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Residual persistence of pesticides on brinjal in different growing seasons

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Abstract
A study was conducted during two *kharif* and two *rabi* 2013-14 and 14-15 in the farm of MARS, Department of Crop Physiology, UAS, Dharwad, Karnataka to evaluate the residues of pesticides and its persistent in brinjal. The samples were also collected from farmers field during survey was conducted to study the farmer perception on residues management in brinjal. The samples collected from farmers field and experimental plots subjected to residue estimation. Four different pesticides (thiodicarb-P1, spinosad-P2, profenophos-P3 and chlorantrinalliprole-P4) were sprayed on four different varieties of brinjal (Malapur local-V1, Kalpataru-V2, Manjula-V3, Manjari-V4) with one nonsprayed control(P0). Experiments laid out in factorial randomized block design with three replication. The pesticides sprayed at recommended dose (thiodicab 75WP@1g^{-1}l,spinosad 45 SC @0.1 ml^{-1}l profenophos50 EC@2ml^{-1}l and chlorantraniliprole 20 SC @ 0.5 ml^{-1}l) which are used to control shoot and borer management suggested by agricultural expert. The developed method (LC-TMS) described above permitted the fast and easy qualitative screening of all pesticides detected. In the survey, samples collected from farmers field were monitored for the level of pesticides residues. Results showed the intensity of pesticides exceeding the approved MRLs among the sample of Dharwad district. The pesticides detected in samples collected from Gadag distict are same as that of Dharwad and Belgavi except one pesticide hexaconozole detected in sample number GB-3. The persistence of thiodicarb, spinosad and clorantraniliprole till 24 hr in brinjal has been reported during both the *Kharifs* and *Rabi* seasons. The persistence of profenophos in brinjal up to 96 hr after spraying has been reported while residue dissipiated completely within 96 hr after spraying found below MRL level fixed by FAO.

Keywords: Pesticides, persistance, thiodicarb, spinasad, profenophos, chlorantraniliprole, maximum recidue limit, recommended dose

1. Introduction

Brinjal (*Solanum melengona*) is one of the most popular and important commercial vegetable crops grown throughout the world. Pesticide residues in food pose both proven and suspected health risk to humans, and they generate much public concern and the Government regulatory action throughout the world. Accurate and precise analytical data of pesticide residues in brinjal would help to fix maximum residue limits of pesticides, their minimum waiting periods in ensuring safe consumption in our daily intake.

Fate refers to the pattern of distribution of an agent, its derivatives or metabolites in an organism, system, compartment or (sub) population of concern as a result of transport, partitioning, transformation or degradation (OECD, 2003) [11]. After pesticides are applied to the crops, they may interact with the plant surfaces, be exposed to the environmental factors such as wind and sun and may be washed off during rainfall. The pesticide may be absorbed by the plant surface (waxy cuticle and root surfaces) and enter the plant transport system (systemic) or stay on the surface of the plant (contact). While still on the surface of the crop, the pesticides can undergo volatilization, photolysis, chemical and microbial degradation. All these processes can reduce the original pesticide concentration but can also introduce some metabolites in the crop.

Volatilization of the pesticide usually occurs immediately after the application in the field which depends on the vapor pressure of the pesticides. Pesticides with high vapor pressure tend to volatilize rapidly into the air, while those with low vapor pressure remain longer on the surface. Volatilization rate also depends on the environmental factors, such as, wind speed and temperature. The faster the wind speed and the higher the temperature, the more the pesticide will evaporate. Photolysis occurs when molecules absorb energy from the sunlight resulting in pesticide degradation. The indirect reaction can also be caused by some other chemicals being broken by the sunlight and their products reacting with pesticides in turn.

Some pesticides may be degraded by microbial metabolism. Micro-organisms can use pesticides as nutrients thereby breaking them into carbon dioxide and other components (Holland and Sinclair, 2004) [4]. Brinjal is most prone to insect and pest especially shoot and fruit borer, it damages the crop from nursery to fruiting. For the management of shoot and fruit borer farmers used lot of pesticides or mixture of pesticide most frequently leads to residue accumulated in fruits. This indiscriminate use of pesticide create toxicity human, animals and plant health. Now a days, it is important to study the Maximum residue limit, below detectable limits and acceptable body intake for different pesticides and its effect on plant growth and development.

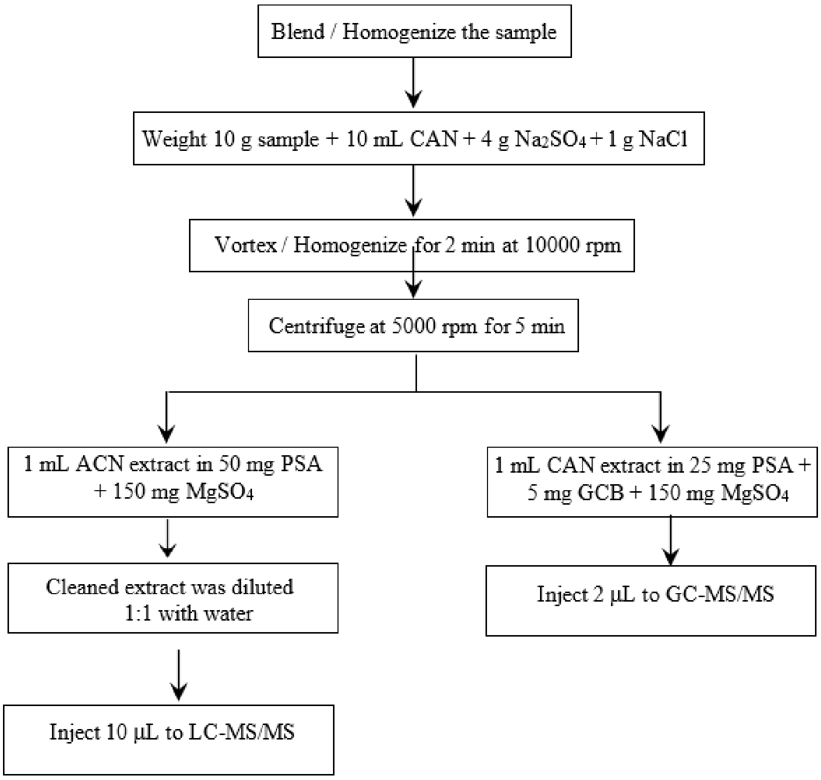
2. Materials and Methods

Standard operating procedure for pesticide residue analysis in Brinjal by LC-MS/MS All pesticide residues analyzed by liquid chromatography and tandem mass spectroscopy and calculated in mg kg^{-1} of fruit weight.

