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Dissipation Behaviour and Effect of Different Decontamination Processes on Reduction of Residues of Novaluron in Tomato (*Lycopersicon esculentum* Mill.)

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A B S T R A C T

Dissipation behaviour of novaluron 5.25% SC was investigated in tomato fruits sprayed at 43.31 (single dose) and 86.62 g a.i. ha^{-1} (double dose). Tomato fruits samples were collected periodically on 0 (1h after application), 1, 3, 5, 7, 10, and 15 days after application. Average recoveries of novaluron in tomato fruits fortified at 0.01 to 0.25 mg kg^{-1} levels ranged from 82.20 to 89.47 per cent. The initial deposits of novaluron were 0.30 and 0.56 mg kg^{-1} at single and double dose, respectively. Dissipation of novaluron fitted well to first order kinetics with half-life values ranging from 1.40 to 1.52 days at single and double doses, respectively. Residues of novaluron decreased substantially during household processing among which peeling was found most effective which resulted 80 % reduction in both the doses. LOD and LOQ were found to be 0.005 and 0.01 mg kg^{-1}, respectively.

Introduction

Pesticides are chemical compounds which are biologically active and used worldwide for the protection of crops, fiber and human health (Malhat *et al.,* 2015). These pesticides tend to degrade after application with their residues remaining not only in the plants but also in various environmental matrices, like water, soil or sediments. Humans main exposure route is via food that contribute five times more than other routes, such as air and drinking water (Claeys *et al.,* 2011; Malhat *et al.,* 2014b). Tomato (*Lycopersicon esculentum* Mill.) is the world's largest vegetable crop

after potato and sweet potato, but it tops the list of canned vegetables (Ganesan *et al.,* 2012). In India tomato is grown over an area of 125,000 hectares, where climate conditions are such that the tomato can be cultivated in any month of the year (NHB 2015). The tomato crop is infested by jassids, aphids, tobacco caterpillar, flea beetles, leaf miner, spider mites and fruit borer (Thamburaj and Singh 2015). Hence, in order to combat the insect pest problem, lots of pesticides are used by the vegetable growers. Insecticide growth regulator (IGR) is the class of pesticide used to control pest species by mostly targeting juveniles rather than adults. Primarily, IGR's

inhibit the development of target species by acting as chitin synthesis inhibitors, ecdysone agonists and juvenile hormone mimics (reviewed by Tasei, 2001). IGR's do not typically exhibit acute effects on adult bees and numerous IGR's including the chitin synthesis inhibitors novaluron and diflubenzuron and ecdysone agonist methoxyfenozide are registered as 'reduced risk' pesticides in various crops (USEPA, 2017).

It was reported by Das *et al.,* (2008) that Novaluron [(±)-1-[3-chloro-4-(1,1,2-trifluoro-2-rifluoromethoxyethoxy)- phenyl]-3-(2,6-difluoro-benzoyl)urea], is a relatively new benzoylphenyl urea insect growth regulator which inhibits the chitin formation on larvae of various insects (Lepidoptera, Coleoptera, Homoptera and Diptera). Insect growth regulators (IGR) insecticides are comparatively safer to beneficial insects and environment and are compatible for use in an integrated pest management system. This compound is coming up as an eco-friendly or green pest-controlling agent. The detailed studies of novaluron have not been undertaken so far on tomato fruits especially in Haryana state. Besides this, information on reduction of residues of novaluron in tomato fruits by kitchen processes like unwashed, washing, boiling, peeling is also lacking. Thus, keeping this in view, the present investigation was undertaken to study the dissipation of novaluron residues and effect of different decontamination processes on reduction of residues in tomato fruits.

