Persistence and decontamination studies of chlorantraniliprole in *Capsicum annum* using GC–MS/MS

Sushil Ahlawat¹ · Suman Gulia¹ · Kamla Malik² · Savita Rani¹ · Reena Chauhan¹

Revised: 16 March 2019 / Accepted: 26 March 2019 / Published online: 6 May 2019
© Association of Food Scientists & Technologists (India) 2019

Abstract Chlorantraniliprole, a new systemic insecticide of anthranilic diamide class gaining popularity among farmers for its effective control of Lepidoptera pest particularly in vegetables. Thus monitoring of chlorantraniliprole (CAP) leftover in vegetables is required and to this end eco-friendly, cost effective, selective and accurate method was developed and validated for quantification of its left over in chilli fruit using gas chromatography–tandem mass spectrometry (GC–MS/MS) in SCAN/MRM mode with a triple Quadrupole analyzer. Two MS–MS transitions were acquired to ensure the reliable quantification and confirmation of the analyte. All calibration curve showed a good linear relationship ($r > 0.99$) with in test ranges (0.005 – $0.5 \mu\text{g ml}^{-1}$). To study its persistence, half-life, waiting period and decontamination behavior the field trial were performed at recommended dose and its double by Central Insecticide Board and Registration Committee (CIBRC). Initial deposits of CAP at recommended (T1) and double (T2) the recommended doses revealed 3.16 and 4.18 mg kg^{-1} with their respective half-lives 1.18 and 2.05 days respectively. According to maximum residual limit i.e. 0.03 mg kg^{-1} by FSSAI, residues persists up to 7th and 15th day if sprayed at fruit setting stage. The extent of removal of CAP using simple decontamination approach showed 62–67% reduction on maximum residue.

Keywords Chlorantraniliprole · Dissipation · Quechers · Half-life · Decontamination · MRM

Introduction

Indian chilli (*Capsicum annum* Linn.) is considered the world famous for its two important commercial qualities namely, colour and pungency levels. The pungency is due to the alkaloid ‘capsaicin’ present in the pericarp. India is the lead producer of chilli followed by China and Pakistan. Chilli is used in every vegetarian/non-vegetarian preparation, curries and pickles. Chilli crop is attacked by a wide range of insect pests including 51 species of insects and 2 species of mites, belonging to 27 families under 9 orders causing high yield loss (Reddy et al. 2007). Since last many years it has been reported that due to severe attack of fruit borers, there is a 90% flower and fruit drop in chilli (Reddy and Reddy 1999). In the race of attaining ever-green revolution, one of the main strategies would be to sustain and further accelerates the gains through minimizing the crop losses due to pest, diseases and weeds. In the spirit of saving product, pesticides are abruptly used to reduce the colossal losses and to enhance availability of quality product. Pesticides are repeatedly applied during the entire growth and development and even some time at the fruiting stage just before the harvest. Continuous and haphazard utilization of the pesticide leads to accumulation in consumable seasonal vegetables. Non target organisms including humans are badly affected through direct or indirect exposure even at micro level. Due to awareness of consumers about the persistence of pesticide left over in food commodities has prompted the advancement of eco-accommodating new molecules to guarantee least hazard to man and condition. Chlorantraniliprole (CAP), an

✉ Sushil Ahlawat
sushilahlawat21@gmail.com

¹ Department of Chemistry, CCS Haryana Agricultural University, Hisar 125004, India