2.1 Sample preparation

The entire laboratory sample was crushed thoroughly in a blender and approximately 10 g of the crushed sample was further homogenized. And extracted with dried magnesium sulphate (4 g) and sodium chloride (1 g) followed by homogenization (2 min at 15000 rpm) and centrifugation at 5000 rpm for 5 min. 1 ml aliquot of supernatant was cleaned by dispersive solid phase extraction with 50 mg PSA and 150 mg MgSO4 and centrifugation at 5000 rpm for 5 min.0.5 ml of supernatant with addition of 0.5 ml of deionised water was passed through 0.2 µm Nylon 66 membrane filter and 10 µl of the extract was injected into LC-MS/MS.

2.2 Method: Standard operating procedure for pesticide residue analysis in Brinjal by LC-MS/MS



2.3 LC-MS/MS analysis

A LC-MS/MS system equipped with API 4000 Qtrap hybrid triple quadrupole/linear ion trap (QqQLIT) mass spectrometer (Applied Biosystem, Foster City, CA, USA), Agilent 1200 series HPLC and analyst (version 1.5) software was used for data acquisition and processing. All experiments were conducted under Turbo Spray (pneumatically assisted electrospray) mode. The chromatographic separation was carried out using an Atlantis dC18 column (100 x 2.1 mm, 5□m) from Waters India Pvt Ltd., Bangalore. The mobile phase composition was (A) Water (100% v) with 5 mM ammonium formate and 0.1 formic acid and (B) methanol (100% v) 5mM ammonium formate and 0.1 formic acid. The column flow rate and temperature was fixed at 0.6 mL min^{-1} and 35°C, respectively. A gradient mobile phase programming of 0-0.5 min/80% A, 0.5-3min/80%-2%A, 3-9min/2% A, 9-10 min/2-80% A and 10-15 min/80% A was used. The source parameters like nebulizer gas (GS1) 40 psi, heater gas (GS2) 60 psi, ion source temperature 550°C and ion spray voltage 4.5KV for negative and 5.5KV for positive polarity were maintained.

3. Results

3.1 Pesticide residues analyzed from farmers field sample during survey

These data indicated that the most commonly detected pesticides in all samples of three districts (Dharwad, Belgavi and Gadag) of Karnataka are chlorantraniliprole, monocrotophos, profenophos, methomyl, myclobutanil, phorate sulfoxide, spinosad, thiodicarb and acetimaprid. The samples contaminated several pesticides from different group whereas, pesticides like monocrotophos, methomyl, myclobutanil, spinosad and phorate sulphoxide reached above MRLs after one week of spraying in all 7 samples analyzed. The other pesticides detected are chlorantriniliprole, profenophos, thiodicarb and acetimaprid reached below

MRLs level.

For the monitoring purpose, out of 20 samples, 7 samples from Belagavi district of Karnataka were collected randomly and selected sample after one week of spraying for analysis. It is clear from table 2, the pesticides detected in samples collected from Belgavi district are same as that of Dharwad district except one pesticide dimethomorph detected in sample number BB-2. The pesticides Myclobutanil, methomyl, phorate sulphoxide, thiodicarb and spinosad reached above MRLs in all samples while, Chlorantraniliprole, profenophos were below MRLs. The brinjal sample collected from farmer's field of Gadag district analyzed and tabulated in table 3 showed contamination of cocktail of pesticides as that of Dharwad and Belgavi samples. Results indicated that all samples (6) from Gadag district farmers field were detected with mixed pesticides except sample number GB-2. The detected pesticides monocrotophos, myclobutanil.

phorate sulphoxide, methomyl were found above MRL while thiodicarb, profenophos and chlorantriniliprole detected were below MRLs.

3.2 Pesticides residue analyzed from experimental plot during different seasons

Study showed that residue of all four pesticides was present in treated samples. It was investigated the persistence and dissipation of pesticide in brinjal where recommended dose applied five times. The persistence of P1, P2 and P4 till 24hr in brinjal has been reported during *kharif*. The persistence of P3 in brinjal up to 96 hr has been reported in which residue dissipated completely within 96 hr. In pesticide treatments, in P1 and P2 residue (0.039 and 0.059 respectively) existed above maximum residue limit fixed in India for thiodicarb and spinosad (0.02 and 0.01 mg kg^{-1}) at 24 hr, further residues P3 (0.102) and P4 (0.148) found below MRL at 24 and 96 hr after spraying.

Pooled data recorded (Table 4) during *kharif* 2013-14 and 14-15 in varieties showed that V3 and V2 (0.112 mg kg^{-1}) found with higher residues and further it reduced in all the varieties until 96 hr. Among interactions V1P1and V1P2; V2P1 and V2P2; V3P1 and V3P2; V4P1 and V4P2 residue reached above maximum residue limit (MRL) at 24 hr after spray. Similarly, the treatment combinations V1P3 and V1P4; V2P3 and V2P4; V3P3 and V3P4; V4P1and V4P4 residues detected below MRLS at 24 hr after spray. At 96 hr after spray, pesticides detected in V1P3, V2P3, V3P3 and V4P4 also found below MRLs.

The data pertaining to influence of both the *rabi* (2013-14 and 14-15) on persistence to of pesticides residues presented in table-5. The persistence study conducted for different pesticides on brinjal varieties that initial residues of P1 (0.029), P2 (0.071) and P3 (0.063) and P4 (0.090) at 24 hours after spraying dissipate to below detectable limit at 96 hr after spraying except profenophos (P3) treatments. The pooled data calculated for residues during different seasons showed that varieties responses to persistence of residues followed different trend in both *kharif* and *rabi*. The maximum residues found in V2 and V3 followed by V4 and least was in V1 during *kharif* while trend was different among varieties as that of *rabi*. The variety V1 (malapur local) indicated found with maximum value of residues at 24 h after spray and it was above the MRLs. Among all interactions between varieties and pesticides, all combinations persists residues at 24 hr after spraying found above MRLs except V1P4, V2P4,V3P1, V4P4,V4P3 and V4P1 treatments.

4. Discussion

4.1 Persistence of pesticides residues in brinjal collected from farmers field samples

The results imply that more pesticides are being used on brinjal grown in studied area during survey. It could be due to conducive climatic conditions for the proliferation factors or this may be due to commercial sources of information that earlier discussed in farmer perception study. The different chromatogram obtained for different samples containing pesticides (plate-1,2 and 3). It is observed that, one sample contaminated 2 to 6 pesticides. With regard to sample investigated from farmer's field, most of the samples contained pesticides residues above MRLs. These residues enter in to the plant body and create stress resulting in interference of residues with physiological and biochemical parameters of plants. Pesticides are used indiscriminately and excessively throughout the globe, and these residues remain in the food material, fruits, vegetable (Baptista *et al.*, 2008 and Lazic *et al.*, 2009) [1, 8]. It is reported that out of twenty samples from farmers field, 12 samples were contaminated with chlorantraniliprole pesticides, all below MRL value after one week of spraying.

