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Dissipation kinetics of flubendiamide and thiacloprid on tomato (*Lycopersicon esculentum* Mill) and soil

Rubaljot Kooner, S.K. Sahoo, Balwinder Singh & R.S. Battu

Department of Entomology, Punjab Agricultural University, Ludhiana, Punjab, India

Keywords
desiodo flubendiamide; dissipation; flubendiamide; half-life; residues; thiacloprid.

Correspondence
R.S. Battu, Department of Entomology, Punjab Agricultural University, Ludhiana-141004, Punjab, India.
Email: rsbattu2007@rediffmail.com

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Abstract

Introduction Flubendiamide, a phthalic acid diamide widely used against the lepidopteran pests and thiacloprid, the first chloronicotinyl insecticide quite effective against the sucking insects, white flies and jassids have recently been used on various vegetable crops in India. *Objectives* Studies on dissipation kinetics of insecticides is very essential to work out their half- lives and waiting periods for the safe consumption of agricultural produce. *Methods* Standardized methodology supported by recovery studies is adopted to estimate residues of flubendiamide and thiacloprid on tomato. Final estimation of residues was accomplished using high performance liquid chromatography by employing C_{18} column and photo diode array at 230 wavelength. *Results* Half-lives values for flubendiamide following its three applications at 10 days intervals @ 48 g a.i. ha^{-1} were observed to be 0.33 and 1.00 days, respectively. Similarly, at the same application rate these values for thiacloprid were found to be 1.18 and 0.95 days, respectively. Flubendiamide and thiacloprid residues were observed to dissipate below their determination limit of 0.01 mg kg^{-1} after 3 and 5 days, respectively, when applied @ 48 g a.i.ha^{-1}. Soil samples collected after 15 days did not show the presence of flubendiamide, desiodo flubendiamide, and thiacloprid at their determination limit of 0.01 mg kg^{-1}. *Conclusion* A waiting period of 5 days is recommended for safe consumption of tomato fruit after application of combination formulation of flubendiamide 24% + thiacloprid 24% (480 SC) @ 200 g ha^{-1}.

Introduction

The increasing awareness of the potential impact of persistent crop protection agents has led to the development of eco-friendly new molecules to ensure minimum risk to humankind and the environment. Flubendiamide, *N*'-[1,1-dimethyl-2-(methylsulphonyl)ethyl]-3-iodo-*N*-{4-[2,2,2tetrafluoro-1-(trifluoromethyl) ethyl]-0-tolyl} phthalimide belongs to a new chemical class, the phthalic acid diamides, and is widely used against lepidopteran pests on a variety of annual and perennial crops (Figure 1a and b). It provides superior plant protection against a broad range of economically important lepidopterous pests including *Helicoverpa* spp, *Heliothis* spp, *Spodoptera* spp, *Plutella* spp, *Trichoplusia* spp and *Hyrotis* spp. Experiments in North America have shown flubendiamide to be hydrolytically stable, relatively immobile in soil and practically non-detectable in key rotated crops. Flubendiamide has a favourable ecological, ecotoxicological and environmental profile with low mammalian toxicity and no genotoxic, mutagenic or oncogenic properties (Shane, 2006). Flubendiamide has been recently introduced in India by Bayer Crop Science and is presently under consideration of approval for use on major crops. Thiacloprid, *N*-{3-[(6-Chloro-3-pyridinyl)methyl]-1,3-thiazolan-2-yliden} cynamide (Figure 1c) is the first chloronicotinyl insecticide to have activity not only against sucking insects such as aphids, whiteflies and some jassids, but also against weevils, leafminers and various species of beetles and it shows good plant compatibility in all relevant crops (Elbert *et al.*, 2000). Tomato is a premier vegetable crop of India and is grown in mainly tropical and subtropical regions. However, no information is available on the persistence of flubendiamide and thiacloprid on tomato. Therefore, the present study was carried out to investigate the persistence and dissipation kinetics of combination formulations of flubendiamide and thiacloprid in tomato and soil.

Materials and methods

The certified reference standards of flubendiamide (purity 93.66%) along with reference standard of desiodo flubendiamide (purity 100%) and thiacloprid (purity 99.6%) were supplied by M/s Bayer Crop Sciences Limited (Mumbai, India). All the solvents used in this study were of laboratory grade. Before use these were redistilled in an all-glass apparatus and their suitability was ensured by running reagent blanks along with actual analysis. Acetonitrile was of high performance liquid chromatography (HPLC) grade. The stock solutions of flubendiamide, desido flubendiamide and thiacloprid were prepared at 1000 μg $\mathrm{mL^{-1}}$ in acetonitrile of HPLC grade.