² Department of Microbiology, CCS Haryana Agricultural University, Hisar 125004, India

anthranilic diamide insecticide with novel mode of action emerged as the most effective insecticide and shows excellent activity against Hemipteran, Thysanopteran and Lepidopteran insects. It is available as trade name as Coragen 18.5% suspension concentrate (SC) in market and has ovicidal, ovo-larvicidal action. Environmental Protection Agency has classified the chlorantraniliprole as a reduced-risk pesticide. The key biological attributes of chlorantraniliprole are its selectivity profile towards non-target organisms and its long-lasting activity against target pest species. CAP is a “reduced risk” pesticide hence recommended as an alternative to pyrethroids for vegetables (EPA 2008). To create specific, low portion, eco-accommodating pesticides to guarantee wellbeing for purchasers it is important to gauge of pesticide constancy, disinfecting, conduct, non-harmful metabolites, half life period and safe holding up period in consumable deliver (Ahlawat et al. 2017; Kumar et al. 2018). Since CAP is a new insecticide, a very little work has been carried out on its residues estimation, therefore present study summarises its dissipation pattern, half life and decontamination effects on chilli fruits from consumer safety point of view.

Materials and methods

Analytical standard of CAP insecticide was purchased from Sigma Aldrich of purity 99.2% under name of chlorantraniliprole having CAS-No[500008-45-7] and the formulation of CAP (Coragen 18.5% suspension concentrate) was procured from E.I Du Pont India Private. Limited. Organic solvents like acetonitrile, dichloromethane, hexane, acetone are from Merck, Germany (Suprasolv), PSA from Agilent and magnesium sulphate from ACROS ORGANIC, New Jersey was used. Stock solution of CAP insecticide was prepared by dissolving 10 mg in 100 ml of acetonitrile. The subsequent 100 µg/mL was utilized to get ready working solutions of range 0.005–0.5 µg mL⁻¹ by serial dilutions technique for calibration and recovery experiments. Working solutions and stock solution was kept in refrigeration at – 4 °C to prevent degradation. All calibration curve showed a good linear relationship ($r > 0.99$) with in test ranges.

The field test was planned out using randomized block design (RBD) at Entomology Research Farm, of Chaudhary Charan Singh Haryana Agricultural University (CCSHAU), Hisar following recommended agronomic practices as per package of practices by the university. To checkout right measure of insecticide for every treatment, the market available formulation was tested for its active compound before application to field. Insecticide spray was made at fruit setting/formation that is 90 days after sowing, the crop is first sown in nursery and then transplanted to

field by picking only healthy plants so that maximum effect i.e. persistence and leaching of pesticide is to be noticed. Spraying is with Knapsack sprayer in plots of size 5 m × 5 m size (three for every treatment). Separate plots were utilized for the recommended (30 g a.i. ha⁻¹) and its two fold portion (60 g a.i. ha⁻¹) application while one plot was kept splashed just with water and utilized as control. Samples were taken in triplicates for both persistence and decontamination studies.

About half kg of chilli sample for dissipation and decontamination studies was collected randomly from the control and treated plots of each treatment at 0 (1 h after treatment), 1, 3, 5, 7, 10, 15 and 20 days after the application of the insecticide. The samples from each treatment plot were packed in polyethylene bags, and brought to the laboratory for processing. Samples were extracted and cleaned up immediately after sampling on the same day. Extraction of CAP was streamlined with two techniques for accomplishing high affectability; exactness and repeatability for low level build up analysis.

Method 1: Liquid–liquid partitioning

Handling of the chilli fruit sample was carried out by the strategy of Gupta et al. (2010). Hexane and dichloromethane were utilized for extraction pursued by cleanup with adsorbent blend of silica + activated charcoal (5 + 0.2 g) in the middle of the two layers of anhydrous sodium sulphate. Column was pre wetted with 40 ml hexane and eluted with 100 ml solution of acetone:hexane (9:1). The final volume was made to 3 ml using n-hexane for analysis.

Method 2: QuEChERS

Samples were extracted using the modified QuEChERS method (Anastassiades et al. 2003). 15 g chopped, macerated chilli fruits was taken as representative sample mixed with 30 ml acetonitrile and homogenised at 14,000 rpm for 3–4 min on low volume homogeniser (Heidolph). To this extract, 5 g sodium chloride was added and vortexed for 2 min to separate water and acetonitrile phase. Vortexed sample was then centrifuged for 5 min at 2500 rpm and upper 18 ml acetonitrile layer was transferred over sodium sulphate to remove any left out moisture traces. For cleaning, dispersive solid phase extraction (DSPE) technique was used with primary secondary amine (PSA) 0.4 g and magnesium sulphate (MgSO₄) 1.15 g as absorbent. The final volume was reconstituted in 3 ml acetonitrile and filtered through a 0.2 micron filter prior to GC–MS/MS analysis.

