

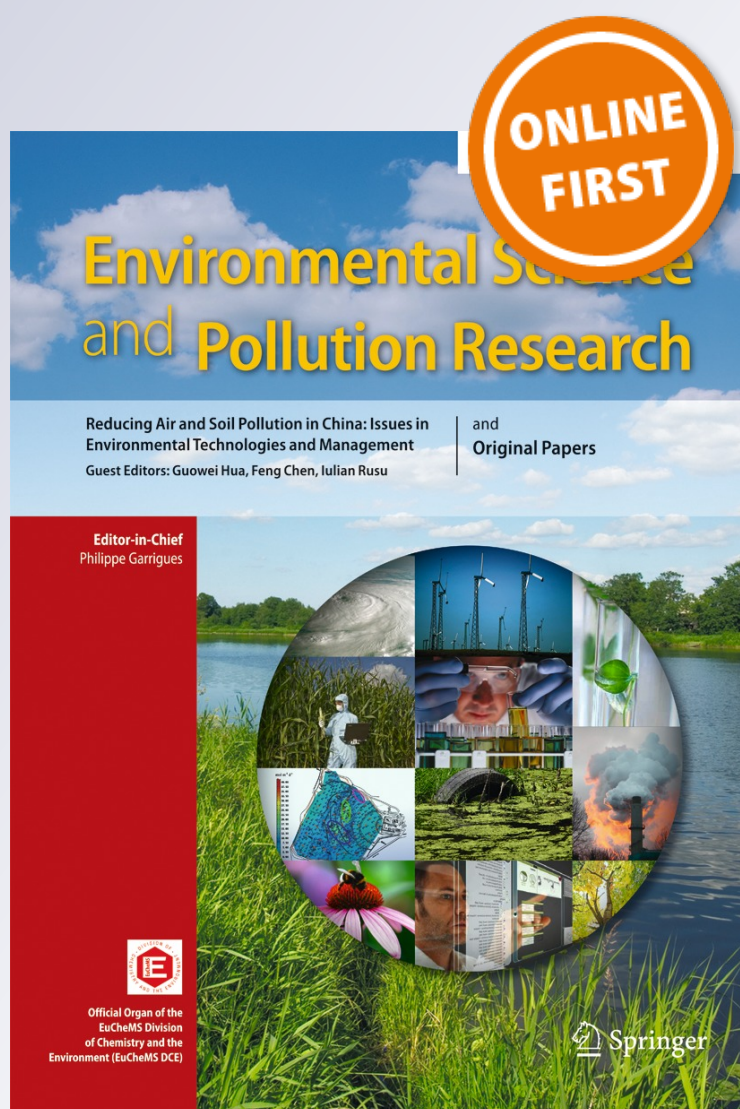
Persistence of tetraniliprole and reduction in its residues by various culinary practices in tomato in India

Ekta Kaushik, Jatiender Kumar Dubey, Surender Kumar Patyal, Sapna Katna, Avinash Chauhan & Nisha Devi

Environmental Science and Pollution Research

ISSN 0944-1344

Environ Sci Pollut Res
DOI 10.1007/s11356-019-04738-6



Your article is protected by copyright and all rights are held exclusively by Springer-Verlag GmbH Germany, part of Springer Nature. This e-offprint is for personal use only and shall not be self-archived in electronic repositories. If you wish to self-archive your article, please use the accepted manuscript version for posting on your own website. You may further deposit the accepted manuscript version in any repository, provided it is only made publicly available 12 months after official publication or later and provided acknowledgement is given to the original source of publication and a link is inserted to the published article on Springer's website. The link must be accompanied by the following text: "The final publication is available at link.springer.com".



Persistence of tetraniliprole and reduction in its residues by various culinary practices in tomato in India

Ekta Kaushik¹ · Jatiender Kumar Dubey ¹ · Surender Kumar Patyal¹ · Sapna Katna¹ · Avinash Chauhan¹ · Nisha Devi¹

Received: 5 July 2018 / Accepted: 27 February 2019
© Springer-Verlag GmbH Germany, part of Springer Nature 2019

Abstract

A field experiment was conducted to study the persistence and dissipation pattern of a new molecule tetraniliprole on tomato fruits and soil. Tetraniliprole was sprayed at the rate of 60 g a.i. ha⁻¹ and 120 g a.i. ha⁻¹ on the tomato crop. Tomato fruit samples were analyzed as per the method described by Bosta and Nageswara (Asian J Res Chem 8:383-388, 2015). The residues of tetraniliprole and its metabolite chinazolinon were estimated on HPLC equipped with RP C₁₈ column and photo diode array detector. Initial deposits of tetraniliprole were 0.865 and 1.747 mg kg⁻¹ on fruits and 0.092 and 0.177 mg kg⁻¹ in the soil, respectively, from the two treatments at the rate 60 g a.i. ha⁻¹ and 120 g a.i. ha⁻¹. The residues on fruits dissipated to half in 2.7 and 3.49 days, respectively. Based on the persistence studies, a waiting period of 15 days is suggested on tomato fruit from consumer's safety point of view. The pesticide residues, left to a variable extent in the tomato after harvesting, are beyond the control of consumers and have deleterious effects on human health; hence, their residues reduction by various culinary processes were highlighted. Treated tomato fruit samples collected at 1, 3, and 5 days after application were also subjected to common household practices. Washing of tomato fruits by tap, lukewarm, and saline water reduce tetraniliprole residues up to 37.63, 44.67, and 61.49%, respectively. Microwave cooking of tomato provided >12% better relief from tetraniliprole residues in comparison with open pan cooking of 72.21%. Chinazolinon residues, a metabolite of tetraniliprole, were not detected in any analyzed processed tomato fruit sample.