Materials and Methods

Field experiment

Experiment was conducted at Research Farm of Department of Entomology, CCS HAU, Hisar in randomized block design (RBD) plots as per good agricultural practice (GAP) in the month of May, 2015. Novaluron was applied in the field on the tomato crop (variety HS-86) at 50% fruiting stage with Knapsack sprayer in plots of size 16 m^2. Two doses of novaluron were used, for single dose 43.31 g a.i. ha^{-1} and for double dose 86.62 g a.i. ha^{-1} was applied, where as one plot was left untreated and used for the sampling of fruits as control in each treatment. About 1 kg of tomato sample was collected randomly and separately from the control and treated plots of each treatment at 0 (1 h), 1, 3, 5, 7, 10 and 15 days after the application of the insecticide. The samples from each treated plot were collected periodically from each plot separately and subjected to household processing like washing, washing followed by boiling/cooking and peeling as explained below. Residues from processed samples were extracted, cleaned and analyzed by gas liquid chromatography (GLC). Residues status was compared with control.

Extraction and clean-up

Tomato fruits samples collected from field were chopped and macerated in Warring blender to make a fine paste. Representative 20 g of tomato sample were extracted in acetone. Then filtered extract was partitioned thrice with dichloromethane and hexane (75, 50, 25 ml) by vigorous shaking for 5 min to remove the non-emulsifying impurities. Each time, organic phase was collected and pooled organic layer was concentrated to 5 ml on Rotary Vacuum Flask Evaporator. For clean-up of extract, adsorbent mixture i.e. silica + activated charcoal (5 + 0.2 w/w) was used as per method of Gupta *et al.,* (2011). The final volume was concentrated and made upto 5 ml in acetone for GC analysis.

Instrumentation

The residues of novaluron were estimated using gas liquid chromatography (Shimadzu

GC-2010) equipped with a fused silica capillary column, Restek -1(30 m x 0.32 mm i.d. x 0.25 μm film thickness) of 5% diphenyl + 95% dimethyl polysiloxane and electron capture detector (ECD).

The operating GC parameters were: injector temperature: 280^0C, detector temperature: 300^0C and oven temperature programe was 150 (5min) increased at 8^0C min^{-1} up to 190 (2min) further increased at 15^0C min^{-1} up to 280^0 (5 min) with split ratio 1:10. Total gas flow rate was 60 ml min^{-1}. Retention time (R_t) for novaluron was 2.329 minute.

Limit of detection and quantification

Residues of novaluron were determined by comparing the peak areas of the reference standards with those of the unknown or spiked samples run under identical working conditions of the instruments employed (Table 1 and Figure 1).

For novaluron half-scale deflection was obtained for 0.5 μg ml^{-1}, which could be easily identified from the baseline as 0.1 μg ml^{-1} of the compound produced 10% deflection, which can be measured. When 1 μL (5 mg) of the sample was injected then did not produce any background interference. Thus, the limit of quantification (LOQ) was found to be 0.01 mg kg^{-1} and the limit of detection (LOD) observed to be 0.005 mg kg^{-1} for tomato fruits.

Recovery

Representative 20 g of chopped tomato fruits were taken in 250 ml Erlenmeyer flasks and were fortified @ 0.01 to 0.25 mg kg^{-1} with standard pesticides. As evident from data given in Table 2, average recoveries from samples of tomato fruits fortified at 0.01, 0.10 and 0.25 mg kg^{-1} levels were 82.20, 87.35 and 89.47 per cent of novaluron.

