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Dissipation, persistence and risk assessment of imidacloprid 17.8 SL on tomato

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ABSTRACT: Studies were conducted to evaluate the persistence, dissipation, and risk assessment of Imidacloprid 17.8 SL in tomato. After the third spray, fruit samples were separately collected from treated and untreated control plots at various intervals. The tomato samples were processed following modified QuEChERS technique and analyzed through UHPLC. When tomato was treated at 35and 70 g a.i. ha^{-1}after the third spray, the average initial deposits of imidacloprid on tomato were reported to be 0.34 and 0.65 mg kg^{-1}, respectively. After five and seven days following the last application at the single dose and double dose, imidacloprid residue in tomato was dissipated at below the LOQ of 0.05 mg kg^{-1}. For risk assessment of imidacloprid on tomato, the TMRC were calculated and compared with MPI. The results showed that, the TMRC values were below MPI in all the sampling days for both the dosages. Marketable size fruits should be plucked before the application of any insecticide so that 2-3 days will required for next picking. Hence, the study suggested aminimum waiting period of three days for safe consumption of tomato when applied with imidacloprid at a single dose.

Keywords: Imidacloprid, waiting periods, half-life, tomato, UHPLC

INTRODUCTION

Tomato (*Solanum Iycopersicum* Linn.) is one of the important major vegetables farmed at a global level (Engindeniz, 2006). It is widely grown in subtropical regions of north India, with 845 thousand ha area, under tomato cultivation and a production of 21181 thousand tonnes with a productivity of 25.07 MT/ha. In Bihar, tomato cultivation covered 62.70 thousand ha area, production 1161.79 thousand tonnes with a productivity of 18.53 MT/ha (Anonymous, 2021). The crop is affected by weeds, pathogens, and insect pest infestation. The fruit borers (*Helicoverpa armigera* (Hübner), aphids (*Aphis gossypii* Glover), and whitefly (*Bemisia tabaci* Gennadius) are the main insect pests that attack tomatoes and cause considerable economic harm to tomato growers. Pesticides are used on tomato crops to prevent pest infestation. The most common method of control of these pests is by the application of insecticides. When we compared from the food categories of plant origin like bread and others, the level of pesticide residue in vegetables and fruits that are mostly consumed as raw or semi-processed would be higher (WHO, 2003). Even though it has been suggested to use conventional insecticides, such as organochlorines, organophosphates, carbamates, and synthetic pyrethroids against a different species of insect pests of tomato (Claeys *et al.,* 2011). While the usage of these insecticides has helped the tomato growers to control the insect pests, it is frequently associated with environmental damage, chemical residues, and the emergence of pesticide resistance. Moreover, imidacloprid has been found to be highly efficient against many insect pests in tomato.

Imidacloprid[1-(6-chloro-3-pyridinylmethyl)-N-nitroimidazolidin-2-ylideneamine] is a broad-spectrum systemic insecticide newly introduced in the Indian sub-continent by Bayer India Ltd.as Confidor 200 g $litre^{-1}$ SL and Gaucho 700 g kg^{-1} WS. It has an ovel mode of action, acting as an agonist of the nicotinyl acetylcholine receptor (Bai *et al.,* 1991; Businelli *et al.,* 1992). This new chloro-nicotinyl compound is effective against various insect pests and is used for seed dressing, soil treatment and foliar treatment in different crops (Mullins, 1993).

For the analysis of pesticide residues is one of the crucial for tackling growing consumer concerns about contamination issues. The two main origins of pesticide residues in food and crops are when pesticide that persist in the soil and pesticide that is directly applied to crops growing in the field (Businelli *et al.,* 1992). Pesticide residue contamination of food sources, particularly vegetables, is one of the biggest hazards to public health. Since there seems to be much information on the residues of imidacloprid on tomato is not available, the current investigation was to focus on the quantification of imidacloprid residues on tomato fruits that is required to fixed consumer and environmental safety. Therefore, the present study was carried out to know the dissipation, persistence, and risk assessment of imidacloprid on tomato.