Keywords Tetraniliprole · Chinazolinon · Persistence · Tomato · HPLC · Culinary practices

Introduction

Tetraniliprole (IUPAC name, 1-(3-chloropyridin-2-yl)-N-[4-cyano-2-methyl-6-(methylcarbamoyl)phenyl]-3-{[5-(trifluoromethyl)-2H-tetrazol-2-yl]methyl}-1H-pyrazole-5-carboxamide) (Fig. 1), a phthalic acid diamide group of insecticide given its ISO name in 2014, is developed by Bayer CropScience and is likely to be introduced in the market by 2019 (Anonymous 2016a). It is a carboxamide cyantraniliprole in which the bromine atom has been replaced by a [5-(trifluoromethyl)-2H-tetrazol-2-yl] methyl group. It is a ryanodine receptor modulator, acts as selective ion channels,

and modulates the release of calcium, thereby, depleting the winternal intracellular calcium stores finally leading to muscle paralysis and death (Anonymous 2017).

The tomato crop is damaged by various insect pests like fruit borer, leaf hoppers, aphids, caterpillars, flea beetle, leaf miner, and spider mite; out of them, fruit borers *Helicoverpa armigera* and *Spodoptera litura* cause severe losses to farmers (Thamburaj and Singh 2015). Anthranilicdiamide insecticide cyantraniliprole has been registered by CIBRC in India to control tomato fruit borer (Anonymous 2017). Cyantraniliprole has a root systemic and translaminar activity against a broad spectrum of sucking and chewing insects. Presently, diamide molecules like cyantraniliprole, chlorantraniliprole, and flubendiamide effectively manage the insect pests population in soybean (Raut et al. 2014; Patil et al. 2014), fruits, and vegetable crops (Cordova et al. 2006; Misra 2015; Tiwari and Stelinski 2013; Caballero et al. 2015). Kousika et al. (2017) reported insecticidal activity of tetraniliprole in the rice ecosystem.

Responsible editor: Philippe Garrigues

✉ JatienderK.Dubey
jkdubey14@yahoo.com

¹ Department of Entomology, Dr. Y.S. Parmar University of Horticulture and Forestry, Nauni, Solan 173 230, India

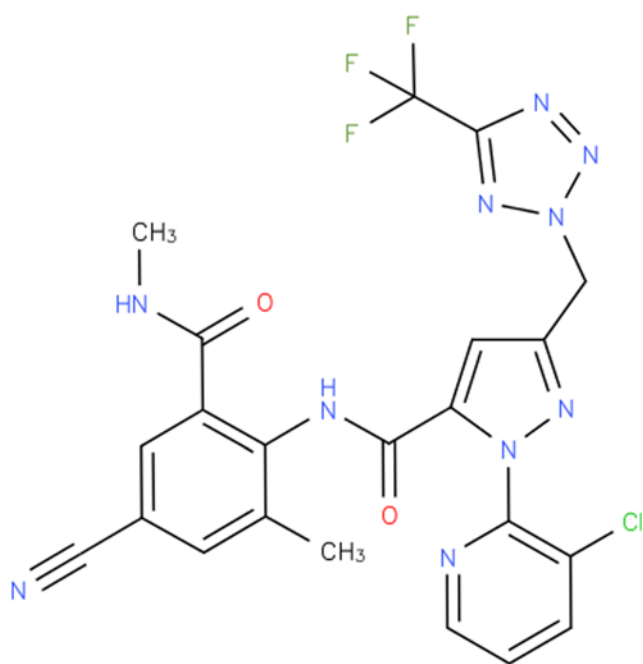


Fig. 1 Chemical structure of tetraniliprole

Alternate insecticides tetraniliprole, as a substitute are required to protect the tomato crop from fruit borer pests, as the insect has the tendency to develop resistance rapidly to insecticides. This will not only avoid the problems of frequent pest outbreaks but also decrease the use of insecticides and the cost of cultivation. However, its application during the fruiting stage may lead to the accumulation of residues in the fruits which are harmful to the ultimate consumers. Tomato constitutes an important component of the Indian diet and not only used as raw but also home cooked or processed as a canned product, juice, paste, etc. Hence, persistent behavior studies for tetraniliprole on tomato crop grown in open field conditions of each growing area are necessary to establish safe waiting period to ensure that their residues are well below the minimum risk level even through household practices like washing, peeling, cooking, and blanching in the tomato produce. Since, no information pertaining to the residue status of tetraniliprole in tomato is available besides commonly adopted household practices; therefore, the present investigation was aimed to study the persistent behavior of tetraniliprole in tomato along with the effect of culinary practices in the reduction of residue level in the farm produce, from consumer's safety point of view.

Material and methods

Reagents and chemicals

Formulated (Tetraniliprole 200 SC) and certified reference materials of tetraniliprole (purity, 99.7%) along with

its metabolite chinazolinon (purity, 99.7%) were supplied by M/s Bayer CropScience Ltd. Primary secondary amine (PSA), particle size 40 μm , was obtained from Agilent Technologies, USA. Anhydrous magnesium sulfate, sodium sulfate, sodium chloride, sodium citrate tribasic dehydrate, sodium hydrogen citrate sesquihydrate, and HPLC grade water were procured from Merck Specialties Pvt. Ltd. Worli, Mumbai. HPLC grade acetonitrile was purchased from by M/s Genetix Biotech Asia Pvt. Ltd., New Delhi. Nylon membrane filters of 13 mm and 47 mm diameter (0.45 μm pore size) were procured from by M/s Rankem, New Delhi.