Results and Discussion

Persistence and dissipation kinetics of novaluron

As clear from experimental data (Table 3), the application of (novaluron 5.25% SC) at single dose (T_1) consisted of 825 g ha^{-1} (equivalent to 43.31 g a.i. ha^{-1}) and the double dose (T_2) consisted of 1650 g ha^{-1} (equivalent to 86.62 g a.i. ha^{-1}) of insecticide on tomato fruits in field conditions resulted an initial deposits in tomato fruits to the extent of 0.30 and 0.56 mg kg^{-1} at single and double dose in novaluron, respectively. The residues of novaluron dissipated with time gradually after application in both the doses. At single dose, residues of novaluron reached below MRL value of 0.01 mg kg^{-1} on 7th day and at double dose it was below MRL on 10th day. Regression equations, half-life values and correlation coefficient of novaluron have also been shown in Table 3 and plot of log [Residues (mg kg^{-1}) x 10^3] and time (in days) were also plotted to study the degradation kinetics of novaluron residues in tomato fruits (Fig. 2). The residues half-life values for novaluron were 1.40 days and 1.52 days at single and double dose, respectively following first order kinetics. The values of correlation coefficient for degradation kinetics in tomato fruits were 0.849 and 0.968 for single and double dose of novaluron in tomato fruits. The results of novaluron were in agreement with those of Malhat *et al.,* (2014a) who studied the dissipation behaviour of novaluron. The method was validated using blank samples spiked at three levels and results showed that recoveries ranged from 93 to 99%. The initial concentration of novaluron residues in tomato was 0.51 mg/kg which dissipated following first-order rate kinetics with half-life of 2.08 days. Das *et al.,* (2007) noted that residues of novaluron rapidly dissipated in chili and brinjal following first-order reaction kinetics at all rates of application with half-lives of

1.80 to 1.95 days (for chili) and 1.8 to 2.08 days (for brinjal), respectively.

Decontamination studies

Food processing techniques are the set of methods and unit operations used to transform raw ingredient into edible form for direct consumption either in the home or by the food processing industry (Tomer and Sangha 2013).

In present investigation when the samples were subjected to washing with simple tap water than residues of novaluron tend to decrease with increase in time duration. Higher per cent reduction was recorded in double dose as compared to single dose on 0 day (1h after treatment). The data presented in

Table 4 and 5 revealed that at single dose after washing treatment residues reduced to 0.24 and 0.09 mg kg^{-1}, after 0 and 1 days, respectively resulting in 20.00 and 10.00 per cent reduction due to washing on 0 (1h after spray) and 1 day after treatment. However, when, sample was subjected to washing + boiling, initial residue level reduced to 0.13, 0.04 and 0.02 mg kg^{-1} on 0 (1h after spray), 1 and 3 days after treatment in tomato fruits resulting in 56.66, 60.00 and 66.66 per cent reduction respectively. When sample were subjected to peeling, residue level reduced to 0.06, 0.03 and 0.03 mg kg^{-1} on 0 (1h after spray), 1 and 3 days after treatment resulting in 80.00, 70.00 and 50.00 per cent reduction. After 5th day residues were below detectable level of 0.01 mg kg^{-1} as shown in figure 3.

Table.1 Standard curve data of novaluron

Amount (ng)	Area of novaluron
0.01	2050
0.025	4260
0.10	14985
0.25	33905
0.50	98405
1.00	192830

Table.2 Per cent recovery of novaluron from tomato fruits

Fortification Levels (mg kg^{-1})	Novaluron Average Recovery* (%) ± SD
0.01	82.20 ± 1.71
0.10	87.35 ± 4.38
0.25	89.47 ± 2.32

*Average of three replicates

Table.3 Residues (mg kg⁻¹) of novaluron in tomato fruits

Days after treatment	Novaluron residues (mg kg⁻¹)				Mean
	T₁ (43.31 g a.i. ha⁻¹)		T₂ (86.62 g a.i. ha⁻¹)		
	Average residues*± SD	% Dissipation	Average residues*±SD	% Dissipation	
0	0.30 ± 0.02	-	0.56 ± 0.04	-	0.43
1	0.10 ± 0.01	66.66	0.23 ± 0.03	58.92	0.17
3	0.06 ± 0.01	80.00	0.11 ± 0.03	80.35	0.09
5	0.01 ± 0.004	96.66	0.05 ± 0.02	91.07	0.03
7	BDL	100.00	0.01 ± 0.003	98.21	0.01
10	-	-	BDL	100.00	
15	-	-	-	-	
Mean	0.12		0.19		
	Correlation coefficient R² = 0.849 Regression equation y =-0.215x +1.372 $t_{1/2}$ = 1.40 days		Correlation coefficient R² = 0.968 Regression equation y =-0.198x + 1.659 $t_{1/2}$ =1.52 days		

