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Residual Behavior and Risk Assessment of Spiromesifen (Oberon 240 SC) on Eggplant (*Solanum melonongena* L) in India: A Multilocational Study

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Spiromesifen (BSN 2060, trade name: Oberon®) [3-(2,4,6-Trimethylphenyl)-4-(3,3-dimethylbutyl-carbonyloxy)-5-spirocyclo-pentyl-3-dihydrofuranon-2] is a novel insecticide/acaricide belonging to the new chemical class of spirocyclic phenyl-substituted tetronic acids, recently introduced by Bayer CropSciences (Fig. 1). Spiromesifen is non-systemic in nature and particularly active against mites and whiteflies (Nauen et al. 2001; Nauen et al. 2002). Spiromesifen has new mode of action that leads to the inhibition of the fat synthesis in the target pest. It acts as lipid biosynthesis inhibitor like its cousin Spirodiclofen, but it has not been confirmed yet (Dekeyser, 2005; Anonymous, 2002).

Spiromesifen is basically active against juvenile stages of whiteflies and mites. However, it also strongly affects fecundity of mite and whitefly adults in a rate-dependent manner by transovariole effects. It shows excellent ovicidal effects in mites, whereas egg hatch in whiteflies was markedly reduced through transovariole effects upon pre-exposure of female adults. Spiromesifen controls white flies (*Bemisia* and *Trialeuroides* spp.) and numerous mite species, including spider mites (*Tetranychus* and *Panonychus* spp.), tersonemid mites and rust mites (Bretschneider et al. 2003).

Review of literature revealed that spiromesifen is a second compound belonging to the tetronic acid group. As spiromesifen is a new molecule and its relevant data are scanty in the literature, this paper is an attempt toward the generation of residues data and to evaluate the risk assessment on eggplant (*Solanum melonongena* L) at different locations in India.

MATERIALS AND METHODS

Supervised field trials on eggplant were conducted at four different locations in Randomized Block Design (RBD). The experiments were carried out in triplicates for eggplant and a control plot was kept aside for each set in which no insecticide was sprayed. All the field trials were carried out using Good Agricultural Practices (GAP). The eggplants were grown in the agricultural fields of Dr.Y.S.Parmar University of Horticulture & Forestry, Solan; Punjab Agricultural University, Rajasthan Agricultural University, Jaipur and Indian Agricultural

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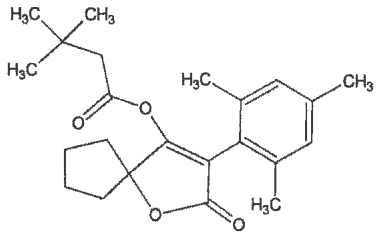

Figure 1. Spiromesifen

Research Institute, New Delhi during the year 2003. The plot size for eggplant was 24 m^2 in Solan and Ludhiana while 25 m^2 in Jaipur and New Delhi. The foliar application of spiromesifen (Oberon 240 SC, obtained from Bayer Crop Science Limited, New Delhi, India) was sprayed on eggplants at the rate of 96 and 192 g ai ha^{-1} (500 L ha^{-1}) at 50% fruiting stage using knapsack sprayer.

Eggplant fruit samples were taken from each plot from all the four locations on day 0 (1h after spray), 1, 3, 5, 7, 10 and 15 days. Soil samples were collected on 15^{th} days after spraying from eggplant field. The important weather parameters during the trial on eggplant are presented in Table 1.

Table 1. Weather conditions during spraying period on eggplant.

Climatic condition	Solan	Ludhiana	Jaipur	New Delhi
Av Min temp (^{0}C)	20.0	25.0	6.0	18.6
Av Max temp (^{0}C)	28.0	35.0	17.0	30.2
Relative humidity (%)	85.0	70.0	80.0	70.0
Rainfall (mm)	Nil	Nil	Nil	Nil
Month of application	June, 2003	Oct, 2003	Dec, 2003	Nov, 2003