Efficiency of two methods was checked by recovery experiments at different spiking levels. QuEChERS was

found better being fast, cheap, less exposure to solvent and better recoveries 85–91% as compared to liquid–liquid partitioning (72–76%). Therefore, QuEChERS was adopted for further study of dissipation and decontamination in chilli fruits. Beside recovery linearity, specificity, repeatability, reproducibility and ruggedness of method was also consider for validation protocol. Six point calibration curve has been constructed with three replicates over a concentration range of 0.005–0.5 $\mu\text{g ml}^{-1}$. Good correlation coefficient was observed which shows goodness of fit within test range of 0.994. The ruggedness of method was checked by small variation in injector port temperature, flow rate of gas and different analyst etc. The effect on GC–MS/MS analysis under these conditions was found with in acceptable range, indicating its ruggedness. Quantification of the leftover of CAP from field experiment and recovery samples was made using triple Quadrupole from Shimadzu (model GCMS-TQ 8040) with following operational parameters:

GC specification		
1.	Software	GC–MS solution version 4.41 (Shimadzu)
2.	Inlet	250 °C; splitless single Taper Gooseneck w/Wool (Restek)
3.	Column	SH-Rxi-5Sil MS (length 30 m, 0.25 mm I.D., film thickness 0.25 µm, Shimadzu)
4.	Column oven temp	80 °C (2 min), 20 °C min ^{−1} to 180 °C, 5 °C min ^{−1} to 300 °C (10 min)
5.	Injection mode	Auto injector, splitless (high pressure injection 250 kPa, 2.30 min)
6.	Carrier gas control	Linear velocity (44.5 cm/s)
7.	Injection volume	1 µL
8.	Column flow	1.46 mL min ^{−1}
MS specification		
1.	Interface temperature	300 °C
2.	Measurement mode	MRM loop MRM
3.	Ion source temperature	200 °C
4.	Loop time	0.4 s
5.	LOD; LOQ	0.005 mg kg ^{−1} ; 0.01 mg kg ^{−1}

The response of scan assessment of CAP revealed peak at m/z 278, 280, 243, 215. The product ion present at m/z 278 and 280 was taken as precursor ion during Multiple Reaction Monitoring (MRM). The GC–MS/MS was operated in the positive ion mode and m/z 249 and 251 with transitions m/z 278 > 249 and m/z 280 > 251 at collision energy 20 eV was selected at quantifier ion. The retention

time (R_t) was found to be 20.37 ± 0.02 min in these conditions as shown in Fig. 1.

Different spiked samples having concentration equivalent to their limit of quantification of CAP were analysed and the area corresponds to resultant peak were plotted against different spiked levels. The limit of detection (LOD) was the concentration that produces a peak with a height three times the level of base line noise. Limit of quantification (LOQ) was calculated by the sample concentration that produce a peak with a height ten times the ratio of signal to noise. Thus LOD and LOQ of CAP in chilli fruit sample was found to be 0.005 and 0.01 mg kg^{-1} respectively. The limit of quantification is always kept higher as compared to limit of detection as with matrix there are co-extractive which interfere the compound of interest elution. The LOQ calculated in present study is with matrix-match (MM) by treating control as sample and applying same procedure as on others, the only change in matrix match calibration is in final make up of samples that is with certified reference material of suitable concentration in matrix match.

The effect of basic culinary practices was utilized for the expulsion of CAP deposits from chilli as explained below:

(i) Washing with tap water.

The whole chilli fruits were kept under running tap water for 60 s by delicate scouring with hands (Fadwa et al. 2014). Blotting paper was used to evacuate excess water and handled for leftover estimation.