For regression equation [residues (mg kg⁻¹)×10³] is taken

*Average residues±SD of three replicates; Below detectable level (BDL): 0.01 mg kg⁻¹

Table.4 Effect of processing on reduction of novaluron residues in tomato fruits at single dose

Days after treatment	Novaluron residues (mg kg⁻¹) at T₁ (43.31 g a.i. ha⁻¹) single dose			
	Average residues* ± SD (mg kg⁻¹)	Washing	Washing + Boiling	Peeling
0	0.30 ± 0.02	0.24 ± 0.04 (20.00)	0.13 ± 0.01 (56.66)	0.06 ± 0.03 (80.00)
1	0.10 ± 0.005	0.09 ± 0.01 (10.00)	0.04 ± 0.03 (60.00)	0.03 ± 0.01 (70.00)
3	0.06 ± 0.01	BDL	0.02 ± 0.005 (66.66)	0.03 ± 0.02 (50.00)
5	0.01 ± 0.004	-	BDL	BDL
7	BDL	-	-	-
10	-	-	-	-
15	-	-	-	-

*Average residues ± SD of three replicates

Figures in parenthesis is per cent reduction of residues

Table.5 Effect of processing on reduction of novaluron residues in tomato fruits at double dose

| Days after treatment	Novaluron residues (mg kg⁻¹) at T₂ (86.62 g a.i. ha⁻¹) double dose			
	Average residues* ± SD (mg kg⁻¹)	Washing	Washing + Boiling	Peeling
0	0.56 ± 0.04	0.43 ± 0.04 (23.21)	0.22 ± 0.03 (60.71)	0.09 ± 0.04 (80.00)
1	0.23 ± 0.03	0.20 ± 0.05 (13.04)	0.07 ± 0.02 (69.56)	0.05 ± 0.03 (78.26)
3	0.11 ± 0.03	0.10 ± 0.02 (9.09)	0.03 ± 0.01 (72.72)	0.04 ± 0.02 (63.63)
5	0.05 ± 0.02	BDL	BDL	BDL
7	0.01 ± 0.003	-	-	-
10	BDL	-	-	-
15	-	-	-	-