Eggplant fruit samples (1 kg) were crushed in a high speed blender and a homogenate of sub-sample equivalent to 25 g was mixed with 80 ml of distilled water in a beaker. Water homogenate mixture was filtered and filtrate was transferred to a separating funnel containing 20 ml NaCl (10 %) solution. The residues left was re-extracted twice with 100 ml of acetone and was transferred to separating funnel containing the filtrate. The aqueous phase was extracted twice with 100 ml mixture of cyclohexane: ethylacetate (1:1, v/v) followed by 75 ml mixture of cyclohexane: ethyl acetate (1:1, v/v). The organic phases were pooled together and passed through the activated anhydrous sodium sulfate for the removal of water traces. The volume of filtrate was reduced under rotary vacuum evaporator up to 5 ml. Again concentrated extract was extracted thrice with 5 ml of ethyl acetate and upper layer was discarded. Collected the extract and dried over anhydrous sodium sulfate, concentrated under rotary vacuum evaporator up to 5 ml and further subjected to column chromatography for removal of co-extractives and impurities. Soil was dried, grounded and sieved through 100 mm mesh. A sub sample of 25 g soil sample was homogenized and extracted as per procedure described for eggplant fruit. The residues in ethyl acetate were then subjected to column cleanup. The column was filled with acetone and then packed

with Florisil (10g) sandwiched between two layers of anhydrous sodium sulfate (2g). The excess acetone was eluted and then concentrate was transferred into the column. The column eluted with 100 ml acetone and the elute was dried over activated anhydrous sodium sulfate. The dried organic layer was concentrated to dryness in a. rotary vacuum evaporator and reconstituted in 5 ml with acetone (HPLC grade solvent) for GC-MS analysis. The concentration of spiromesifen was measured by Thermo Finnigan (Trace) GC coupled with mass detector (Fisons MD-800, quaderpole mass detector) equipped with capillary column (J&W, DB-17, 30m x 0.32mm ID x 0.25μm). Helium was used as a carrier gas with flow rate of 1 ml min^{-1}. The injector temperature was maintained at 260^0C and oven was in temperature programming from 175 (1 min hold) to 250^0C at the rate of 20^0C min^{-1}. Injection volume was 1μl in split mode (1:10). Residues were estimated using Selective Ion Monitoring (SIM) mode and the most stable ion of the fragmentation molecules was found to be in the range of 271-274 m/z. The retention time (Rt) of spiromesifen (99.0 % purity, obtained from Bayer Crop Science Limited, New Delhi, India) was 6.95 min. Limit of detection (LOD) and limit of determination (LOQ) were 0.01 and 0.03 mg/kg respectively.

The eggplant fruit and soil samples were spiked at 1.0, 0.5, 0.1, 0.05 and 0.01 mg/kg levels in triplicate. For the recovery study, samples were extracted and cleaned up as per the method described above.

RESULTS AND DISCUSSION

Fortified eggplant fruit and soil samples were analysed in triplicate and average results showed good reproducibility and accuracy of the method. The average per cent recovery of the method in eggplant fruit was 83.00, 88.00, 90.00, 94.00 and 96.00 per cent at fortification level of 0.01, 0.05, 0.1, 0.5, and 1.0 mg/kg, respectively. Likewise the average recovery in case of soil was 85.00, 89.00,

Table 2. Residues of spiromesifen on eggplant fruit on recommended doses (96 g a.i./h) at four locations.

Residues (mg/kg)[a] (% dissipation)				
Days	Solan	Ludhiana	Jaipur	New Delhi
0	0.592	0.692	0.682	0.688
1	0.521 (11.99)	0.488 (29.47)	0.443 (35.04)	0.478 (30.52)
3	0.321 (45.77)	0.312 (54.91)	0.274 (59.82)	0.302 (56.10)
5	0.213 (64.02)	0.190 (72.54)	0.194 (71.55)	0.189 (72.52)
7	0.176 (70.27)	0.144 (79.19)	0.134 (80.35)	0.134 (80.52)
10	0.046 (92.22)	0.038 (94.50)	0.041 (93.98)	0.036 (94.76)
15	ND (100)	ND (100)	ND (100)	ND (100)
15 (Soil)	ND	ND	ND	ND

[a] Mean of triplicate, ND< 0.01 mg/kg

90.00, 93.00, and 95.00 per cent at fortification level of 0.01, 0.05, 0.1, 0.5, and 1.0 mg/kg, respectively. The data of spiromesifen residues detected on eggplant fruit and soil at different intervals at recommended and double the recommended dose are presented in Table 2 and 3. In eggplant fruit initial deposits of spiromesifen was found to be 0.592 and 0.910 mg/kg at Solan; 0.692 and 0.822 mg/kg at Ludhiana; 0.682 and 0.809 mg/kg at Jaipur and 0.688 and 0.842 mg/kg at Delhi at recommended and double the recommended dose, respectively.

