice into 50 mL dichloromethane and was dried over anhydrous sodium sulfate. The combined organic layers were collected into 500 mL beaker through 1.5″ layer of anhydrous sodium sulfate supported on a pre washed glasswool placed in a filtering funnel. The combined extract was concentrated to about 5 mL under *vacuum* on rotary evaporator. The dried dichloromethane extract was treated with 500 mg activated charcoal for about 2–3 h to remove coloured impurities and filtered through Whatman filter paper No.1 along with rinsings of acetonitrile. The filtrate was concentrated to near dryness on a rotary evaporator under *vacuum* and the final volume was constituted with HPLC grade acetonitrile to 5 mL. The residues were determined by using HPLC (Shimadzu) equipped with C_{18} column with photo diode array (PDA) detector. The instrument was set at wavelength 268 nm, mobile phase methanol with pump flow @ 1 mL min^{-1}. Residues of imidacloprid were quantified by comparison of peak height/peak area of standards with that of unknown or spiked samples run under identical conditions. Under these operating conditions the retention time of imidacloprid was found to be 2.87 min. Soil samples were collected at 15 days after spraying and processed by following the methodology as described above.

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 each for β-cyfluthrin and imidacloprid. The limit of quantification (LOQ) was found to be 0.01 mg kg^{-1} for both the insecticides. Brinjal and soil samples were spiked with β-cyfluthrin and imidacloprid at different levels viz. 0.10, 0.05 and 0.01 mg kg^{-1} and analyzed separately as per the methodologies described above. Per cent recovery of β-cyfluthrin and imidacloprid in brinjal and soil was found to be consistent and more than 80 per cent (Table 1). The persistence of β-cyfluthrin and imidacloprid 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 β-cyfluthrin and imidacloprid was calculated using Hoskins (1961) formula.

Table 1 Recovery studies of β-cyfluthrin and imidacloprid on brinjal and soil

Substrate	Insecticides	Level of fortification (mg kg^{-1})	Recovery (%)[a]
Brinjal	β-cyfluthrin	0.10	85.00 ± 3.00
		0.05	90.67 ± 1.15
		0.01	80.00 ± 1.00
	imidacloprid	0.10	86.90 ± 1.01
		0.05	84.90 ± 3.00
		0.01	86.00 ± 1.72
Soil	β-cyfluthrin	0.10	89.43 ± 1.17
		0.05	86.43 ± 1.30
		0.01	90.50 ± 2.88
	imidacloprid	0.10	85.47 ± 4.00
		0.05	94.00 ± 4.58
		0.01	85.33 ± 3.51
		0.10	85.47 ± 4.00

[a] Mean ± SD of three determinations

Results and Discussion

The overall results of the analysis of brinjal fruits following three application of Solomon 300 OD (β-cyfluthrin 9% + imidacloprid 21%) @ 18 and 36 g a.i. ha^{-1} are presented in Table 3. The mean initial deposits of β-cyfluthrin were 0.07 and 0.13 mg kg^{-1} on the fruits following 3rd application of β-cyfluthrin at minimum effective and double the effective dosages, respectively. These deposits dissipated to 0.02 and 0.04 mg kg^{-1} after 3 days at single dose and double dose respectively, thereby showing a loss of about 71 and 69 per cent following application of β-cyfluthrin @ 18 and 36 g a.i. ha^{-1}. These residues reached below the detectable limit of 0.01 mg kg^{-1} in 5 and 7 days at single and double dose, respectively, following application of β-cyfluthrin at both the dosages (Table 2). The results were similar with findings of Singh and Singh (2007) who reported safe waiting periods of 3 and 5 days, following two applications of β-cyfluthrin on chickpea @ 12.5 and 25 g a.i. ha^{-1}, respectively. Soil samples collected after 15 days did not reveal the presence

Table 2 Residues of β-cyfluthrin (mg kg^{-1}) in brinjal and soil at different time intervals after the application of Solomon 300 OD (β-cyfluthrin 9% + imidacloprid 21%) @ 200 and 400 mL ha^{-1}