*Average residues ± SD of three replicates

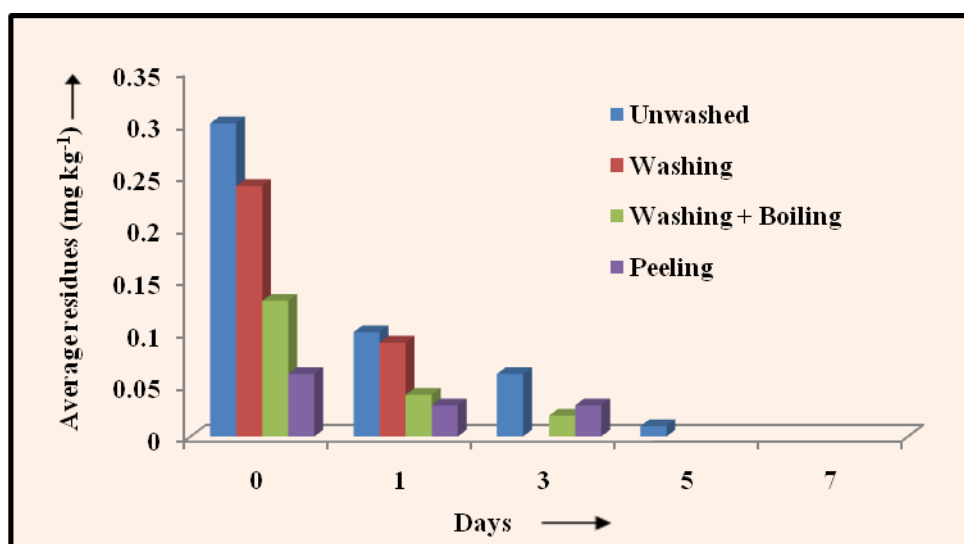Figures in parenthesis is per cent reduction of residues
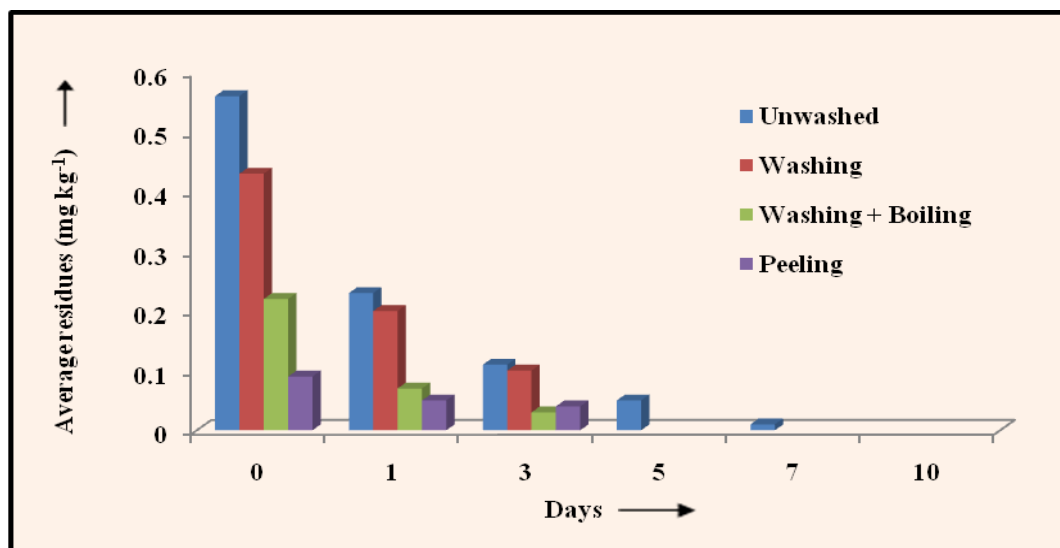
Fig.1 Standard curve of novaluron
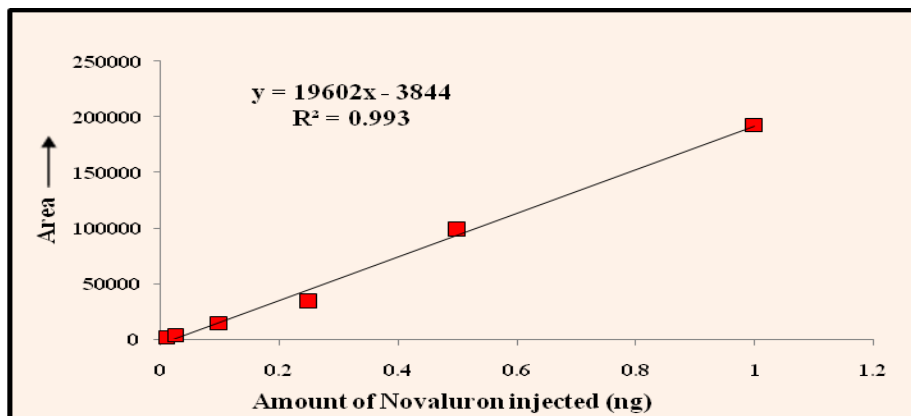
Fig.2 Semi Logarithm graph showing dissipation kinetics of novaluron in tomato fruits
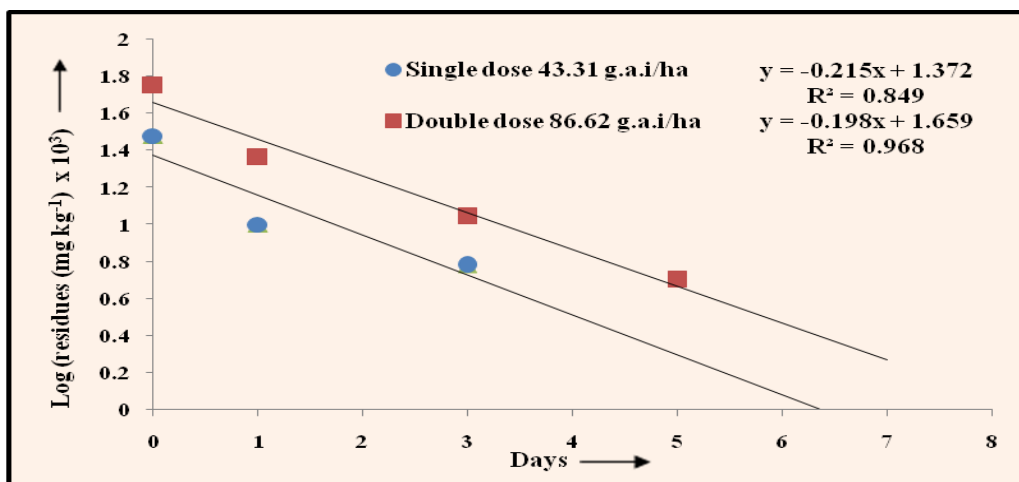
Fig.3 Effect of processing on reduction of residues of Novaluron in tomato fruits at single dose