Instrumentation

Tetraniliprole and its metabolite chinazolinon residues were estimated on high-performance liquid chromatograph LC-20AT along with degasser DGU-20A5, auto-injector SIL-20_{AHT}, and SPD-M20A; photo diode array detector (PDA) was supplied by Shimadzu Corporation, Kyoto, Japan. BONDAPAKTM reverse phase (RP) C₁₈ column (2.0 mm×30 cm) was procured from Waters India Pvt. Ltd. Robot Coupe high volume homogenizer (Blixer® 6 V.V) and Heidolph Laborota 4002 Rotary evaporator were from Heidolph, Germany. Centrifuge (Model 5804) was procured from M/s Eppendorf India Ltd., Chandigarh.

Experiment layout

The experiment was laid out in a randomized block design (RBD) at the experimental farm of the Department of Entomology, Dr. Yashwant Singh Parmar University of Horticulture and Forestry Nauni, Solan (HP), during the kharif season of the year 2016. Tomato (*Solanum lycopersicum* L.) variety Solan Lalima raised in a 3×2 m² plot as per university standard package of practices (Anonymous 2016b). Tetraniliprole was sprayed on tomato crop at the recommended rate (X) 60 g a.i. ha⁻¹ and double the recommended rate (2X) 120 g a.i. ha⁻¹ using the Knapsack sprayer fitted with hollow cone nozzle. The tomato crop was sprayed twice at 10 days at the fruit development stage. Untreated plots were sprayed with water only. Each treatment was replicated thrice. Weather parameters during the experimental period were between 20.56 and 27.3 °C temperatures, and rainfall was measured 274.40 mm with an average relative humidity of 82.28%.

Sample collection for persistence

After the second foliar application, tomato fruit samples (1 kg) from each replication were collected randomly at 0- (2 h after spray), 1-, 3-, 5-, 7-, 10-, 15-, and 20-day intervals and transported to the Pesticide Residue Laboratory for the residue analysis. To study the persistent behavior of tetraniliprole in the soil, the samples (1 kg) were collected

from all the treatments on 0, 3, and 7 days after the last application of tetraniliprole.

Extraction and cleanup

Tetraniliprole and its metabolite chinazolinon residues were extracted and purified from tomato fruits as per the method of Bosta and Nageswara (2015). The tomato fruit sample (1 kg) was homogenized in a low-speed high-volume homogenizer. Homogenized 20 g sample was taken in a 250-ml conical flask containing 100 ml acetonitrile water mixture (9:1 v/v). The sample was shaken on the Eppendorf flask shaker for 30 min and then filtered through Whatman No. 1 filter paper. The extraction was repeated twice with 50 ml of acetonitrile water mixture (9:1). Filtrates were combined, evaporated to dryness in the rotary evaporator at 50 °C, and dissolved residues in 20 ml acetonitrile water mixture (9:1) for further cleanup. The extract (20 ml) was passed through a 5-g silica gel chromatographic column and eluted with 100 ml acetonitrile water (8:2) mixture. The eluant was evaporated to dryness in the rotary evaporator at 50 °C, the residues were dissolved in 20 ml acetonitrile water mixture (9:1), filtered through 13-mm nylon filter paper (0.45 µm pore size), and finally injected 20 µl into HPLC. A soil sample (10 g) was extracted and analyzed as per Asensio-Ramos et al. (2010) with 20 ml acetonitrile along with 4 g magnesium sulfate, 1 g of sodium chloride, and to improve further recovery by the addition of 1 g of sodium citrate tribasic dihydrate and 0.5 g of sodium hydrogen citrate sesquihydrate. The representative aliquot was subjected to dispersive solid-phase cleanup by using magnesium sulfate anhydrous (1.15 g) and PSA (0.4 g) and analyzed by HPLC.

HPLC PDA analysis

Tetraniliprole and its metabolite chinazolinon residues were determined on liquid chromatograph using mobile phase acetonitrile and water (90:10) run in an isocratic mode at a flow rate of 1 ml/min. Wavelength ($\lambda_{\max}$) was set at 254 nm. Under these operating parameters, the retention time of tetraniliprole and its metabolite chinazolinon was observed at 8.652 and 5.270 min.

Data analysis

The residue data were subjected to statistical analysis according to Hoskins (1961) to compute the residue half-life and waiting period. Log residues were regressed on time interval to determine the role of time after the spray on residue dissipation. Residue half-life (RL_{50}) was calculated as $T_{1/2} = \log 2/b$ whereas $T_{1/2}$ =residue half-life (RL_{50}) in days and b =rate constant/slope. Waiting period (WP) was calculated by using the following formula: $\log$ of initial deposit– $\log$ of LOQ (Limit of Quantification)/ b (slope of the regression equation).

Decontamination studies

Tomato fruit samples collected at 1, 3, and 5 days after the last foliar application of tetraniliprole at X dose in the field were also processed with common household practices viz. washing with running tap water, lukewarm water, and saline water, and cooking in open pan and microwave. Each culinary treatment/process adopted the following:

- (i) Washing the fruits with running tap water: Washed tomato fruits under running tap water and hand rubbed for 2 min;
- (ii) Lukewarm water washing: Tomato fruit samples dipped in lukewarm water (50 °C) for 5 min;
- (iii) Washing with saline water: Tomato fruits dipped in 2% NaCl solution for 5 min followed by tap water washing;
- (iv) Open pan cooking: Unwashed tomato fruit sample chopped into small pieces and put in an open pan of 1-l capacity containing 250 ml water and boiled till softness for 10–15 min. Fifteen-gram equivalent fruit material was taken for residue estimation; and
- (v) Microwave cooking: Unwashed tomato fruit samples kept in the microwave for 5 min at 500 W.