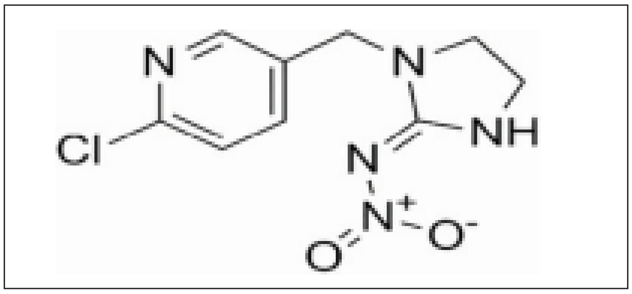
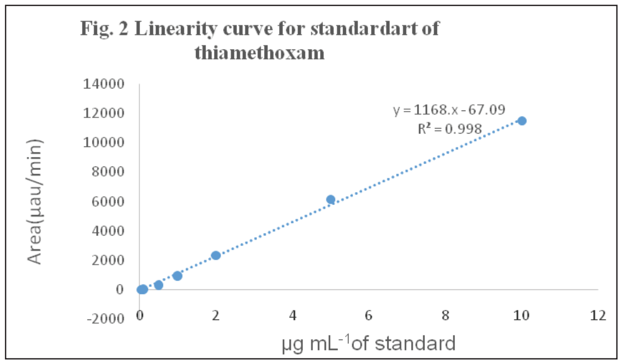


Fig. 1 Depicting chemical structure of imidacloprid



MATERIALS AND METHODS

Chemicals and reagents

Imidacloprid certified reference materials with a purity rating of 99.80% were provided by Dr Ehrenostrofer, Germany. Analytical grade solvents were used to prepare the standard solution and to extract the sample. Imidacloprid stock solutions were made in a concentration of 400.00 µg mL^{-1} in acetonitrile. To obtain concentrations of 100, 10, 2, 1, 0.5, 0.1, and 0.05 µg mL^{-1}, these solutions were serially diluted. Seven different concentrations of the standard solution (10, 5, 2, 1, 0.5, 0.1, and 0.05 µg mL^{-1}) were injected during the linearity study (Fig. 2).

Experimental sites

The field experiment was carried out in 2021 at the Dr. Rajendra Prasad Central Agricultural University in Pusa (Samastipur), Bihar, India, as a supervised field trial using standard agronomic practices for production of tomato (var. Kashi Vishesh), were planted under a Randomized Block Design (RBD) with three treatments, including untreated control. In control plots, insecticides were not used, and in another two treatment, the approved dose 35 and double of the approved dose 70 g a.i. $ha^{-1}$of imidacloprid insecticides were applied. Three times at ten-day intervals, imidacloprid was sprayed on the plants, the first spray starting at the fruit initiation stage. Each and every plot included a 50 m^2 area and three replications of each treatment. 500 g of tomato fruits were taken at random after the last application at the following times *viz.,*0 (2 hours), 1, 3, 5, 7, 10, and 15 days. Samples were brought to the lab for the analysis of pesticide residues for further extraction, cleaning, and quantification.

Extraction and cleanup

The tomato fruit samples were processed following modified Quick, Easy, Cheap, Effective, Rugged and Safe (QuEChERS) technique and analyzed through Ultra High Performance Liquid Chromatography (UHPLC). The sample brought from the field was cut and crushed using a mixer, and 15 g of brinjal and tomato fruits were weighed separately from the representative crushed sample into a 50 mL centrifuge tube and added with 30 mL of acetonitrile followed by addition of 10 ± 0.1 g of sodium chloride (NaCl) and centrifuged. An aliquot of 15 mL was added to a tube containing 10 ± 0.1g of anhydrous sodium sulphate (Na_2SO_4). Dispersive solid phase extraction was used to clean up the acetonitrile extract.The contents of a test tube containing 6 mL of acetonitrile, 0.15 ± 0.01 g of primary secondary amines

Table 1. Residue of imidacloprid in tomato after 3rd spray @ 35 and 70 g a.i. ha^{-1}

Days After Spraying (DAS)	Amount of Residue (mg kg^{-1})			
	35 g a.i. ha^{-1}		70 g a.i. ha^{-1}	
	Mean ± SD	Per cent Dissipation	Mean ± SD	Per cent Dissipation
Before application	<LOQ*	-	<LOQ	-
0 (2hrs after spray)	0.34 ± 0.02	-	0.65±0.05	-
1	0.23 ± 0.04	32.35	0.31± 0.03	52.30
3	0.09 ±0.006	73.53	0.18±0.02	72.30
5	<LOQ	-	0.08±0.02	87.69
7	<LOQ	-	<LOQ	-
10	<LOQ	-	<LOQ	-
15	<LOQ	-	<LOQ	-

*(LOQ = Limit of Quantification 0.05 mg kg^{-1})

Table 3. Theoretical maximum residue contributions (TMRC) on tomato fruits for Imidacloprid 17.8 S