Fig.4 Effect of processing on reduction of residues of novaluron in tomato fruits at double dose

In case of double dose (T_2), the initial residues reduced to 0.43, 0.20 and 0.10 mg kg^{-1}, respectively on 0 (1h after spray), 1 and 3 days after treatment due to washing and thus showed 23.21, 13.04 and 9.09 per cent loss at corresponding time intervals (Table 5). Due to washing + boiling residues reached to the levels of 0.22, 0.07, 0.03 mg kg^{-1} on 0 (1h after spray), 1 and 3 days and BDL on 5 days, while per cent loss of novaluron residues in ready pre-mix formulation at corresponding time intervals were 60.71, 69.56 and 72.72 per cent. Due to peeling residues level reduced to 0.09, 0.05 and 0.04 mg kg^{-1} on 0 (1h after spray), 1 and 3 days after treatment resulting 80.00, 78.26 and 63.63 per cent loss of novaluron residues at corresponding time intervals shown in figure 4.

Similar investigation was carried out by Mirani *et al.,* (2013) on tomato reported that unwashed unprocessed samples contained the residues of lufenuron up to 1.75 ppm which was far above the MRL of 0.5 ppm. The results further revealed that among the traditional processing plain water washing reduced the lufenuron residues up to 29.71%, whereas detergent washing reduced the residues up to 48%. Impact of peeling on carbamate pesticides in raw tomato fruits was shown by Rowayshed *et al.,* (2013). Peeling by hot water at 95˚C for 2 min eliminated about concentration of 0.797, 0.628, 0.916, 0.468 and 1.069 ppm and caused the reduction of the previous pesticides in prepared tomato fruits by 67.27, 68.43, 67.69, 75.22 and 63.43%, respectively. Various analytical techniques were reviewed by Anita and Bharti Sharma (2018) on vegetables to evaluate effect of reduction of pesticides residues present in/on vegetables. Important mechanisms which lead to residue alteration during storage, other household and industrial food preparation processes of raw agro-produce are dissolution, heat degradation, hydrolysis, metabolism, oxidation, penetration, photo degradation, volatilization and co-distillation and physical change of the concentration of the pesticide residues due to possible 184 changes in the agro-produce (Kousika *et al.,* 2009). The above investigation was in agreement with the researches which show gradual decrease in the reduction of residues on processing.

From the research it was concluded that residues of novaluron were found below MRL value of 0.01 mg kg^{-1} on 7th day at single dose

and on 10th day at double dose. Residues of novaluron decreased substantially during household processing among which peeling was found most effective which resulted 80 % reduction.

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