Tomato (var. Rupali) crop was raised during *Rabi* 2007 according to recommended agronomic practices at Entomological Research Farm (Punjab Agricultural University, Ludhiana, India), using a randomized block design. The first application of combination mixture (flubendiamide 24%+ thiacloprid 24%) 480 SC at 48 and 96 g a.i. $\mathrm{ha^{-1}}$ each with respect to flubendiamide and thiacloprid was made at 50% flowering stage using Aspee Knapsack sprayer fitted with hollow cone nozzle. Subsequently the second and third applications were made at 10-day intervals. Each treatment was replicated thrice and the size of each plot was 50 $\mathrm{m^2}$. In control plots, only water was sprayed.

About 1 kg of marketable size tomatoes were collected from each treated and control plot at 0 (2 h), 1, 3, 5, 7 and 10 days after the last application. Soil samples were collected after 15 days following the last application. Samples were extracted immediately after sampling.

The extraction and clean-up of tomato and soil samples for residues of flubendiamide, its metabolite desiodo flubendiamide and thiacloprid were carried out as per procedure reported by Battu *et al.* (2008). Samples of tomato fruits were chopped and finely blended and a representative 50 g sample was dipped overnight into 100 mL acetonitrile in an Erlenmayer flask. The extract was filtered into 1 L separatory funnel along with rinsing of acetonitrile. The filtrate in the separatory funnel was diluted with 600 mL brine solution and partitioned the contents three times into 100, 50 and 50 mL chloroform. The chloroform fractions were combined, dried over anhydrous sodium sulphate.

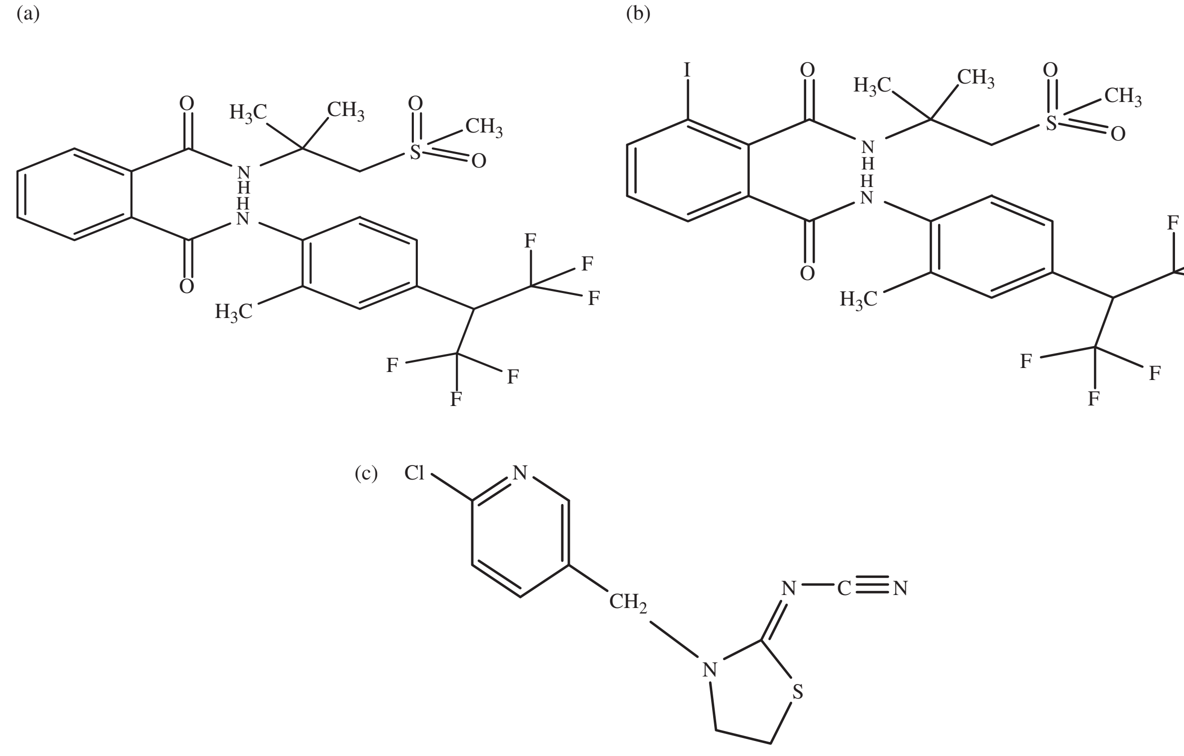

Figure 1 Chemical structure of (a) desiodo flubendiamide (b) flubendiamide (c) thiacloprid.