The tomato fruit samples processed with the abovementioned culinary methods were analyzed for residue estimation as per the analytical procedure described by Bosta and Nageswara (2015).

Validation of analytical methodology

It is important to establish that the method employed is optimum for producing reliable results. The efficiency/validity of an analytical method is determined by the agreement between the true value of an analyte in the sample and the value obtained by its analysis. The measure of accuracy is expressed as a percentage of the analyte recovered of the true value of the amount of spiking (Tiryaki 2016). To establish the efficiency of the method validity, recovery studies were carried out by fortifying the tomato fruit and soil samples with tetraniliprole and its metabolite chinazolinon at 0.05, 0.25, 0.50, and 1.00 mg kg⁻¹ levels, and each spiking level was replicated five times (Fig. 2). The accuracy values were evaluated by using four low to high concentrations of pesticides in tomato fruits and soil. Linearity worked out by running five concentration levels replicated five times between 0.05–1.00 mg kg⁻¹ of tetraniliprole and its metabolite chinazolinon. The precision of the method was expressed as the percent relative standard deviation (% RSD) for replicate analysis of the spiked samples. Limit of detection (LOD) is the minimum concentration of the analyte that can be detected with acceptable certainty and is determined by

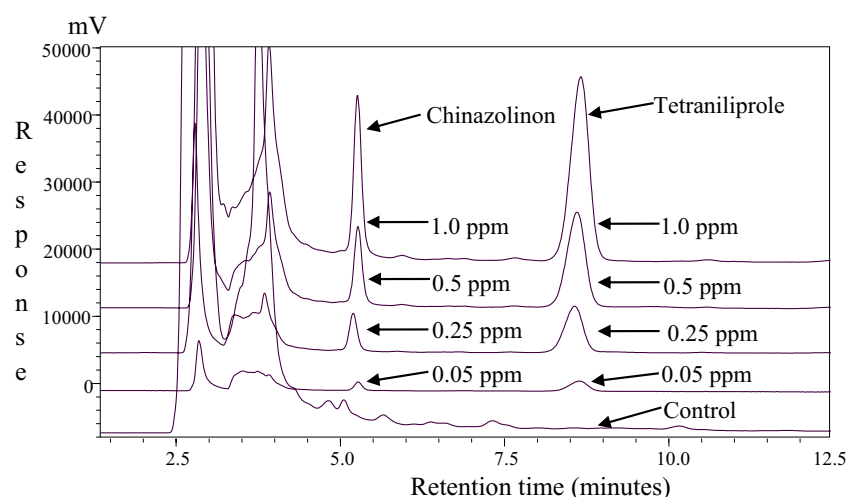


Fig. 2 Overlay chromatographic response of different concentrations of tetraniliprole and its chinazolinon metabolite in tomato

considering a signal to noise ratio of three times, whereas, the limit of quantification (LOQ) was determined by considering the signal to noise ratio of 10 (SANTE 2015).

Results and discussion

Method validation

Data presented in Table 1 depicts the reliability of analytical method tested by spiking of untreated tomato fruit and soil samples at different concentrations. Recovery of tetraniliprole in fruits was between 97.60 and 120.80%, and, in the soil, the percent recovery ranged from 94 to 97%. The recovery of chinazolinon was between 97.84 and 119.60% from fortified tomato fruit and 92.80–100.00% in spiked soil. The results are in the agreement with the investigation of Malhat et al. (2012), who reported recovery of chlorantraniliprole (a diamide insecticide) between 98.00 and 104.00% from tomato fruits. The recovery of chlorantraniliprole from cauliflower curd was reported between 89.60 and 95.80% at 0.10–1.00 mg kg⁻¹ fortification levels (Kar et al. 2013). In

our investigations, the average recovery of tetraniliprole and its metabolite chinazolinon was within the acceptable range of 70–120% both in tomato fruit and soil as documented in SANTE guidelines (SANTE 2015). The precision of the analytical method was determined by the relative standard deviation (RSD), and RSD for its repeatability ranged from 1.63–10.00 for tetraniliprole and chinazolinon for different spiking levels as shown in Table 1. The calibration curves were linear over the test range of tetraniliprole and chinazolinon as correlation coefficients (R^2) were >0.99 for both analytes. The cleanup procedure for this method was found to be efficient enough and as such no significant matrix effect was observed. The limit of quantification (LOQ) for tetraniliprole and its metabolite, chinazolinon, in tomato fruit and soil was observed to be at 0.05 mg kg⁻¹ and LOD was 0.017 mg kg⁻¹.

Persistence

The initial deposits of a pesticide depend upon a number of factors like concentration, formulation, weather conditions, substrate characteristics, type of sprayer used, the distance

Table 1 Recovery of tetraniliprole and chinazolinon from fortified tomato fruits and soil

Fortification levels (mg kg ⁻¹)	Mean per cent recovery* (%RSD)			
	Fruits		Soil	
	Tetraniliprole	Chinazolinon	Tetraniliprole	Chinazolinon
0.05	120.80 (8.33)	119.60 (10.00)	95.00 (1.88)	100.00 (9.20)
0.25	97.60 (2.45)	97.84 (1.63)	94.00 (3.33)	92.80 (5.65)
0.50	102.36 (3.90)	100.04 (3.00)	97.00 (6.40)	97.20 (3.46)
1.00	99.18 (2.11)	103.90 (4.42)	95.50 (6.11)	97.20 (4.24)