The MRL value of some pesticides, especially, monocrotophos, thiodicarb, myclobutanil, methomyl, acetimaprid, spinosad exceeded from MRL value resulting with fruits unfit for human consumption after one week of spray. It could be due to high frequency of application, higher dosage, cocktails of pesticides applied which affects degradation or dissipation pattern of pesticides. In contrast to this study, residue analyzed from sample collected from experimental plot applied with recommended dosage of four different pesticides detected slightly above MRL at 24 hr after spraying and reached below MRL at 96 hr of spraying. The results revealed that in farmers samples persistance of different pesticides were not constant and residue persisted even after one week of spraying and results are not consistent with the residues extracted from experimental plot brinjal sample during all of four seasons. It could be due to high dosage applied by farmers and its frequency. According to Tomkins *et al.* (1999) [16] the half-lives for both spinosyns were not constant with rate, with lower persistence at the lower application rates. The residues from the lower rate treatments (1.2 and 2.4 g/ 100 liters) became non-detectable after 7-14 days. There was an indication that the residues from the higher rate treatments remained after 28 days and were more persistent than in the initial period.

4.2 Influence of growing seasons on the persistence of pesticide residue in brinjal varieties at 24 and 96 hr after the spray

Residues of thiodicarb (P1), spinosad (P2), profenophos (P3) and chlorantraniliprole (P4) were analyzed by liquid chromatography and tandem mass spectroscopy in pesticide residue analysis laboratory at National Research Center for Grapes, Pune, Manjari farm, Maharashtra. All four pesticide residues in brinjal sample which were drawn from experimental plot were analyzed after 24 and 96 hr after fifth spraying are given in table. In this study, it was observed that at 24 hr all four pesticides were detected and later all residue reached below detectable level on 96 hr after spraying except in P3 (profenophos) in both *kharif* and *rabi*. After two weeks, no detectable residues of profenophos were measured on brinjal fruits. Among all, profenophos treatment combinations, V1P3 detected with residues concentrations which was below MRL while V2P3, V3P3 and V4P3 contained residues above MRL. It was also observed that V1 (Malapur local) with lesser amount of pesticides while V4 (Manjiri) contained higher amount of pesticides. It was due to the fact that plant may vary in the level of tolerance to pesticide exposure (Luo *et al.*, 2002). The corresponding half life values of profenophos were 1.74 and 1.96 days respectively. It was also reported that the profenophos residues dissipation ranged from 26.67 to 94 per cent from zero to 6 days respectively and after two weeks residue reached below detectable limits (Radwan *et al.*, 2004) [12]. Gupta, *et al.* (2011) [3] reported that residues of profenophos dissipated with half-life of 2.2-5.4 days, and Sahoo, *et al.* (2004) [14] reported that profenophos spray on tomato at 500 g. a.i. ha^{-1} first at 50% flowering stage and subsequently at 15 days intervals, resulted in initial deposit of 1.37 mg kg^{-1} dissipating to BDL in 15 days, and similar results were also reported by Ahmad, *et al.* (2009) on tomato. Experimental results of Radwan, *et al.* (2004) [12] shows that at application of very high dose *i.e.* 1280 g. a.i. ha^{-1} on three crops *viz.*, green pepper, hot pepper and brinjal results in very high initial deposit of 10-11 mg kg^{-1} on pepper, and 4.50 mg kg^{-1} on brinjal, which dissipated to BDL in 2 weeks. However, the studies conducted by various workers (Gupta *et al.*, 2001, Katroju *et al.*, 2014 and Renuka *et al.*, 2006) [6, 13] on dissipation on profenophos on different crops clearly indicate that when applied at recommended dose, the initial deposits are less than 3 mg kg^{-1} and dissipate to BDL in 7-10 days depending on the crop.

Initial dissipiation in profenophos (P3) is slow in contrast to that observed in thiodicarb (P1), spinosad (P2) and chlorantraniliprole (P4) respectively. Results showed that residues of thiodicarb disappeared rapidly in the first 3 days after spraying while, residues of profenophos were detected even after 3 days after spraying. The results may be attributed to the fact that dissipation is greatly influenced by the agro climatic conditions and plant responses to pesticides (Yadava and Gupta, 1975) [17].

From results obtained, it is revealed that among all four spinosad (P2) sprayed treatment combinations V3P2 contained higher amount of spinosad residues and lesser was detected in V2P2, V3P2 and V4P2 respectively. All four combinations, contained above maximum residue limit at 24 hr after spraying and no residues was detected at 96 hr after spraying. This might be due to accumulation of pesticides in brinjal at 24 hr and later residues of spinosad on brinjal surface dissipated at moderate to rapid rate, primarily due to sunlight photolysis. Results indicated that spinosad residues did not persist after 3 days in brinjal when it sprayed at recommended dose. Saunders and Bret (1997) [15] also observed, dissipation of half lives of 2-16 days for residues on leaf and fruit surfaces, with rate dependent on the amount of sunlight received and degree of shading. Several studies were conducted to investigate the dissipation and fate of spinosad applied to foliage. It was already demonstrated that spinosyn A and D rapidly dissipated from plant surfaces and that photolysis was the predominant mechanism of dissipation. Department of pesticide regulation (1995) revealed that half life of spinosad A on crop like apples; cabbage and turnip was found to be 2.61 to 5.27 days after spraying on leaves and spinosyn D was not detected in case of apples while, half life for cabbage and turnip was 4.64 and 6.31 days after spraying. The proposed photo-degradation or metabolism pathway for spinosyn A and D involves the initial formation of non-polar photoproduct through N-demethylation of rhamnose sugar. With further photo- degradation, polar and non extractable metabolites are found that are subject to biochemical processes and incorporations into natural components of plants (Kollman, 2002) [7].