		Tomato					
		35 g a.i. ha^{-1}			70 g a.i. ha^{-1}		
Interval (days)	*MPI (µg/ $person^{-1}$ day^{-1})	**Average residues (µg g^{-1})**	#TMRC (µg/ $person^{-1}$ day^{-1})		**Average residues (µg g^{-1})**	TMRC (µg/ $person^{-1}$ day^{-1})	
			Rural	**Urban**		**Rural**	**Urban**
0	3300	0.34	9.52	9.86	0.65	18.52	18.85
1	3300	0.23	6.44	6.67	0.31	8.68	8.99
3	3300	0.09	2.52	2.61	0.18	5.04	5.22
5	3300	≤0.05*	-	-	0.08	2.24	2.32
7	3300	≤0.05	-	-	≤0.05	-	-
10	3300	≤0.05	-	-	≤0.05	-	-
15	3300	≤0.05	-	-	≤0.05	-	-

*(LOQ = Limit of Quantification 0.05 mg kg^{-1})

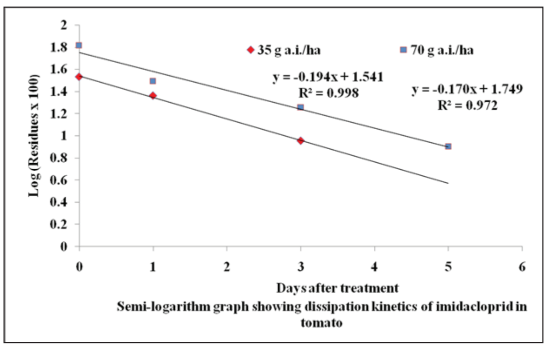


Fig 3. Semi-logarithm depicting dissipation kinetics of imidacloprid in tomato

(PSA) sorbent, and 0.90 ± 0.01 g of anhydrous $MgSO_4$ was extensively vortexed and centrifuged for three minutes. This acetonitrile extract was separated into three milliliters and used for analysis.

Instrumentation and estimation

Imidacloprid residues was analyzed throughUHPLC equipped with PDA (Photo Diode Array)detector with C18 column.The residues were calculated by comparing the peak area of the standards to samples performed under equilibrium conditions.The solvent system used was acetonitrile: HPLC water at 70:30 with a flow rate of 0.3 ml min^{-1}. The retention time was observed 3.097 min.

RESULTS AND DISCUSSION

Effectiveness of the developed techniques

Fortification studies were performed at various concentration prior to the field trial to evaluate the effectiveness of the method. To achieve this, untreated control samples of tomato fruits were fortified with imidacloprid concentrations of 0.05, 0.25, and 0.5 mg kg^{-1}, and the samples were evaluated using the aforementioned techniques.The plots of the untreated control samples and the reagent blanks were both evaluated in the same way in order to look for interferences caused by the substrate and reagents utilized, respectively. The residues data were presented as such as the recovery rate was higher than 80% in all the replicates.

Dissipation and persistence of imidacloprid on tomato

The residue's data are presented in mg kg^{-1} and dosein g a.i. ha^{-1}. After thirddays of treatment (DAT) on tomato, the average preliminary deposits of imidacloprid were found to be 0.34 and 0.65, respectively. On the first day following the last treatment, these residues decreased in tomatoes (0.23 and 0.31) showing per cent dissipation of 32.35 and 52.30, respectively.On 3rd day, in tomato the residuesdissipatedatapproveddosage73.53%and72.30% at the double of the approved dose. The residues at both dosages reached below the LOQ of 0.05 mg kg^{-1} within a week of the last application, as demonstrated in (table1 and fig. 3). According to the aforementioned results, imidacloprid residues increased with larger application rates. These findings are very similar to those of (Manal *et al.,* 2022), who investigated the imidacloprid residue on tomato. The average preliminary deposits of imidacloprid were found to be 0.921 and 0.641 mg/kg in the leaves and fruit.The dissipation of imidacloprid in cucumber fruits after application also studied by (Hassanzadeh *et al.*, 2012), who reported that, The average initial deposits of imidacloprid on the cucumber fruits were found to be 1.93 and 3.65 mg kg^{-1} at the single and double dosages,

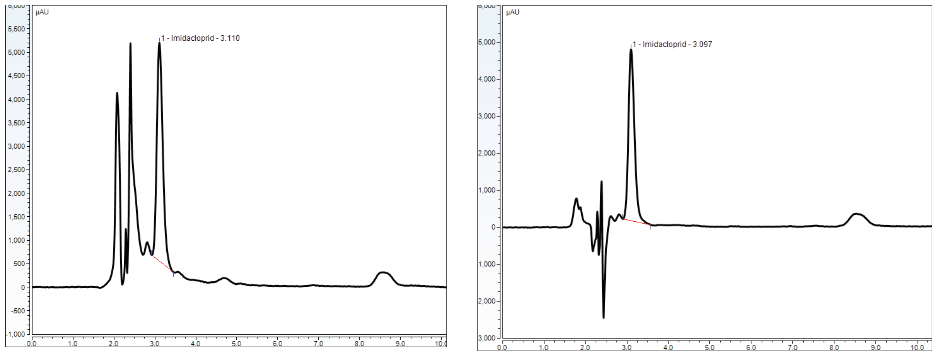


Fig. 3 UHPLC chromatograms for imidacloprid standard 0.05 µg/ml andtomato samples for single dose after 3rd application of imidacloprid