Days after application	β-cyfluthrin @ 18 g a.i. ha^{-1}			β-Cyfluthrin @ 36 g a.i. ha^{-1}		
	Replicates	Mean ± SD	Dissipation (%)	Replicates	Mean ± SD	Dissipation (%)
Before application	BDL	BDL	–	BDL	BDL	–
	BDL			BDL		
	BDL			BDL		
0	0.08	0.07 ± 0.01	–	0.15	0.13 ± 0.02	–
	0.06			0.12		
	0.07			0.11		
1	0.05	0.05 ± 0.006	28.57	0.08	0.08 ± 0.01	38.46
	0.04			0.08		
	0.05			0.06		
3	0.02	0.02 ± 0.006	71.43	0.04	0.04 ± 0.006	69.23
	0.02			0.03		
	0.01			0.04		
5	BDL	BDL	–	0.02	0.01 ± 0.006	92.31
	BDL			0.01		
	BDL			0.01		
7	BDL	BDL	–	BDL	BDL	–
	BDL			BDL		
	BDL			BDL		
Soil samples after 15 days	BDL	BDL	–	BDL	BDL	–
	BDL			BDL		
	BDL			BDL		
$t_{½}$ (days)	1.74			1.39		

BDL Below determination limit of 0.01 mg kg^{-1}

Table 3 Residues of imidacloprid (mg kg^{-1}) in brinjal and soil at different time intervals after the application of Solomon 300 OD (β-cyfluthrin 9% + imidacloprid 21%) @ 200 and 400 mL ha^{-1}

Days after application	Imidacloprid @ 42 g a.i. ha^{-1}			Imidacloprid @ 84 g a.i. ha^{-1}		
	Replicates	Mean ± SD	Dissipation (%)	Replicates	Mean ± SD	Dissipation (%)
Before application	BDL			BDL		
	BDL	BDL	–	BDL	BDL	–
	BDL			BDL		
0	0.26	0.24 ± 0.02	–	0.32	0.37 ± 0.04	–
	0.22			0.39		
	0.24			0.38		
1	0.15	0.17 ± 0.02	29.17	0.23	0.25 ± 0.02	32.43
	0.19			0.27		
	0.18			0.26		
3	0.14	0.14 ± 0.01	41.67	0.18	0.18 ± 0.01	51.35
	0.14			0.20		
	0.13			0.17		
5	0.11	0.12 ± 0.006	50.00	0.14	0.13 ± 0.01	64.86
	0.12			0.12		
	0.12			0.12		
7	0.05	0.04 ± 0.006	83.33	0.11	0.09 ± 0.01	75.67
	0.04			0.09		
	0.04			0.08		
10	BDL	BDL	–	BDL	BDL	–
	BDL			BDL		
	BDL			BDL		
Soil samples after 15 days	BDL	BDL	–	BDL	BDL	–
	BDL			BDL		
	BDL			BDL		
$t_{½}$ (days)	2.31			2.18		

BDL Below determination limit of 0.01 mg kg^{-1}

of β-cyfluthrin at LOQ of 0.01 mg kg^{-1}. Half-life ($T_{1/2}$) values of β-cyfluthrin calculated as per Hoskins 1961 were observed to be 1.74 and 1.39 days, respectively, when applied @ 18 and 36 g a.i. ha^{-1}. Similar results were reported by Dikshit et al. (2001).

The average initial deposits of imidacloprid on brinjal were found to be 0.24 and 0.37 mg kg^{-1}, respectively, following three applications at 7 days interval of Solomon 300 OD (a combination mixture of β-cyfluthrin 9% + imidacloprid 21%) @ 42 and 84 g a.i. ha^{-1} w.r.t. imidacloprid. Residues of imidacloprid dissipated below detectable level of 0.01 mg kg^{-1} after 10 days at both the dosages (Table 3). Similarly, Mukherjee and Gopal (2000) reported that imidacloprid residues persisted up to 10 days following its application at 20 and 40 g a.i. ha^{-1} in brinjal. Half-life ($T_{1/2}$) of imidacloprid were observed to be 2.31 and 2.18 days, respectively when applied @ 42 and 84 g a.i. ha^{-1}. The maximum residue limit (MRL) of 0.2 mg kg^{-1} has been prescribed for imidacloprid on brinjal. Following application of imidacloprid @ 42 g a.i. ha^{-1} in/on brinjal the residues were found to be below the MRL after 1 day of its application. Soil samples collected after 15 days did not reveal the presence of imidacloprid at LOQ of 0.01 mg kg^{-1}.

The present studies suggest that the use of combination mixture of β-cyfluthrin and imidacloprid at the recommended and double the recommended dosages does not seem to pose any hazards to the consumers if a waiting period of 3 days is observed before consumption of brinjal fruits.

Acknowledgments The authors are thankful to Indian Council of Agricultural Research, New Delhi, India for sponsoring the project. Authors are also thankful to the Head, Department of Entomology, PAU, Ludhiana for providing research facilities.

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