The chloroform fractions of both the tomato and soil samples were 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 about 20 mL HPLC grade acetonitrile added and again concentrated using rotary vacuum evaporator at 30 °C. The process was repeated to completely evaporate chloroform and the final volume was reconstituted to about 5 mL using HPLC grade acetonitrile.

The cleaned extracts were estimated on HPLC by employing Phenomenex Luna C_{18} column at 230λ (wavelength) and using acetonitrile:water (60:40, v/v) mixture as the mobile phase at 1.0 mL min^{-1}. Under these operating conditions the retention times of flubendiamide, desiodo flubendiamide and thiacloprid were found to be 10.87, 15.04 and 3.83 min, respectively.

Both tomato and soil samples were spiked at 0.01, 0.05, 0.1 and 0.2 µg g^{-1} levels. The samples were extracted and cleaned up as per the procedure given above.

The limit of detection was determined as the concentration having a peak area three times higher in relation to the noise of the base line at the retention time of the peak of interest. 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 10 ng for thiacloprid and flubendiamide and the limit of quantification (LOQ) was found to be 0.01 mg kg^{-1}. The $T_{1/2}$ of flubendiamide and thiacloprid were calculated using the Hoskins (1961) formula.

Results and discussions

The selected method provided good recoveries of flubendiamide, its metabolite desiodo flubendiamide and thiacloprid residues, 82–98% from tomato fruits in the concentration ranges 0.20–0.01 µg g^{-1}. At the 0.20 µg g^{-1} fortification level the recovery of flubendiamide in tomato was found to be 90.00 ± 0.01% and of desiodo flubendiamide it was 87.50 ± 0.007%. At the same level the per cent recovery for thiacloprid in tomato was found to be 95.00 ± 0.01. In the case of soil the per cent recovery was found to be 97.50 ± 0.008 for flubendiamide, 96.50 ± 0.02 for desiodo flubendiamide and 98.50 ± 0.004 for thiacloprid at the 0.20 µg kg^{-1} fortification level (Table 1).

The residues of flubendiamide, desiodo flubendiamide and thiacloprid were confirmed by HPTLC. This technique was able to identify and quantify 100 ng each of flubendiamide, desiodo flubendiamide and thiacloprid. Cleaned-up sample extracts of different substrates were spotted on precoated silica gel 60F plates along with reference standards visualized through scanner (TLC Scanner 3, D_2 lamp with wavelength range of 190–400 nm: CAMAG, Muttenz, Switzerland) and quantified by comparison of the peak height/area of the sample with that of reference standards under similar conditions.

The average initial deposits of flubendiamide on tomato were found to be 0.08 and 0.16 mg kg^{-1}, respectively, following three applications of the combination mixture (flubendiamide 24% + thiacloprid 24%) 480 soluble concentrate at 48 and 96 g a.i. ha^{-1}. Residues of flubendiamide dissipated below LOQ of 0.01 mg kg^{-1} in 3 and 5 days at single and double dosages, respectively. Desiodo flubendiamide was not detected at 0.01 mg kg^{-1} level in tomato samples collected at different time intervals. Soil samples collected at 15 days after the last spraying did not reveal the presence of flubendiamide and its metabolite desiodo flubendiamide (Table 2).

The average initial deposits of thiacloprid on tomato were found to be 0.16 and 0.29 mg kg^{-1}, respectively, following

Table 1 Fortification and recovery of flubendiamide, its metabolite desiodo flubendiamide and thiacloprid in tomato and soil

Substrate	Level of fortification (mg kg^{-1})	Recovery %* Flubendiamide	Desiodo flubendiamide	Thiacloprid
Tomato	0.20	90.00 ± 0.01	87.50 ± 0.007	95.00 ± 0.01
	0.10	85.00 ± 0.005	92.00 ± 0.002	85.00 ± 0.004
	0.05	86.00 ± 0.04	82.00 ± 0.003	88.00 ± 0.004
	0.01	82.00 ± 0.0005	90.00 ± 0.0004	85.00 ± 0.0005
Soil	0.20	97.50 ± 0.008	96.50 ± 0.02	98.50 ± 0.004
	0.10	90.00 ± 0.003	87.00 ± 0.004	93.00 ± 0.003
	0.05	88.00 ± 0.003	98.00 ± 0.04	96.00 ± 0.003
	0.01	86.00 ± 0.0004	89.00 ± 0.0006	85.00 ± 0.0004

*Mean ± SD of three replicates determinations.