Results obtained showed that residue levels of profenofos throughout sampling period were higher than thiodicarb (P1), spinosad (P2) and chlorantriniliprol (P4), respectively in brinjal in both the seasons (*kharif* and *rabi*). Considering that differences in weather conditions during 45 days experimental period for brinjal plants were almost different in all four seasons of *kharif* and *rabi*. Sampling during 1st and 4 th days after spraying, exposed to different climatic conditions of *kharif* 2013-14 (max temp 31.0 to
27.7 0 C; max relative humidity 96 to 85% ; wind speed 4 to 6 and rainfall at 1 st day
after spray in last 24 hr was 17.6 mm) and *kharif* 2014-15 (max temp 31.0 to 31.5 ^{0}C; max relative humidity 88 to 83%; wind speed 4 to 7 and rainfall at 4 th day after spray in last 24 hr was 0.6 mm) respectively. The experiments were conducted in two different *rabi* season also exposed to different climatic conditions of 2013-14 (max temp 31.5 to 31.0 ^{0} C; max relative humidity 83 to 77%; wind speed 3 to 5 and rainfall at 4 th day after spray in last 24 hr was 0.6 mm) and 2014-15 (max temp 25 to 27.7 ^{0} C; max relative humidity 80 to 98% ; wind speed 2 to 6 and no rainfall at 4 th day after spray in last 24 hr). Maghalhes *et al.* (1989) [9] revealed that different crops respond differently to the same pesticides at the same rate of applications. The difference in level of cypermethrin residues may also be attributed to higher temperature during tomato and okra trials as compared to lower temperature during the cauliflower trials. Brinjal is sunloving vegetable plant require warm to hot conditions over five to six month of growing period will retard plant growth and reduce yields.

The MRL specified for thiodiocarb by Environmental plant protection agency (EPA) (USA) is 0.1 ppm. Initial residues of thiodiocarb dissipated to its half life within a period of 1 to 1.2 days. The MRL of 0.1 ppm was reached in 4.21 to 7.85 days with an average of 5.96 days after application. But in present study P1 found below detected limit at 4 th after spraying may be because of less exposure, rain fastness and non systemic nature. Karabhantanal *et al.* (2006) [5] stated that thiodiocarb dissipation pattern also depends on the environmental condition. His study indicated a highly negative significant relation between maximum temperature and loss of residue from the tomato fruits during two *kharif* seasons 2001 and 2002 seasons, respectively. Morning RH in 2001, afternoon in 2002 and pooled data had a positive significant correlation. On the contrary, a negative non significant correlation was observed during 2001 with respect to evening RH. Results obtained in present study are in accordance with Murthy *et al.* (1982) [10] who noticed that rapid dissipation of malathion, endosulfan, phosolone and carbaryl from cauliflower could be possible under high temperature, low RH and bright sun light.

5. Conclusion

- It can be concluded that, in comparison study between farmer sample and experimental plot sample during different seasons, number of pesticides detected in farmer samples above MRL even after week of spraying while in contrast to that experimental sample all below detectable limit at 4 days after spaying. Therefore, from the present study it can be suggested to farmers to use recommended dose of pesticides to reduce residues from brinjal fruits at some extent.

- Brinjal production is substantially reduced by infestations of various insect pests and specially shoot and fruit borer from seedling stages to harvest. The pest infestation causes 35-45 per cent losses to the marketable yield and sometimes losses are as high as 60-70 per cent. Therefore, from this study we can be suggested to the farmers that the pesticides used in study can control the fruit and shoot borer effectively at recommended dosage especially profenophos, chlorantriniliprole and spinosad respectively, because dosage used by farmers found injudicious and indiscriminate application of pesticides to crops it results in residues accumulation in brinjal with consequential hazard to consumers.
- The residues of all four pesticides found all below MRL at 4 days after spraying can be minimized considerably or eliminated if these residues are kept below their prescribed safe level (*i.e.*, MRLs). The profenophos residues were found to have half lives 1-4 days and 1-3 days for thiodicarb, spinosad and chlorantraniliprole. In present study, among all pesticides profenophos persisted after 4 th day of spraying but nondetectable amounts while, chlorantriniliprole, spinosad, thiodicarb persisted about 3 rd day of the spraying and not dectable after three days of spraying.
- Withholding periods (defined as number of days required to elapse between the pesticide application and harvest) were calculated. Based on dissipation pattern of residues from different pesticides in relation to their prescribed maximum residue limits, withholding periods of 3 to 4 days for thiodicarb, spinosad and chlorantraniliprole while, 4 to 6 days for profenophos with respect to different varieties of brinjal. Out of all samples analyzed, all samples were contaminated with different pesticides treated. Of these, all below maximum residues limit after 4 days of spraying. The samples could not pose health hazard to the consumers. The picking of brinjal fruits without taking into account their withholding period may lead to residues higher than the tolerance limits. This is mainly attributed to illiteracy of the farmers and lack of effect of legislation in the country. Majority of brinjal growers (*i.e.* more than 80 per cent) consult pesticide dealer for recommendation of pesticides.
- The recommended dose (fixed by agriculture expert) used in all four experiments resulted minimum residues as compared to farmers dosage used for brinjal. Also it was found safe after 3 to 4 days of spraying in experimental plot but in farmer field collected samples it was detected after 8 days of spraying. In view of an increasing trends in pesticides used in India, continuous monitoring for pesticides residues is needed in brinjal in order to protect from health hazard involved in misuse of pesticides and to generate base line data upon which future plans could be developed.
- Based on the residual dissipation of the selected pesticides studied in field experiments on brinjal, it can be recommended to farmers that following withhold period or pre-harvest interval (PHI), after the pesticides application as the safe period for picking the respective fruits of different brinjal varieties.
- Spinosad had very high activity after profenophos and chlorantraniliprole against fruit borer and activity on the treated fruits persisted for 3 days, at 4 days after application the residues found below detected limits. There was a strong relationship between the biological activity of treated fruits and level of residues persisted in the fruit material which enables further studies on different dosages and its persistence related with metabolism of plant relationships for this promising new pesticides.

Table 1: Residues of different pesticides estimated from brinjal collected during survey from farmer's field (mg kg^{-1}) after a week of spraying

Sl. No.	Location	Compound detected	Quantity mg kg^{-1}
Sample number DB1	Dharwad	Chlorantraniliprole	0.048
		Methomyl	0.051
		Myclobutanil	0.042
		Monochrotophos	0.025
		Phorate sulphoxide	0.012
		Profenophos	0.159
		Thiodicarb	0.136
Sample number DB2		Chlorantraniliprole	0.074
		Monocrotophos	0.078
		Phorate sulfoxide	0.093
		Myclobutanil	0.036
		Spinosad	0.114
Sample number DB3		Chlorantraniliprole	0.012
		Myclobutanil	0.066
		Monocrotophos	0.036
		Phorate sulfoxide	0.010
		Thiodicarb	0.016
Sample number DB4		Chlorantraniliprole	0.737
		Myclobutanil	0.036
		Monocrotophos	0.063
		Phorate sulfoxide	0.010
		Profenophos	0.022
Sample number DB5		Chlorantraniliprole	0.015
		Methomyl	0.137
		Phorate sulfoxide	0.029
		Myclobutanil	0.048