(ii) Washing with hot water.

One litre of Luke warm water (40 °C) was taken in a beaker and chilli fruits were dipped in it for 40 s by gentle rubbing with hands. Washed chillies were dried using blotting paper and further processed for residue estimation.

(iii) Washing with 5% sodium chloride solution.

Chillies were dipped in 5% sodium chloride solution and gently rubbed with hand for 40 s. Here time for washing/dipping was kept same in all processes for sake of better comparison. Blotting paper was used to remove excess water and samples were processed in similar manner as explained above.

The degradation rate equation was calculated graphically by plotting time frame against level of concentration and R^2 i.e. Maximum Square of correlation coefficient was obtained. Exponential relations were applied and corresponds to first-order rate equation calculated from: $C_t = C_0 e^{-kt}$, where C_t is the concentration at time t , C_0 is the initial concentration on 0 day i.e. 1 h after the spray and k is the degradation rate constant. The half-life ($t_{1/2}$) was determined by formula $t_{1/2} = \ln(2)/k$.

Fig. 1 a, b Mass spectra showing various mass-to-charge (m/z) fragmentation during SCAN and MRM mode; c, d full SCAN and MRM chromatogram of chlorantraniliprole with retention time

Results and discussion

Efficiency of the method

The explanatory technique utilized for extraction of Chlorantraniliprole in chilli fruit was approved according to as per SANTE/11813/2017 rules. The strategy approval criteria depended on linearity, recovery studies, repeatability, reproducibility and ruggedness. Recovery experiments were performed at different fortification concentrations up to limit of quantification to set up the reliability and validity of the analytical method and to know the proficiency of extraction and clean-up methodology. Precision was assessed by intra and inter day tests with RSD < 2.0%, recovery in between 72 and 91% with RSD < 2.00%. The ruggedness i.e. small variation in test condition of method is properly checked and found in test ranges. Limit of quantification (LOQ) was found to be 0.01 mg kg⁻¹ and limit of detection (LOD) being 0.005 mg kg⁻¹ with matrix match to including effect of co-extractives.

Persistence of chlorantraniliprole in chilli fruit

Chlorantraniliprole @ 30 (T₁) and 60 (T₂) g.a.i ha⁻¹ was sprayed once and the dissipation dynamics was studied in open field by collecting samples at 0 (1 h after treatment), 1, 3, 5, 7, 10, 15 and 20 days. Results are presented in Table 1. For T₁ (single dose), initial deposits were 3.16 mg kg⁻¹ at 0 (1 h after spray) day, which dissipated

to 2.16, 1.39, 0.42 and 0.043 mg kg⁻¹ in 1, 3, 5 and 7 days after treatment, respectively, thereby recording 31.64, 56.01, 86.70 and 98.73 per cent degradation during this period. Residues further reached below quantification limit of 0.01 mg kg⁻¹ on 10th day after application. The regression equation, R² and half-life was $y = -0.254x + 3.653$, R² = 0.905, t_{1/2} = 1.18 days, respectively. At T₂ (double dose), initial deposits of 4.68 mg kg⁻¹ at 0 (1 h after treatment) day reached to 0.79, 0.37, 0.09 and 0.04 mg kg⁻¹ level on 5, 7, 10 and 15 days after application of insecticide with dissipation per cent of, 83.11, 92.09, 98.07 and 99.14 respectively during this period. On 20th day, the residues of CAP reached to below quantification limits. The regression equation, R² and half life was $y = -0.146x + 3.637$, R² = 0.977, t_{1/2} = 2.05 days, respectively. The above findings presume that higher rate of use that is two-fold of recommended dose of chlorantraniliprole brought about higher initial deposits. As with other insecticides, the residues of chlorantraniliprole on chilli fruit declined with time and genuinely high rate of dissemination was observed. The outcomes are in concurrence with those of Vijayasree et al. (2013), who reported the CAP persistence on cowpea fruits and reported the half-life of CAP (18.5% SC) for 30 g a.i. ha⁻¹ dose to be 1.31 days. Waiting period was 0.62 days following first order kinetics and Below Quantitation Limit (BQL) came on 10th day. The results are in agreement with those of Malhat (2012) who reported the fate of CAP in the grape fruit by using high-performance liquid chromatography with photodiode array detector