*Mean of 5 replications

between the nozzle and plant surface, and properties of the carrier. Besides these factors, plant type (erect or prostrate), shape of plant parts (broad, narrow, or linear), and growth of plant parts (slow or fast) influence the deposits persistence on plant surface (Ebling 1963) whereas the dissipation of insecticides depends upon crop factors like stage of crop, type of fruit surface, and internal material, weather factors like moisture, temperature, and rain, and surface characteristics to hold deposits. The dissipation pattern of tetraniliprole in tomato fruit is shown in Table 2. The average initial deposits of tetraniliprole on tomato fruits were 0.865 and 1.747 mg kg⁻¹ at the application rate of 60 and 120 g a.i. ha⁻¹, respectively. The initial deposits were dissipated to 0.052 and 0.077 mg kg⁻¹ in 10 and 15 days at X and 2X dose, thereby showing losses of about 93.98 and 95.59% residues, respectively (Table 2). The computing of graph between log values of residues and interval in days yielded regression equations with a correlation coefficient (R^2) of -0.987 and -0.983 at the respective dose level (Table 2). The tetraniliprole deposits dissipated to half in 2.70 days at X dose as compared with 3.49 days at 2X dose which indicate the imminence in dissipation behavior of this insecticide at both doses. Sun et al. (2012) also observed 2.9 to 6.4 days half-life value of cyantraniliprole deposits on pakchoi after the application at the rate of 60 g a.i. ha⁻¹. The half-life value of chlorantraniliprole reported to be 1.31 days on cowpea (Vijayasree et al. 2013), 1.58–1.80 days on brinjal, 1.69–1.70 days on okra fruits (Vijayasree et al. 2015), 3.30 days (Malhat et al. 2012), and 2.44–2.98 days on tomato fruits (Ali et al. 2015). Since no MRL has been fixed for tetraniliprole, therefore, a safe waiting period was calculated on the basis of the limit of quantification (LOQ). The safe waiting periods determined

at LOQ of 0.05 mg kg⁻¹ were worked out to be 11.77 and 14.86 days for tetraniliprole at X and 2X doses, respectively. Malhat et al. (2012) also suggested a waiting period of 8 days for chlorantraniliprole on tomato fruits. Whereas Vijayasree et al. (2015) suggested a waiting period of 0.6 and 2.38 days for chlorantraniliprole on brinjal fruits after the application at the rate of 30 and 60 g a.i. ha⁻¹, where the initial deposits were 0.72 and 1.48 mg kg⁻¹, respectively. Chinazolinon residues were not found in any analyzed tomato fruit sample.

The transport, persistence, or degradation of pesticides in soil depends on the behavior of the pesticide as well as physical, chemical, and biological properties of the soil (Beevi et al. 2014). Residue dissipation pattern of tetraniliprole in soil is presented in Table 3, and the analysis showed that when tetraniliprole applied at the rate of 60 g a.i. ha⁻¹, the average initial deposits of 0.092 mg kg⁻¹ in tomato cropped soil was found below the level of determination on the third day of application. Tetraniliprole applied at 120 g a.i. ha⁻¹ on crop gave initial average deposits of 0.177 mg kg⁻¹ in the soil which degraded to 0.056 mg kg⁻¹ on the third day of application. The residues degraded by 68.61% on the third day and were not further detected at successive intervals of sampling. Our results are in close proximity with Malhat et al. (2012) who observed the initial deposits of chlorantraniliprole from tomato cropped soil as 4.55 mg kg⁻¹, dissipated to 0.165 mg kg⁻¹, which showed 96.37% residue dissipation within 15 days of application. Sharma et al. (2014) observed the mean initial deposits of chlorantraniliprole on sugarcane field soil as 0.88 and 1.59 mg kg⁻¹ when applied at 100 and 200 g a.i. ha⁻¹, which supports the present investigation. No residues of chinazolinon were found in any soil sample.

Table 2 Persistence and dissipation pattern of tetraniliprole in tomato

Interval (Days)	X dose=60 g a.i. ha ⁻¹		2X dose=120 g a.i. ha ⁻¹	
	Mean residue (mg kg ⁻¹) ± SD	Dissipation (%)	Mean residue (mg kg ⁻¹) ± SD	Dissipation (%)
0	0.865±0.007	-	1.747±0.016	-
1	0.457±0.008	47.16	0.864±0.005	50.55
3	0.330±0.003	61.84	0.715±0.003	59.08
5	0.247±0.004	71.44	0.394±0.005	77.44
7	0.115±0.005	86.70	0.281±0.007	83.92
10	0.052±0.001	93.98	0.152±0.005	91.29
15	BDL	-	0.077±0.004	95.59
20		-	BDL	-
RL ₅₀ (Days)	2.70		3.49	
Regression equation	y= -0.13- 0.11 x		y= 0.09- 0.08 x	
Correlation coeff. (r^2)	-0.987		-0.983	

BDL Below Determination Limit

Table 3 Dissipation of tetraniliprole residues in tomato cropped soil

Interval (Days)	X dose= 60 g a.i. ha ⁻¹		2X dose = 120 g a.i. ha ⁻¹	
	Mean residue (mg kg ⁻¹) ± SD	Dissipation (%)	Mean residue (mg kg ⁻¹) ± SD	Dissipation (%)
0	0.092 ± 0.005	-	0.177 ± 0.003	-
3	BDL	100	0.056 ± 0.005	68.61
7	-	-	BDL	100

BDL Below Determination Limit

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). Important mechanisms which lead to residue alteration during storage and other household and industrial food preparation processes of raw agro-produce are dissolution, heat degradation, hydrolysis, metabolism, oxidation, penetration, photodegradation, volatilization, co-distillation, and physical change of the concentration of the pesticide residues due to possible change in the agro-produce (Kaushik et al. 2009; Holland et al. 1994).