		Profenophos	0.165
		Thiodicarb	0.146
Sample number		Acetimaprid	0.013
DB6		Myclobutanl	0.039
		Profenophos	0.014
		Spinosad	0.107
Sample number DB7		Acetimaprid	0.013
		Myclobutanl	0.039
		Profenophos	0.026
		Spinosad	0.009

DB – Sample collected from Dharwad location

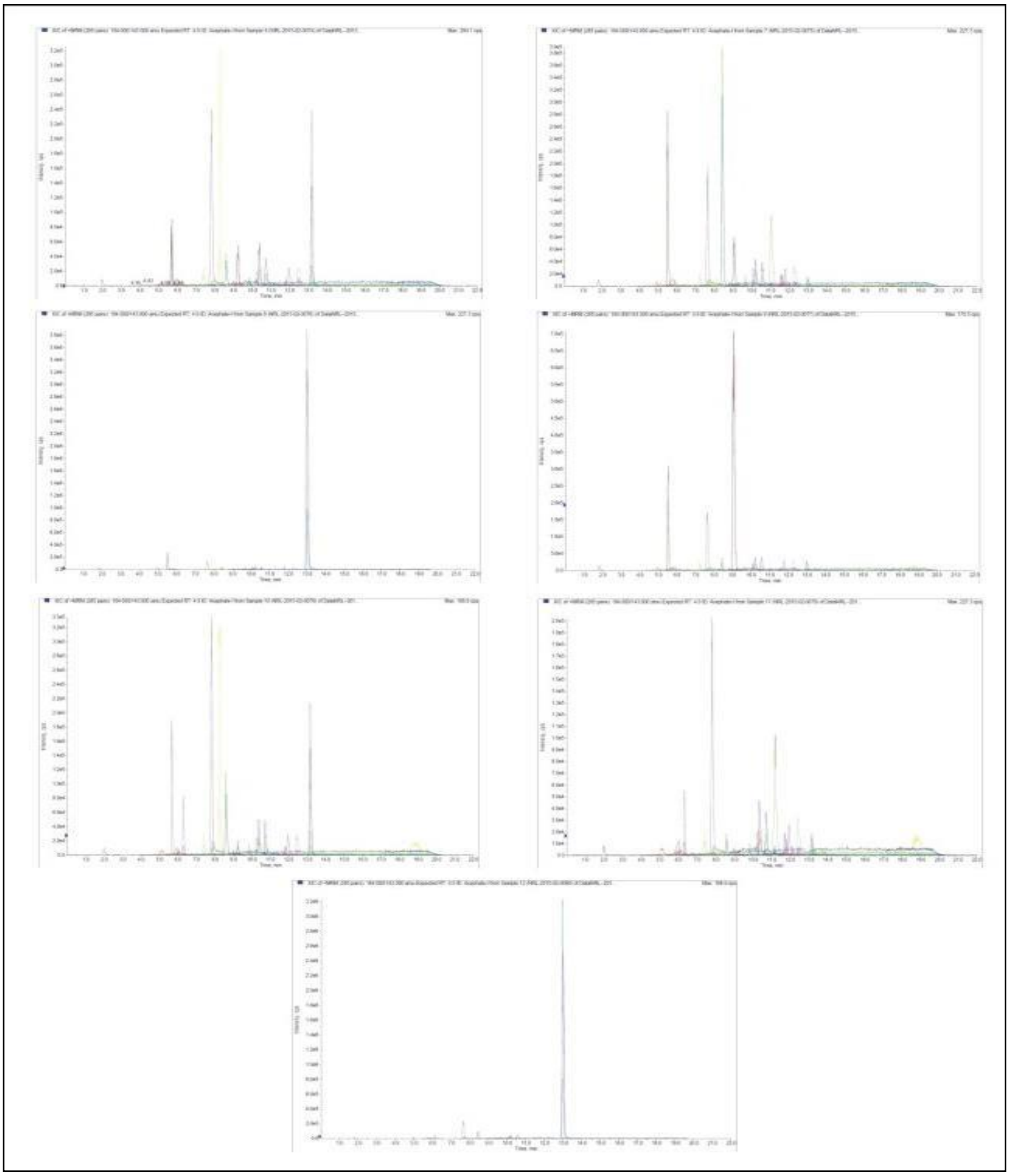


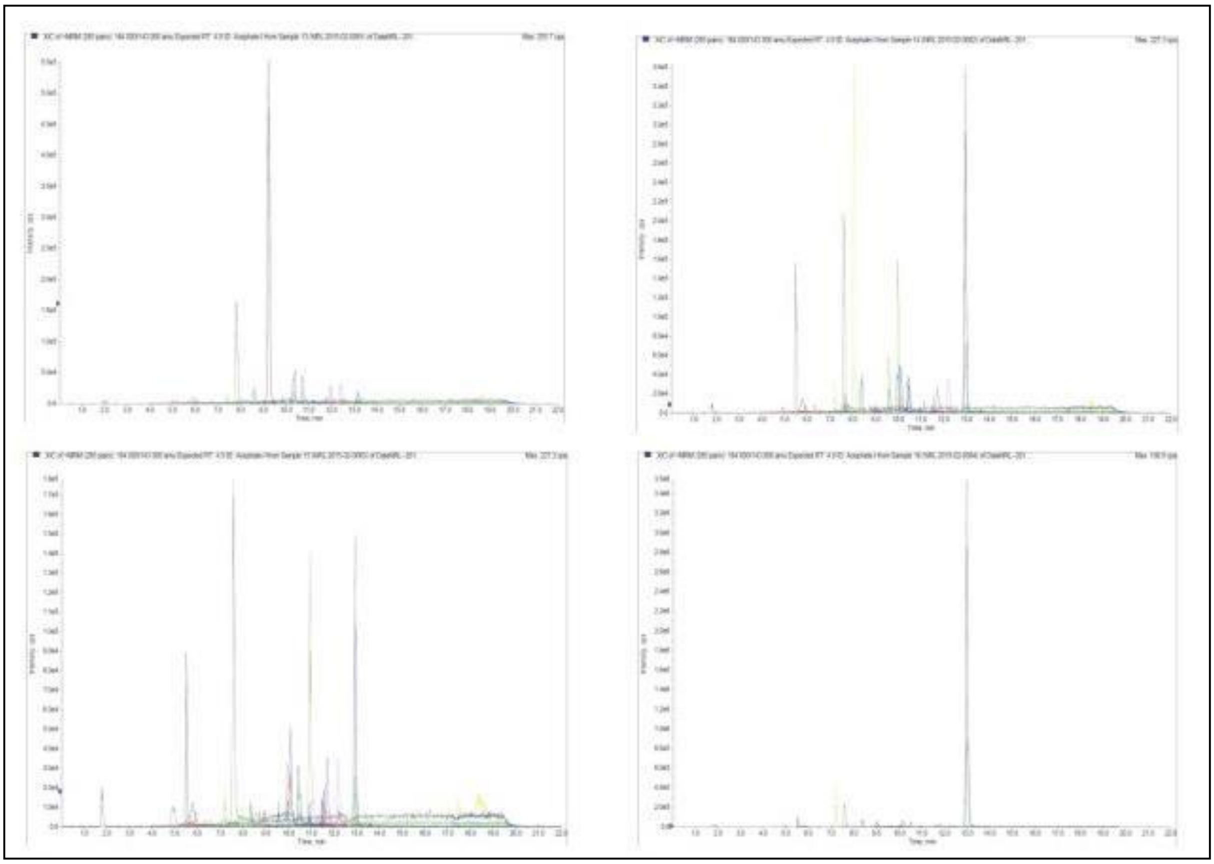
Plate 1: Chromatogram of pesticides detected in sample number DB1 to DB7