Table 2. Dissipation parameters of imidacloprid residues in tomato

Dissipation parameters	**3rd spray (MRL = 0.5 mg kg^{-1})**	
	Single dose (35g a.i. ha^{-1})	**Double dose (70 g a.i. ha^{-1})**
K_1 (b)	-0.194	-0.170
K_2 (a)	1.541	1.749
$T_{1/2}$	1.55	1.77
T_{tol}	-	0.29
R^2	0.998	0.972
Y	-0.194x + 1.541	-0.170x + 1.749

K_1 = "Slope of the regression line",K_2 = "Initial deposit obtained as in the regression equation, $T_{1/2}$ = "Residual half-life (in days)", T_{Tol}= "Time (in days) required for the pesticide residue to reach below the maximum residue limit (MRL) of 0.6 mg kg^{-1} ", R^2 = "Coefficient of determination".

respectively. The average preliminary deposits of imidacloprid were found to be 1.33 and 2.38 mg kg^{-1}, respectively, following the application of imidacloprid in tomato (Dharumarajan *et al.,* 2009).

Waiting period for imidacloprid in tomato

The data depicted regarding dose of the imidacloprid in (table 2) in g a.i.ha^{-1}. Half-life value ($T_{1/2}$) is often described simply and broadly as the time required to dissipate initial residues to half (Gunther and Blinn, 1955). According to Hoskins formula (1961),time was taken for residue to reach below Maximum Residue Limit (MRL) (T_{tol}) and half-life value ($T_{1/2}$) was calculated in days.

"Maximum residue limit (MRL)" of thiamethoxam in tomato was approved at 0.5 mg/kg (Anonymous, 2022). Determination of dissipation kinetics regarding residues of imidacloprid in tomato after third application is expressed in the form of semi-logarithm graphs (fig. 4 for imidacloprid, a linear relationship was obtained by plotting log concentration of residue multiplied by 100) against time. It confirms that, declination in residues of imidacloprid shows first order kinetic reaction.

After the third application of imidacloprid the half-life values in tomato were found to be 1.55 and 1.77 day resulting from the dose of single and double accordingly. When applied at the approved dose, initial deposit of imidacloprid in tomato was below the MRL. However, three days waiting period is suggested as picking interval for tomato is 2-3 days (table 2).

Risk assessment of imidacloprid in tomato fruit samples

The data demonstrated in (table 3)regarding MPI(µg/ person^{-1} day $^{-1}$), TMRC (µg/ person^{-1} day $^{-1}$) and dose of imidacloprid in (g a.i. ha-^{1}).A moderately toxic pesticide is more likely to cause risk assessment to occur from high exposure than from low exposure to a very toxic pesticide. The Theoretical Maximum Residue Contributions (TMRC) of imidacloprid residues in tomato fruits were estimated at different time intervals and compared to the Maximum Permissible Intake (MPI) in order to determine the risk (table 3). The Acceptable Daily Intake (ADI) values of imidacloprid were 0.06 mg kg^{-1} body weight (Anonymous, 2022).Taking the average daily consumption of tomato fruit as 28 g for rural diet and 29 g for urban diet (Anonymous, 2022), the average residues of imidacloprid on tomato were used to calculate TMRC value. MPI was calculated by multiplying ADI with the weight of an average person (55 kg), the value of MPI which came out to be 3300, respectively. TMRC values of tomato for imidacloprid applied at single and double doses were determined to be 9.52 and 18.52for a rural diet, and 9.86 and 18.85for an urban diet. After treating samples of tomato fruit with imidacloprid at both applied dosages, it was reported that the TMRC values were lower than MPI for all the sampling days. But, considering the picking interval, minimum three day waiting period may be suggested before consumption of tomato.

CONCLUSION

Imidacloprid half-life (t½) is values on tomato were found to be 1.55 and 1.77 days, respectively, after three applications of imidacloprid 17.8SL. Theoretical maximum residue contributions for imidacloprid were reported to be much lower than MPI on tomato fruits at 0 (2 hours DAT) for both dosages, according to residue data. Therefore, a minimum three days waiting period is advised before tomato can be consumed safely when used at the recommended dose in order to avoid any harm to consumers' health.

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