Table 1 Residues (mg kg⁻¹) of chlorantraniliprole in chilli fruits at single and double dose

Days after treatment	Chlorantraniliprole residue (mg kg ⁻¹)			
	Single dose (30 g a.i. ha ⁻¹)		Double dose (60 g a.i. ha ⁻¹)	
	*AR ± SD (mg kg ⁻¹)	D%	*AR ± SD (mg kg ⁻¹)	D%
0	3.16 ± 0.026	–	4.68 ± 0.026	–
1	2.16 ± 0.026	31.64	3.45 ± 0.044	26.28
3	1.39 ± 0.010	56.01	1.79 ± 0.026	61.75
5	0.42 ± 0.046	86.70	0.79 ± 0.046	83.11
7	0.04 ± 0.026	98.73	0.37 ± 0.046	92.09
10	< LOQ	–	0.09 ± 0.01	98.07
15	–	–	0.04 ± 0.01	99.14
20	–	–	< LOQ	
Mean	1.43		1.60	
t _{1/2}	1.18 days		2.05 days	
Correlation coefficient	r = - 0.9512		r = - 0.9889	
Regression equation	y = - 0.254x + 3.653		y = - 0.146x + 3.637	
	R ² = 0.905		R ² = 0.977	
MRL (as per FSSAI)			0.03 mg kg ⁻¹	

AR average residue, D dissipation

*Average of three replicates; ± SD (standard deviation)

(HPLC–DAD). The half-life of chlorantraniliprole in grapes was found to be 2.70 days. Residue reached below detection limit of 0.02 mg kg^{-1} on 21st day after spray treatment with pre-harvest interval of 4 days. Malhat et al. (2012) also studied the dissipation behavior of CAP in tomato fruits and soil and reported the half-life value of 3.30 days at recommended dose in tomato. Pre-harvest interval (PHI) was of 8 days after the treatment.

Half-life of chlorantraniliprole in chilli fruit

Half-life ($t_{1/2}$) or DT 50 is the time taken by any pesticide to end up half of its underlying stores. The degradation dynamics of the chlorantraniliprole in chilli fruit was determined by plotting left over amount against days, and the maximum squares of correlation coefficients found were used to determine the equations of best fit curves. Half-life of CAP calculated was observed to be 1.18 and 2.05 days @ 30 and 60 g a.i. ha^{-1} respectively (Table 1). The outcomes are in concurrence with (Malhat et al. 2012) who revealed the half-life of chlorantraniliprole on tomato fruit was 3.30 days after application. Half-life ($t_{1/2}$) of chlorantraniliprole on cauliflower curds worked out to be 1.36 and 1.25 days, respectively when applied @ 9.25 and 18.50 g.a.i ha^{-1} (Kar et al. 2012).

Decontamination behaviour

Pesticides leave certain amount of residues, which may prove hazards to the health of the consumers, and most commonly used household process such as washing by tap water, hot water and with brine solution can reduce residue level. The results pertaining to the effect of washing on the removal of CAP applied @ 30 and 60 g a.i. ha^{-1} on samples of chilli fruit are presented in Table 2. All the