Vegetable washing with water is the most traditional and preliminary operation at house level to remove dirt and debris from vegetables prior to consumption either as raw or cooked as well in commercial food preparation. Water washing is mostly prevalent in every household as it is the cheapest and easiest method of vegetable cleaning (Krol et al. 2000). In the modern era of life, vegetables are mostly washed under running tap water with slight hand rubbing prior to cutting and cooking. In the present investigation,

washing of 1, 3, and 5 days old treated tomato fruits under running tap water caused 30.12, 30.30, and 29.32% relief from tetraniliprole residues, respectively. Washing of tomato fruit samples in lukewarm water further increased relief from tetraniliprole residues to 41.94, 42.63, and 42.43% from 1, 3, and 5 days old treated samples, respectively (Fig. 3). The statistical analysis of the data in Table 4 revealed a significant reduction in tetraniliprole residues level due to different culinary processes at respective intervals. Efficacy of chlorantraniliprole (a diamide insecticide) residues, a sister chemical of tetraniliprole, removal by water washing is reported to be 69.17–57.81% in cowpea by Vijayasree et al. (2013), 86.38–88.78% in brinjal, and 56.35–66% in okra by Vijayasree et al. (2015). Removal of pesticides from the raw agricultural commodities depends upon the solubility of the chemical which in general increases with the increase in the level of commodity temperature depending upon pesticide binding with the matrices which ultimate leads to affect the partitioning coefficient. Removal of chlorpyrifos residues from tomato fruits was increased upon lukewarm water washing (38.98–43.09%) in comparison with washing tomato fruits under running tap water to the tune of 35.99–40.02% (Banshtu and Patyal 2015). Cauliflower washing with plain

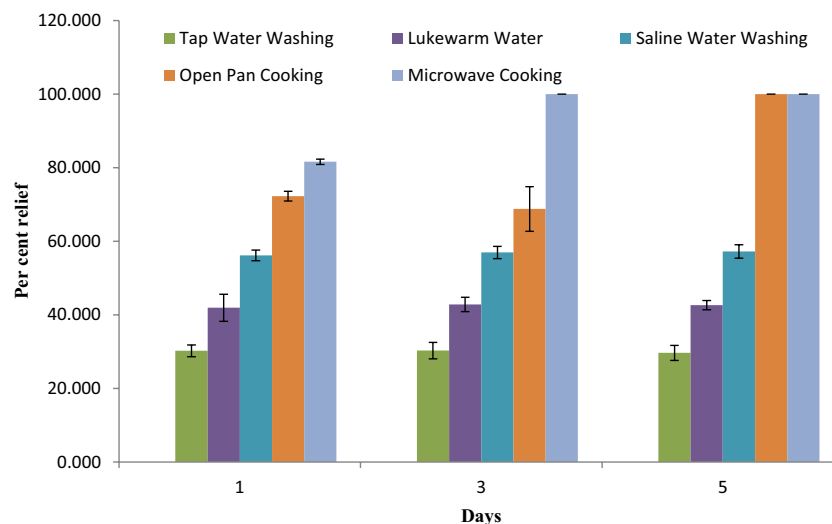
**Fig. 3** Effect of culinary processes on the tetraniliprole residues in tomato

Table 4 Effect of culinary processes on the residues of tetraniliprole in tomato

Interval (days)	Residue (mg kg ⁻¹)						Mean
	Un-processed	Tap Water Wash-ing	Lukewarm Water	Saline Water Wash-ing	Open Pan Cook-ing	Microwave Cook-ing	
1	0.457 (1.207)	0.319 (1.148)	0.265 (1.125)	0.200 (1.096)	0.127 (1.061)	0.084 (1.041)	0.242 (1.113)
3	0.330 (1.153)	0.230 (1.109)	0.189 (1.09)	0.142 (1.069)	0.093 (1.045)	<0.050 (1.00)	0.164 (1.078)
5	0.247 (1.117)	0.174 (1.083)	0.142 (1.068)	0.106 (1.052)	<0.050 (1.00)	<0.050 (1.00)	0.111 (1.053)
Mean	0.345 (1.159)	0.241 (1.114)	0.199 (1.095)	0.149 (1.072)	0.073 (1.036)	0.028 (1.014)	

BDL= <0.050 mg kg⁻¹, Figures in parentheses are square root transformed values

CD_{p=0.001}: Effect of processing (P)= 0.002, Days (D) = 0.002, Interaction (P x D) = 0.004

water reduced fat soluble residues of bifenthrin, endosulfan, and profenofos by 25%, 28.1%, and 14.32%, respectively. The degree of reduction on plain water washing on water-soluble pesticides namely diafenthiuron and imidacloprid in cauliflower were 40.69%, 39.07%, and 2117% (Panhwar and Sheikh 2013), respectively. Deltamethrin was reduced by washing up to 35% in tomato, 32% in cauliflower, 26% in potato, and 10% in spinach (Randhawa et al. 2008). Washing reduced cypermethrin residues by 33.42–35% and decamethrin by 25–27.90% in brinjal. Lambda cyhalothrin residues were reduced in the range of 37–40% by washing tomato fruits (Chauhan et al. 2012).