Table 2: Residue of different pesticides estimated from brinjal collected during survey from farmer's field (mg kg^{-1}) after a week of spraying

Sl. No.	Location	Compound detected	Quantity mg kg^{-1}
Sample number BB1	Belagavi	Chlorantraniliprole	0.481
		Myclobutanil	0.044
		Profenophos	0.017

Sample number BB2		Dimethomorph	0.038
		Myclobutanil	0.040
		Thiodicarb	0.145
		Profenophos	0.297
Sample number BB3		Monocrotophos	0.022
		Myclobutanil	0.042
		Profenophos	0.117
		Spinosad	0.103
Sample number BB4		Chlorantraniliprole	0.055
		Methomyl	0.010
		Monocrotophos	0.023
		Myclobutanil	0.045
		Phorate sulfoxide	0.020
		Thiodicarb	0.023
Sample number BB5		Chlorantraniliprole	0.505
		Monocrotophos	0.086
		Myclobutanil	0.037
		Thiodicarb	0.033
		Profenophos	0.018
Sample number BB6		Chlorantraniliprole	0.020
		Methomyl	0.046
		Phorate sulfoxide	0.089
		Myclobutanil	0.035
		Profenophos	0.089
		Thiodicarb	0.090
Sample number BB7		Chlorantraniliprole	0.015
		Myclobutanl	0.050
		Phorate sulfoxide	0.011
		Spinosad	0.121
		Profenophos	0.014

BB - brinjal samples collected from Belagavi district



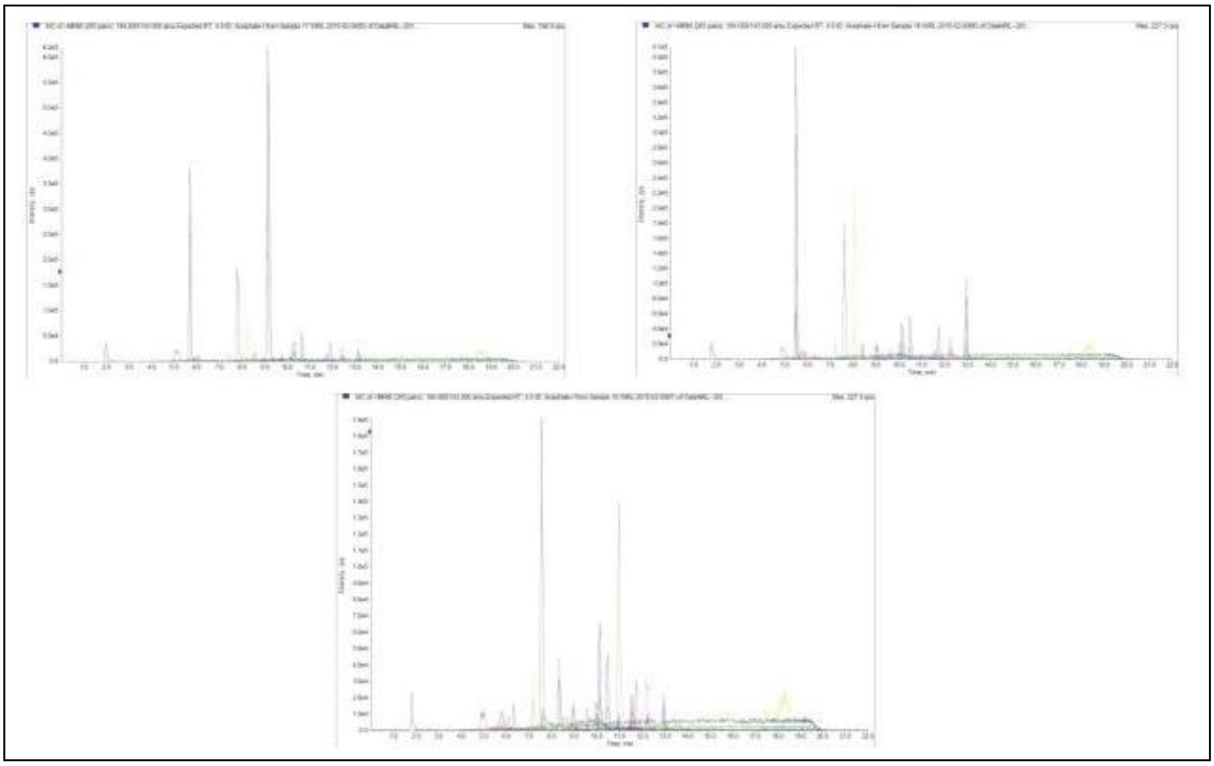
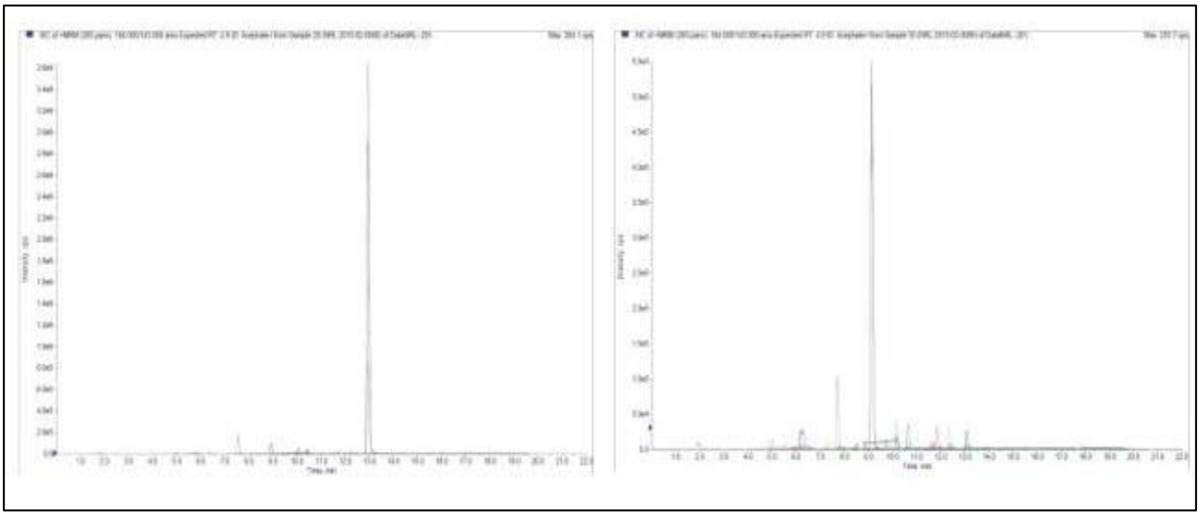