Table 2 Mean and range of flubendiamide residues (mg kg^{-1}) in tomato and soil at different time intervals after the third application of (flubendiamide 24%+thiacloprid 24%) 480 SC (w/v) at 48 and 96 g a.i. ha^{-1}

Days after application	Flubendiamide (48 g a.i. ha^{-1})	% dissipation	Flubendiamide (96 g a.i. ha^{-1})	% dissipation
Before third application	BDL		BDL	
	(BDL–BDL)	-	(BDL–BDL)	-
0	0.08 ± 0.02		0.16 ± 0.02	
	(0.05–0.10)	-	(0.14–0.19)	-
1	0.01 ± 0.01		0.08 ± 0.01	
	(0.01–0.02)	87.50	(0.07–0.09)	50.00
3	BDL		0.02 ± 0.01	
	(BDL–BDL)	-	(0.02–0.03)	75.00
5	BDL		BDL	
	(BDL–BDL)	-	(BDL–BDL)	-
Soil samples after 15 days	BDL		BDL	
	(BDL–BDL)	-	(BDL–BDL)	-
$T_{1/2}$ (days)	0.33		1.00	

BDL < 0.01 mg kg^{-1}.
SC, soluble concentrate.
Figures in parentheses are range of flubendiamide residues.

Table 3 Mean and range of thiacloprid residues (mg kg^{-1}) in tomato and soil at different time intervals after the third application of (flubendiamide 24%+thiacloprid 24%) 480 SC (w/v) at 48 & 96 g a.i. ha^{-1}

Days after application	Thiacloprid (48 g a.i. ha^{-1})	% dissipation	Thiacloprid (96 g a.i. ha^{-1})	% dissipation
Before trhird application	BDL		BDL	
	(BDL–BDL)	-	(BDL–BDL)	-
0	0.16 ± 0.01		0.29 ± 0.04	
	(0.15–0.18)	-	(0.25–0.33)	-
1	0.11 ± 0.01		0.14 ± 0.01	
	(0.09–0.12)	31.25	(0.13–0.15)	51.72
3	0.03 ± 0.01		0.05 ± 0.01	
	(0.02–0.04)	81.25	(0.04–0.06)	82.76
5	BDL		0.03 ± 0.01	
	(BDL–BDL)	-	(0.02–0.03)	89.65
7	BDL		BDL	
	(BDL–BDL)		(BDL–BDL)	
Soil samples after 15 days	BDL		BDL	
	(BDL–BDL)	-	(BDL–BDL)	-
$T_{1/2}$ (days)	1.18		0.95	

BDL < 0.01 mg kg^{-1}.
SC, soluble concentrate.
Figures in parentheses are range of thiacloprid residues.

three applications of the combination mixture (flubendiamide 24%+thiacloprid 24%) 480 soluble concentrate. Residues of thiacloprid dissipated below LOQ of 0.01 mg kg^{-1} in 5 and 7 days at single and double dosages, respectively. Thiacloprid residues were not detected at 0.01 mg kg^{-1} level in soil samples collected 15 days after last spraying (Table 3).

Following the application of profenofos at 500 g a.i. ha^{-1}, the residues of profenofos in/on tomato were found to be below the (maximum residue limit) of 0.5 mg kg^{-1} after 3 days of application (Sahoo *et al.*, 2004).

After two applications of mancozeb at 10 days intervals on tomato at 1250 and 2500 g a.i. ha^{-1}, the residues of mancozeb dissipated below its MRL of 5.25 mg kg^{-1} just 1 day after its application (Chahal *et al.*, 1996).

Singh *et al.* (1980) reported that residues of quinalphos on tomato took 4 days to dissipate below its MRL of 0.25 mg kg^{-1} when sprayed at 0.250 kg a.i. ha^{-1}. Whereas phosalone residues on tomato reached below the prescribed MRL of 1 mg kg^{-1} in one day when sprayed at 0.437 kg a.i. ha^{-1}.

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