Pesticides residues loosely bound to the exposed surface of vegetables can be easily removed with reasonable efficiency by varied type of washing processes (Street 1969). Washing with a dilute salt solution can be a convenient method to lower the load of pesticides from fruits and vegetable surfaces. Washing of 1, 3, and 5 days treated harvested tomato fruit with saline water (2% NaCl) produce relief to the level of 56.16, 56.87, and 57.16%, respectively, from tetraniliprole residues. This procedure can be recommended as being practical for household practices for adoption. Vijayasree et al. (2013) also observed 74.64 and 52.17% chlorantraniliprole residues removal by 2% common salt from cowpea fruits in 0 and 3 days fruits, respectively. Banshtu and Patyal (2015) reported 41.89–45.10% from chlorpyrifos residues removal by washing of tomato fruits in 2% sodium chloride solution. Chlorothalonil was reported to be removed from Chinese cabbage by 1% saline exposure for 10 min (Lee and Chou 1995).

Foods are subjected to heat treatment during preparation and preservation. Heat treatment includes pasteurization, boiling, and cooking depending upon the nature of food and aim of processing. The loss of pesticide residues during heat processing may be due to evaporation, co-distillation, and thermal degradation, which may vary with the chemical nature of the individual pesticide (Sharma

et al. 2005). The effect of tomato fruit cooking on tetraniliprole revealed maximum relief (81.62%) from tetraniliprole residues by microwave in comparison with 72.21–71.92% relief in open pan cooking (Fig. 3). The disappearance of pesticide residues from boiling extract could be due to decomposition by the heat effect, the stronger adsorption of pesticide onto plant tissues, and/or the poor solubility of pesticides in water (Abou and Abou 2001; Ali 1983). Microwave cooking of rice and beans containing trifluralin, chlorpyrifos, decamethrin, cypermethrin, and dichlorvos residues at powers of 500 W and 800 W for 15–45 min resulted in the elimination of 92 to 99% pesticides residues (Castro et al. 2003).

Conclusion

It is clear from the above study that analytical procedure has been validated for the estimation of pesticide residues of tetraniliprole before putting into use in tomato fruits. Persistence of tetraniliprole largely depends upon the weather parameters like moisture, temperature, rain, and plant characteristics to hold insecticide deposit. Faster dislodging and degrading capabilities of initial deposits of tetraniliprole on tomato fruits due to the two treatments at the rate of 60 g a.i. ha⁻¹ and 120 g a.i. ha⁻¹ with the half-life of 2.7–3.49 days provide safety to human health. A safe waiting period of 15 days is suggested for tetraniliprole on tomato from consumer's safety point of view.

Pesticide residues carried from field produce to kitchen can be reduced to a greater extent from a minimum level to a higher level based upon the culinary processes adopted right from washing tomato fruits under running water, followed by more effective processes in an increasing trend for reducing tetraniliprole residues like lukewarm water washing, open pan cooking, and finally microwave cooking, which has a direct bearing effect on human health besides boosting the export of tomato fruit.