Plate 2: Chromatogram of pesticides detected in sample number BB1 to BB7

Table 3: Residues of different pesticides estimated from brinjal collected during survey from farmer's field (mg kg^{-1}) after a week of spraying

Sl. No.	Location	Compound detected	Quantity mg kg^{-1}
Sample number GB1	Gadag	Chlorantraniliprole	0.481
		Myclobutanil	0.044
Sample number GB2		Chlorantraniliprole	0.052
Sample number GB3		Profenophos	0.031
		Myclobutanil	0.028
		Methomyl	0.125
		Hexaconazole	0.297
Sample number GB4		Chlorantraniliprole	0.017
		Methomyl	0.010
		Myclobutanil	0.034
		Monocrotophos	0.064
		Thiodicarb	0.010
Sample number GB5		Profenophos	0.100
		Chlorantraniliprole	0.782
		Myclobutanil	0.031
		Phorate sulfoxide	0.015

GB - brinjal samples collected from Gadag district



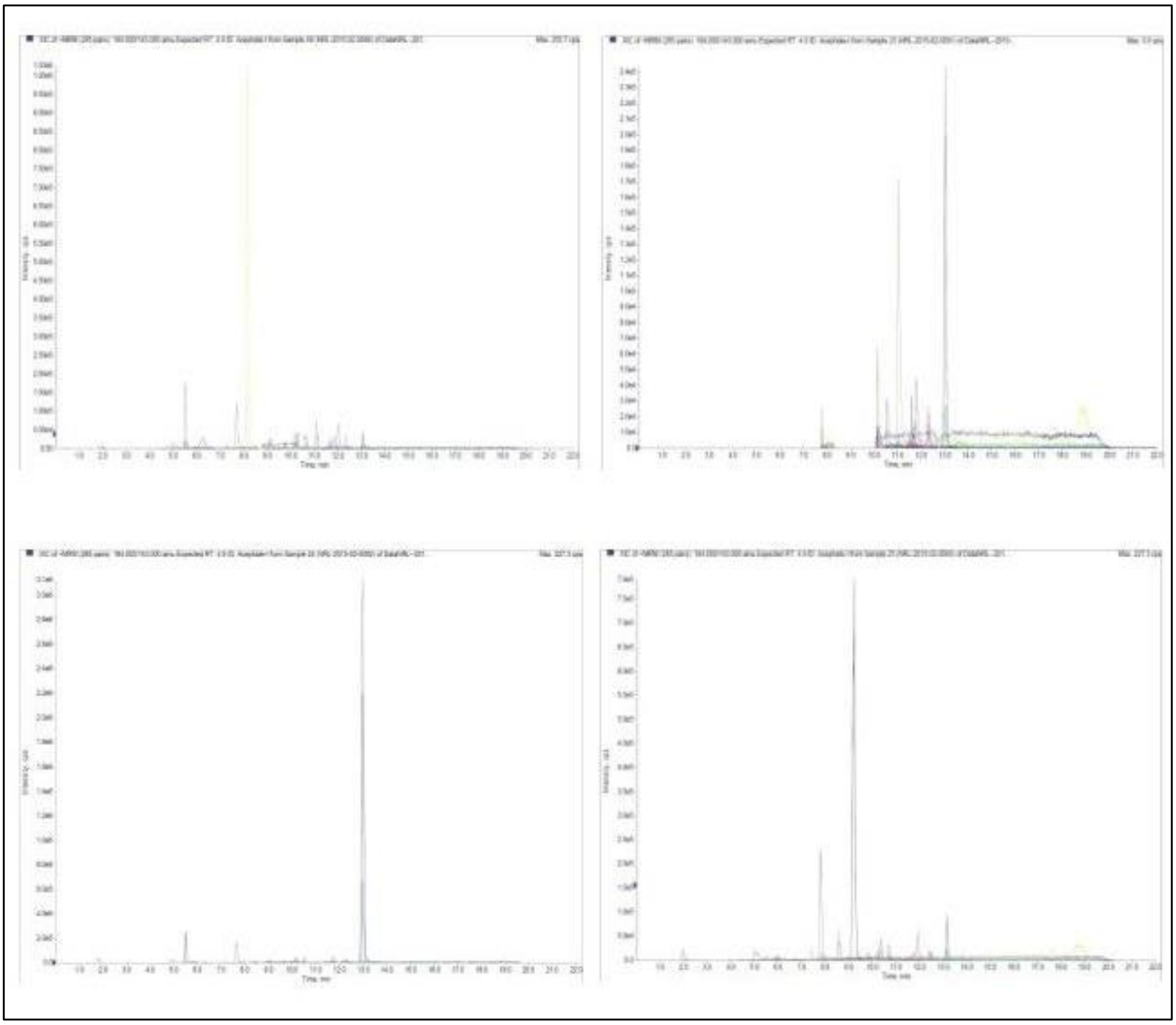


Plate 3: Chromatogram of pesticides detected in sample number GB1 to GB7

Table 4: Influence of growing seasons on the persistence of pesticide residues (mg kg^{-1}) in brinjal varieties at 24 and 96 hr after the spray