culinary processes used in expelling the CAP deposits were found effective expelling the CAP contamination from chilli fruits on initial days which reduces with time as it may leach inside the fruit. Washing with 5% sodium chloride was found most effective irrespective of dose showed maximum 62.02 and 67.94% reduction on 0 day, followed by washing with hot water and simple tap water. Hot water treatment showed 59. 40–58.54% and simple tap water indicated 53.79–50.80% reduction in residues from initial on 0 day. Culinary processes were effective only up to 5th day after that result was below quantification level. Results obtained in this study are in agreement by Kar et al. (2012) where in around 17–40% of CAP residues got reduced from cabbage and cauliflower when treated with tap water and by boiling. Similarly, Vijayasree et al. (2013), tried households solutions, viz. vinegar 2%, turmeric 1%, baking soda 2%, tamarind 2%, slaked lime 2%, and common salt 2% solution, to decline the CAP residues on cowpea fruits and reported of 44.56–91.70% reduction. Sunayana et al. (2015) also reported efficiency of washing i.e. 40–60% in dislodging pesticides in chilli fruit samples.

The quantification of impact of pesticide on human health is very precise procedure as affected by difference in the time frame and level of exposure, type and nature of pesticide with respect to its toxicity level, the geographical and meteorological characteristics of the agriculture area under consideration (Damalas and Eleftherohorinos 2011; Patel et al. 2016). Considering human health due to pesticide toxicity and exposure particularly for food crops and vegetables the residue above maximum residue limit (MRL) directly affect their biological system and also constitute barriers to export and domestic consumption. Thus, risk assessment study conducted was found to be valuable for calculating waiting period which can be suggested to farmers for adoption after application of

Table 2 Effect of washing on reduction of residues of chlorantraniliprole in chilli

Days after treatment	Chlorantraniliprole residues (mg kg^{-1})							
	Single dose (30 g a.i. ha^{-1})				Double dose (60 g a.i. ha^{-1})			
	*Initial AR $\pm$ SD (mg kg^{-1})	Washing with tap water (R%)	Washing with hot water (R%)	Washing with 10% NaCl solution (R%)	*Initial AR $\pm$ SD (mg kg^{-1})	Washing with tap water (R%)	Washing with hot water (R%)	Washing with 10% NaCl solution (R%)
0	3.16 ± 0.026	1.46 (53.79)	1.31 (58.54)	1.20 (62.02)	4.68 ± 0.026	2.30 (50.80)	1.90 (59.40)	1.50 (67.94)
1	2.16 ± 0.026	1.18 (45.37)	0.98 (54.62)	0.90 (58.33)	3.45 ± 0.044	1.90 (44.92)	1.84 (46.66)	1.80 (47.82)
3	1.39 ± 0.010	0.90 (35.25)	0.87 (37.41)	0.80 (42.44)	1.79 ± 0.026	1.10 (38.54)	1.05 (41.34)	0.10 (44.13)
5	0.42 ± 0.046	0.31 (26.19)	0.31 (26.19)	0.30 (28.57)	0.79 ± 0.046	0.60 (24.05)	0.52 (34.17)	0.46 (41.77)
7	0.04 ± 0.026	< LOQ	< LOQ	< LOQ	0.37 ± 0.046	< LOQ	< LOQ	< LOQ

AR average residue, R reduction

*Average of three replicates; $\pm$ SD (standard deviation)

insecticide to reduce contamination in their final product for ensuring safety towards man kind. Therefore, present study suggested that there is no threat to human being if they consume chilli fruit treated with formulation of CAP after 10th and 15th day of application at recommended and double of recommended dose and residue effect are further declined if washed before consumption.

Conclusion

The dissipation of chemical residues on crops depends on condition, sort of application, plant species, doses and stage of crop at the time of application. A maximum residue level (MRL) is the highest level of a pesticide residue that is legally tolerated in or on food or feed established by Food Safety and Standards Authority of India (FSSAI) and European commission in India and Europe and for CAP it is 0.03 and 0.02 mg kg⁻¹ respectively. Chlorantraniliprole showed good linearity and acceptable recovery in the method validation protocol. The limit of quantification (LOQ) determined in presented work is 0.01 mg kg⁻¹ which is lower than the MRL. It can thus be concluded if spray of the insecticide is to be made on fruit setting stage of chilli, the residue reaches below MRL at 10th and 20th day at recommended (30 g a.i. ha⁻¹) and double of recommended (60 g a.i. ha⁻¹) doses. Therefore, a safe waiting period of 10 and 20 days is suggested to reduce the risk before consumption of chilli fruit samples after following Good Agricultural Practices (GAP) for ensuring full safety of consumers. Since the developed method is simple, sensitive, selective and repeatable it can be extended for CAP based standardization of various formulations in pesticide industries. Sterilization with simple and financially savvy family practices like washing further diminishes the danger of deposits and hence advisable to pursue these techniques before use and utilization.