Table 3. Residues of spiromesifen on eggplant fruit on double recommended doses (192g ai h^{-1}) at four locations.

Residues (mg/kg)[a] (% dissipation)				
Days	Solan	Ludhiana	Jaipur	New Delhi
0	0.910	0.822	0.809	0.842
1	0.713 (21.65)	0.616 (24.88)	0.626 (22.72)	0.623 (25.83)
3	0.489 (46.26)	0.522 (36.34)	0.474 (41.48)	0.512 (39.04)
5	0.287 (68.46)	0.284 (65.37)	0.274 (66.17)	0.274 (67.38)
7	0.194 (78.68)	0.179 (78.17)	0.187 (76.91)	0.169 (79.88)
10	0.064 (92.97)	0.043 (94.76)	0.051 (93.70)	0.041(95.11)
15	ND (100)	ND (100)	ND (100)	ND (100)
15 (Soil)	ND	ND	ND	ND

[a]Mean of triplicate, ND< 0.01 mg/kg

The regression equation and half-life of spiromesifen on eggplant fruit are presented in Table 4. The half-life of spiromesifen residues was calculated by using the formula given by Hoskins, 1966. Dissipation of spiromesifen on eggplant followed first order kinetics at all the four locations. In the case of eggplant fruit, half-life ranged between 2.52-2.88 days at recommended dose, while correlation coefficient (r) found to be 0.97-0.98.

Table 4. Statistical data on regression analysis and half-life for the dissipation of spiromesifen on eggplant fruit.

Location	Dose	Regression equation (y)	Half life (Days)	(r)
Solan	SD	-0.1044 x +1.822	2.88	0.97
	DD	-0.1114 x +1.991	2.70	0.99
Ludhiana	SD	-0.1173 x +1.848	2.60	0.98
	DD	-0.1213 x +1.986	2.48	0.97
Jaipur	SD	-0.1124 x + 1.811	2.67	0.98
	DD	-0.114 x +1.960	2.64	0.98
New Delhi	SD	-0.1195 x +1.844	2.52	0.98
	DD	-0.1297 x +1.992	2.32	0.97

Human health risk situations are a function of hazard and exposure to that hazard. If the hazard is small and fixed, then the risk will be proportional to the exposure, which can be reduced to low and occasional (Bates, 2002). To evaluate the risk to the consumers for spiromesifen on eggplant fruit in India, the Theoretical Maximum Residues Contribution (TMRC) were calculated and compared with Maximum Permissible Intake (MPI). The prescribed Acceptable Daily Intake

(ADI) of spiromesifen by European Union is 0.022 mg/kg /body weight/ day. European Union (EU) has also fixed 0.2, 0.3, 0.3, 1.0, 1.0 and 0.1mg/kg maximum residue limit (MRL) of spiromesifen on cucumber/courgetee, tomato/eggplant, sweet pepper, bean, strawberry and melon, respectively. Maximum permissible intake (MPI) obtained by multiplying the ADI with the weight of average Indian person (55 kg) (Mukherjee and Gopal, 2000). The MPI was calculated to be 1.21 mg/person/day. Based on spiromesifen residue field trials on eggplant, data reflecting maximum residues that may occur under worst condition on recommended dose (96 g ai ha^{-1}), the TMRC values on 0 day were found to be 0.047, 0.055, 0.054 and 0.055 mg/person/ day from Solan, Ludhiana, Jaipur and New Delhi, respectively. The TMRC has been calculated at considering recommended consumption of vegetable as 80 g in Indian context (Anonymous, 1999). The Theoretical Maximum Residues Contribution (TMRC) were calculated from residue data generated from all four locations were found to be well below than MPI on eggplant fruit. TMRC values were also found to be less than MPI even if double doses are considered. Based on the experimental facts and evaluation, the consumer health risks are minimal at the recommended dose on vegetables in Indian context. Soil samples (0-15 cm), collected from eggplant field (15 day) did not show the presence of spiromesifen residues and therefore no downward movement is expected.

Therefore, application of spiromesifen at the recommended level on eggplant could be taken as safe from the crop protection and environmental contamination point of view.

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