Treatments	*kharif* 2013-14		*kharif* 14-15		Pooled data	
	24 hr	96 hr	24 hr	96 hr	24 hr	96 hr
Varieties(V)						
V1	0.020	0.002	0.044	0.001	0.031	0.001
V2	0.008	0.003	0.222	0.002	0.112	0.003
V3	0.162	0.002	0.069	0.002	0.112	0.002
V4	0.062	0.004	0.128	0.003	0.093	0.003
Mean	0.063	0.003	0.116	0.002	0.087	0.002
S.Em±	0.001	0.001	0.003	0.002	0.001	0.001
LSD @ 5%	0.003	0.002	0.008	NS	0.004	0.001
Pesticides						
P0	ND	ND	ND	ND	ND	ND
P1	0.018	ND	0.061	ND	0.039	ND
P2	0.045	ND	0.073	ND	0.059	ND
P3	0.049	0.010	0.173	0.008	0.102	0.009
P4	0.140	ND	0.157	ND	0.148	ND
Mean	0.063	0.010	0.116	0.008	0.087	0.009
S.Em±	0.001	0.000	0.002	0.000	0.001	0.000
LSD @ 5%	0.003	0.000	0.007	0.001	0.003	0.000
Interactions(V×P)						
V1P0	ND	ND	ND	ND	ND	ND
V1P1	0.026	ND	0.093	ND	0.061	ND
V1P2	0.009	ND	0.125	ND	0.065	ND
V1P3	0.042	0.010	0.059	0.009	0.047	0.008
V1P4	0.056	ND	0.016	ND	0.037	ND
V2P0	ND	ND	ND	ND	ND	ND
V2P1	0.011	ND	0.070	ND	0.039	ND
V2P2	0.006	ND	0.108	ND	0.057	ND

V2P3	0.015	0.017	0.857	0.013	0.429	0.017
V2P4	0.019	ND	0.447	ND	0.223	ND
V3P0	ND	ND	ND	ND	ND	ND
V3P1	0.035	ND	0.147	ND	0.092	ND
V3P2	0.127	ND	0.144	ND	0.137	ND
V3P3	0.165	0.016	0.113	0.012	0.115	0.013
V3P4	0.754	ND	0.056	ND	0.405	ND
V4P0	ND	ND	ND	ND	ND	ND
V4P1	0.045	ND	0.094	ND	0.071	ND
V4P2	0.156	ND	0.108	ND	0.133	ND
V4P3	0.107	0.024	0.126	0.019	0.090	0.022
V4P4	0.105	ND	0.528	ND	0.323	ND
Mean	0.084	0.003	0.154	0.003	0.116	0.003
S.Em±	0.010	0.001	0.025	0.002	0.012	0.001
LSD @ 5%	0.028	0.003	0.071	NS	0.035	0.003

Pesticides were detected only at 24 and 96 hr after the spray. No further detection was seen
NS – Non-significant ND-Not detected
V1 – Malapur local P0 – Control (water sprayed)
V2 – Kalpataru P1 – Thiodicarb 75 WP @ 1g/L
V3 – Manjula P2 - Spinosad 45 SC @ 0.1 ml/L
V4 – Manjari P3 - Profenophos 50 EC @ 2 ml/L
P4 – Chlorantraniliprole 20 SC @ 0.5 ml/l

Table 5: Influence of growing seasons on the persistence of pesticide residues (mg kg^{-1}) in brinjal varieties at 24 and 96 hr after the spray

Treatments	***rabi* 2013-14**		***rabi* 2014-15**		**Pooled data**	
	24 hr	**96 hr**	**24 hr**	**96 hr**	**24 hr**	**96 hr**
Varieties(V)						
V1	0.121	0.001	0.101	0.001	0.108	0.002
V2	0.025	0.002	0.068	0.002	0.046	0.002
V3	0.046	0.002	0.041	0.002	0.044	0.002
V4	0.061	**0.003**	0.066	**0.003**	0.067	**0.004**
Mean	0.063	0.002	0.069	0.002	0.066	0.003
S.Em±	0.001	0.000	0.007	0.002	0.003	0.001
LSD @ 5%	0.002	NS	NS	NS	0.009	0.001
Pesticides						
P0	ND	ND	ND	ND	ND	ND
P1	0.029	ND	0.030	ND	0.029	ND
P2	0.071	ND	0.052	ND	0.061	ND
P3	0.063	0.008	0.093	0.008	0.081	0.010
P4	0.090	ND	0.102	ND	0.094	ND
Mean	0.063	0.008	0.069	0.008	0.066	0.010
S.Em±	0.001	0.000	0.006	0.000	0.003	0.000
LSD @ 5%	0.002	0.001	0.017	0.001	0.008	0.000
Interactions(V×P)						
V1P0	ND	ND	ND	ND	ND	ND
V1P1	0.134	ND	0.134	ND	0.136	ND
V1P2	0.115	ND	0.115	ND	0.113	ND
V1P3	0.083	0.007	0.106	0.008	0.091	0.010
V1P4	0.473	ND	0.321	ND	0.381	ND
V2P0	ND	ND	ND	ND	ND	ND
V2P1	0.034	ND	0.028	ND	0.029	ND
V2P2	0.103	ND	0.103	ND	0.103	ND
V2P3	0.012	0.015	0.282	0.015	0.145	0.016
V2P4	0.020	ND	0.038	ND	0.030	ND
V3P0	ND	ND	ND	ND	ND	ND
V3P1	0.014	ND	0.016	ND	0.016	ND
V3P2	0.117	ND	0.080	ND	0.096	ND
V3P3	0.160	0.013	0.162	0.014	0.162	0.015
V3P4	0.017	ND	0.016	ND	0.017	ND
V4P0	ND	ND	ND	ND	ND	ND
V4P1	0.011	ND	0.019	ND	0.015	ND
V4P2	0.141	ND	0.051	ND	0.096	ND
V4P3	0.164	0.020	0.066	0.018	0.141	0.025
V4P4	0.090	ND	0.305	ND	0.197	ND
Mean	0.084	0.003	0.092	0.003	0.088	0.003
S.Em±	0.008	0.002	0.062	0.002	0.029	0.001
LSD @ 5%	0.022	NS	0.176	NS	0.083	0.003

Pesticides were detected only at 24 and 96 hr after the spray. No further detection was seen NS – Non-significant

ND-Not detected
V1 – Malapur local P0 – Control (water sprayed)
V2 – Kalpataru P1 – Thiodicarb 75 WP @ 1g/L
V3 – Manjula P2 - Spinosad 45 SC @ 0.1 ml/L
V4 – Manjari P3 - Profenophos 50 EC @ 2 ml/L
P4 – Chlorantraniliprole 20 SC @ 0.5 ml/L

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