Acknowledgements The authors are thankful to CCS Haryana Agricultural University, Hisar and Indian Council of Agricultural Research (ICAR), New Delhi, for providing necessary facilities during the study.

References

- Ahlawat S, Rani S, Chauhan R (2017) Study of organophosphates residue in vegetables using gas chromatography–tandem mass spectrometry. *J Entomol Zool Stud* 5:1954–1959
- Anastassiades M, Lehotay SJ, Stagnbahr D, Schenck FJ (2003) Fast and easy multiresidue method employing acetonitrile extraction/partitioning and “dispersive solid-phase extraction” for the determination of pesticide residues in produce. *J AOAC Int* 86:412–431
- Damalas CA, Eleftherohorinos IG (2011) Pesticide exposure, safety issues and risk assessment indicators. *Int J Environ Res Public Health* 8:1402–1419
- EPA (2008) Pesticide fact sheet. <http://www.epa.gov/opprd001/factsheets/chloran.pdf>. Registered 2008 April
- Fadwa AT, Yang C, Jack C (2014) Reduction of pesticide residues in tomatoes and other product. *J Food Prot.* <https://doi.org/10.4315/0362-028x.jfp-12-240>
- Gupta S, Gajbhiye VT, Sharma RK, Gupta RK (2010) Dissipation of cypermethrin, chlorpyrifos and profenofos in tomato fruits and soil following application of pre-mix formulations. *Environ Monit Assess* 174:337–345
- Kar A, Mandal K, Singh BC (2012) Decontamination of CAP residues on cabbage and cauliflower through household processing methods. *Bull Environ Contam Toxicol* 88:501–506
- Kumar P, Ahlawat S, Chauhan R, Kumar A, Singh R, Kumar A (2018) In vitro and field efficacy of fungicides against sheath blight of rice and post-harvest fungicide residue in soil, husk, and brown rice using gas chromatography–tandem mass spectrometry. *Environ Monit Assess* 190:503
- Malhat FM (2012) Determination of chlorantraniliprole residues in grape by high-performance liquid chromatography. *Food Anal Methods* 5:1492–1496
- Malhat FM, Abdallah H, Hegazy I (2012) Dissipation of chlorantraniliprole in tomato fruits and soil. *Bull Environ Contam Toxicol* 88:349–351
- Patel BV, Chawala S, Gor H, Upadhyay P, Parmer KD, Patel AR, Shah PG (2016) Residue decline and risk assessment of flucypram + tebuconazole (400 SC) in/on onion (*Allium cepa*). *Environ Sci Pollut Res* 23:20871–20881
- Reddy MRS, Reddy GS (1999) An eco-friendly method to combat *Helicoverpa armigera* (Hub.). *Insect Environ* 4:143–144
- Reddy KN, Satyanarayana S, Reddy KD (2007) Persistence of some insecticides in chillies. *Pesticide Res J* 19:234–236
- Sunayana S, Sushil A, Kumari B (2015) Persistence of fipronil and effect of processing on fipronil plus its metabolite’s residues in Chilli (*Capsicum annum* linn). *Pestic Res J* 27:88–95
- Vijayasree V, Bai H, Beevi SN, Mathew TB, Kumar V, George T, Xavier G (2013) Persistence and effects of processing on reduction of chlorantraniliprole residues on Cowpea fruits. *Bull Environ Contam Toxicol* 90:494–498

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