References

- Abou AAK, Abou DMA (2001) Pesticide residues in some Egyptian spices and medicinal plants as affected by processing. *Food Chem* 72:439–445
- Ali SL (1983) Bestimmung der pestiziden Ruckstande und anderbedenklicherer untreinigungen-wietoxische Metallspuren in Arzneipflanzen1. Mitt: Pestizid-Ruckstande in Arzneidrofen. *Pharm Ind* 45:1154–1156
- Ali MSEL, Mohamed MA, Monir MA, Ibrahim AG, Hanim MS (2015) Chlorantraniliprole behaviour in tomatoes under climatic changes of temperature and humidity. *Egypt Sci J Pestic* 1(2):1–8
- Anonymous (2016a) Focus on innovation crop science. Annual report (2016) augmented Version. <http://www.annualreport2016.bayer.com/management-report-annexes/about-the-group/research-development-innovation/crop-science.html>. Accessed 25 Aug 2017
- Anonymous (2016b) Package of practices for vegetable crops. Dr Y S Parmar University of Horticulture and Forestry, Solan
- Anonymous (2017) CIBRC. www.cibrc.nic.in. Accessed 31 Aug 2017
- Asensio-Ramos M, Hernandez-Borges J, Ravelo-Perez LM, Rodriguez-Delgado MA (2010) Evaluation of modified QuEChERS method for the extraction of pesticides from agricultural, ornamental and forestal soils. *Anal Bioanal Chem* 396:2307–2319
- Banshtu T, Patyal SK (2015) Effect of decontamination processing on the removal of chlorpyrifos and cypermethrin residues from tomato fruits. *Int J Food Ferment Technol* 5:25–31
- Beevi SN, Paul A, George T, Mathew TB, Kumar NP, Xavier G, Kumar GTP, Rajith R, Ravi KP, Kumar SV (2014) Pesticide residues in soils under cardamom cultivation in Kerala, India. *Pestic Res J* 26:35–41
- Bosta P, Nageswara RT (2015) A new validated HPLC method for determination of cyantraniliprole and its metabolite residues in tomato fruits. *Asian J Res Chem* 8:383–388
- Caballero R, Schuster DJ, Peres NA, Mangandi J, Hasing T, Trexler F, Kalb S, Portillo HE, Macron PC, Annan IB (2015) Effectiveness of cyantraniliprole for managing *Bemisia tabaci* (Hemiptera: Aleyrodidae) and interfering with transmission of tomato yellow leaf curl virus on tomato. *J Econ Entomol* 108:894–903
- Castro MFPM, Oliveira JJV, Rodrigues J, Scartuchio DLI (2003) A study on the persistence of trifluralin, chlorpyrifos, decamethrin, cypermethrin and dichlorvos in rice and beans after cooking in a commercial microwave oven. In: Credland PF, Armitage DM, Bell CH, Cogan PM, Highley E (eds) Proceedings of the 8th international working conference on stored product protection, 22–26 July 2002, York UK, pp 517–521
- Chauhan SS, Negi S, Singh N, Bhatia G, Srivastava A (2012) Monitoring of pesticides residues in farmgate vegetables of Uttarakhand, India. *Wudpecker J Agric Res* 1:250–256
- Cordova D, Benner EA, Sacher MD, Raul JJ, Sopa JS, Lahm GP (2006) Anthranilic diamides: a new class of insecticides with a novel mode of action, ryanodine receptor activation. *Pestic Biochem Phys* 84:196–214
- Ebling W (1963) Deposition, degradation, persistence and effectiveness of pesticides. *Resi Rev* 3:35–163
- Holland PT, Hamilton D, Ohlin B, Skidmore MW (1994) Effects of storage and processing on pesticide residues in plant products. *Pure Appl Chem* 66:335–356
- Hoskins WM (1961) Mathematical treatment of loss of pesticide residues. *Plant Prot Bull (FAO)* 9:163–168
- Kar A, Mandal K, Singh B (2013) Environmental fate of chlorantraniliprole residues on cauliflower using QuEChERS technique. *Environ Monit Assess* 185:1255–1263
- Kaushik G, Satya S, Naik SN (2009) Food processing a tool to pesticide residue dissipation—a review. *Food Res Int* 42:26–40
- Kousika J, Kuttalam S, Kumar MG (2017) Evaluation on the effect of tetraniliprole 20 SC, a new chemistry of pyridine derivative to the rice arthropod biodiversity. *J Ent Zool Stud* 5:133–143
- Krol WJ, Arsenault TL, Pylypiw H, Incorvia MMJ (2000) Reduction of pesticide residues on produce by rinsing. *J Agri Food Chem* 48:4666–4670
- Lee YS, Chou SS (1995) Reduced pesticide residues in vegetables by various methods of washing. Conf Proc IFT Annual Meeting 1995. Food Sci. Program, Univ. of the District of Columbia, Washington, DC 20008, USA
- Malhat FM, Abdallah H, Hegazy I (2012) Dissipation of chlorantraniliprole in tomato fruits and soil. *Bull Environ Contam Toxicol* 88:349–351
- Misra HP (2015) Cyantraniliprole (Cyazypyr)—a new anthranilic diamide insecticide against tomato fruit borer, *Helicoverpa armigera*. *Indian J Plant Prot* 43:1–5
- Panhwar AA, Sheikh SA (2013) Assessment of pesticide residues in cauliflower through gas chromatography-μECD and high performance liquid chromatography (HPLC) analysis. *Int J Agric Sci Res* 3:7–16
- Patil MU, Kulkarni AV, Gawkare O (2014) Evaluating the efficacy of novel molecules against soybean defoliators. *Bioscan* 9:577–580
- Randhawa MA, Anjum FM, Randhawa MS, Ahmed A, Farooq U, Abrar M, Randhawa AR (2008) Dissipation of deltamethrin on supervised vegetables and removal of its residue by household processing. *J Chem Soc Pak* 30:227–231
- Raut AS, Barkhade UP, Bhalkare SK, Borkar UH (2014) Efficacy of newer insecticides against major pests of soybean. *Trends Biosci* 7:3133–3138
- SANTE (2015) Guidance document on analytical quality control and method validation procedures for pesticide residues analysis in food and feed. SANTE/11945/2015. https://ec.europa.eu/food/sites/food/files/plant/docs/pesticides_mrl_guidelines_wrkdoc_2017-11813.pdf. Accessed 09 Jan 2018
- Sharma J, Satya S, Kumar V, Tewary DK (2005) Dissipation of pesticides during bread making. *Chem Health Saf* 12:17–22
- Sharma N, Mandal K, Kumar R, Kumar B, Singh B (2014) Persistence of chlorantraniliprole granule formulation in sugarcane field soil. *Environ Monit Assess* 186:2289–2295
- Street JC (1969) Methods of removal of pesticide residues. *Can Med Assoc J* 100:154–160
- Sun J, Feng N, Tang C, Qin D (2012) Determination of cyantraniliprole and its major metabolite residues in pakchoi and soil using ultra-performance liquid chromatography–tandem mass spectrometry. *Bull Environ Contam Toxicol* 89:845–852
- Thamburaj S, Singh N (2015) Vegetables, tubercrops and spices. Directorate of Knowledge Management in agriculture, Indian Council of Agriculture Research, New Delhi 469p
- Tiryaki O (2016) Validation of QuEChERS method for the determination of some pesticide residues in two apple varieties. *J Environ Sci Health B* 51:722–729
- Tiwari S, Stelinski LL (2013) Effects of cyantraniliprole, a novel anthranilic diamide insecticide, against Asian citrus psyllid under laboratory and field conditions. *Pest Manag Sci* 69:1066–1072
- Tomer V, Sangha JK (2013) Vegetable processing at household level: effective tool against pesticide residue exposure. *IOSR J Environ Sci Toxicol Food Technol* 6:43–53
- Vijayasree V, Hebsy B, Beevi SN, Mathew TB, Kumar V, George T, Xavier G (2013) Persistence and effect of processing on reduction of chlorantraniliprole residues on cowpea fruits. *Bull Environ Contam Toxicol* 90:494–498
- Vijayasree V, Hebsy B, Beevi SN, Mathew TB, George T, Xavier G (2015) Persistence and effect of processing on reduction of chlorantraniliprole residues on brinjal and okra fruits. *Environ Monit Assess* 187:299

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.