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ORIGINAL ARTICLE

Residue study of imidacloprid in grapes (*Vitis vinifera* L.) and soil

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Abstract

Introduction Grape, an important fruit crop of India, is affected by thrips that is a destructive sucking insect of grapevine. Imidacloprid, a neonicotinoid insecticide, gives very good control of this insect. *Objectives* Study of the residue persistence of imidacloprid on grapes, to estimate its residue deposit, half-life of degradation, safe pre-harvest interval and harvest time residues for consumption of this fruit after its multiple applications. *Methods* Extraction with acetonitrile, partitioning into dichloromethane, clean up with neutral alumina and estimation of residues with high-pressure liquid chromatography, using a UV-VIS detector at wavelength of 270 nm. *Results* Initial residue deposit of imidacloprid on grape berries following treatment of Confidor 200 SL at the recommended and double the recommended dose of 80 and 160 g a.i. ha^{-1} were 0.74 and 1.26 mg kg^{-1}, respectively. Residues remained in the fruits up to 60 days but at a low level of 0.056 and 0.108 mg kg^{-1}. The residues dissipated with the half-life of 16.6 days from both the treatments. *Conclusion* The pre-harvest interval recommended for safe consumption of grape berries is 60 days. Residues of imidacloprid in grape berries and soil at harvest (105 days after the last treatment) were observed to be below detectable limit of 0.05 mg kg^{-1} from both the treatments.

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Introduction

Grape (*Vitis vinifera* L.) is one of the most intensively cultivated commercial fruit crops in sub-tropical regions of India. Among all the fruit crops, grape has emerged as the most successful commercial crop in the recent years. Thrips (*Rhipiphorothrips cruentatis*) is a severe pest of grapes, which causes 50–100% marketable yield loss. It is found in major grape growing regions of India (Grape Profile, http://www.nrcgrapes.nic.in). Thrips are found throughout the year, but in epidemic form during flowering and early berry formation stage. Imidacloprid, 1-(6-chloro-3-pyridyl-methyl)-*N*-nitroimidazolidin-2-ylideneamine, is a highly systemic chloronicotinoid insecticide extensively used for the control of wide range of insects and pests at various stages of grape cultivation (http://nrcgrapes.nic.in/zipfiles/POP-Diseases_InsectPests-Grapes.pdf). It is recommended for use against grape thrips (Sunitha *et al.*, 2008). Besides thrips it is also used as soil drench for control of mealybug, which is a severe vineyard pest of peninsular India as well as other grape growing nations (Fu-Castillo *et al.*, 2004; Daane *et al.*, 2008). In a study by Frank & Nick (2006) on uptake and persistence of imidacloprid in grapevines it was found out that in younger vines uptake of imidacloprid was most rapid at the highest rates of application (281 and 562 g ha^{-1}), reaching target threshold levels within the xylem fluid of 10 µg L^{1} in 2 days while in older vines it was 6–8 days. Despite the initial delay in uptake, once the target threshold was reached, it was maintained throughout the season. This makes imidacloprid an ideal insecticide for both spray and drench applications to vineyards for control of a number of major pests of grape. When applied as seed treatment, translocation of imidacloprid happened within the plant leading to contamination of sunflower pollen (Laurent & Rathahao, 2003). Although imidacloprid is being used against a wide range of insect pests of grapevine no information is available to our knowledge on its persistence on grape berries under Indian climatic conditions. Therefore this experiment was carried out to evaluate behavior of this insecticide on grape berries and soil.

Materials and methods

Analytical grade imidacloprid (purity 98%) and its formulation Confidor 200 SL were obtained from Bayer Crop Science Limited. Standard solution of imidacloprid was prepared with high-pressure liquid chromatography (HPLC) gradient grade acetonitrile and suitably diluted to obtain the working standards. The residue study of imidacloprid 200 SL on grapes was carried out at the experimental farm of Indian Institute of Horticultural Research, Bangalore, India, during the year 2007. The treatments were untreated control, recommended and double the recommended dose of Confidor 200 SL at 80 and 160 g a.i. ha^{-1}. Imidacloprid spray application was given four times starting from 15 days after October pruning to berry setting stage. For every treatment 10 plants were selected. The spray volume taken was 1000 L ha^{-1}. Untreated control plants were sprayed with water.

Analysis of the grape berry samples was carried out after the fourth spray for a period 2 months, i.e. on 0(1 h), 1, 3, 6, 10, 15, 20, 25, 30, 40, 50 and 60 days and at harvest. Soil samples were analyzed at harvest (105 days after the last spray). On every sampling day from each vine a bunch weighing approximately 250 g was collected. A total of 2.5 kg of each sample was collected, pooled together and representative 50 g samples in triplicate were processed for imidacloprid residues. From each plot soil samples were collected from 3 × 3 grid with total 10 sampling sites. At each site two soil plugs of about 15 cm depth and 3–5 cm diameter were collected using a soil augur. The soil samples were mixed thoroughly. A representative 100 g sample in triplicate was processed for imidacloprid residues.

Extraction and clean up of imidacloprid from grape and soil was carried out as per methodology described by Mukherjee and Gopal (2000). A 50 g portion of grape representative sample was homogenized with 100 mL acetonitrile in a Waring blender and filtered under vacuum through a Buchner funnel. The container and the filter cakes were washed twice with 100 mL acetonitrile and the combined extracts were collected in a 500 mL flask. The acetonitrile fraction was concentrated under reduced pressure in a rotary vacuum evaporator. The aqueous extracts were transferred into a 1 L separatory funnel and diluted with 80 mL of distilled water. The aqueous phase was partitioned into 150 mL dichloromethane (50 mL × 3) after adding 25 mL saturated sodium chloride solution and dried over 25 g anhydrous sodium sulfate. The combined dichloromethane portion was concentrated and subjected to column chromatography. The column was packed with 5 g of neutral alumina in between 1 inch layer of anhydrous sodium sulfate. Imidacloprid was eluted with 100 mL of hexane+acetone (1+1, v/v). The eluate was concentrated to dryness and redissolved in 10 mL of gradient HPLC grade acetonitrile for analysis by HPLC. The soil samples were processed in a similar manner.

Analysis of imidacloprid residues was carried out by HPCC Shimadzu (Shimadzu Corporation, Kyoto, Japan), model LC 10A Dual Pump with the UV-VIS detector using the reversed phase C-18, (Purospher Star RP-18, 250-4 mm i.d., 5 μm; Merck, Darmstadt, Germany) column. The mobile phase consisted of acetonitrile:water (40:60, v/v) with the solvent flow rate of 1 mL min^{-1} and the detector was set at a wavelength of 270 nm. The injection volume was 20 μL. With the above parameters the retention time of the imidacloprid was 3.45 min. The residue data were subjected to statistical analysis as per Hoskins (1961) to compute the residual half-life ($t_{1/2}$) and safe pre-harvest interval. The percent recovery study of pesticide at different fortification levels was evaluated in order to assess the extraction efficiency of the method. The recovery study was carried out at the fortification level of 0.05, 0.1, 0.5 and 1.0 mg kg^{-1} in grape and soil.

Results and discussion

The percent recovery of imidacloprid in grape berries and soil is given in Table 1. By following the analytical method

Table 1 Recovery of imidacloprid residues in grape berries and soil at various fortification levels

	Mean recovery (%)* ± SD	
Fortified concentration (mg kg^{-1})	Grape berries	Soil
0.05	89.50 ± 0.018	89.55 ± 0.016
0.10	90.00 ± 0.002	90.44 ± 0.008
0.50	91.12 ± 0.013	91.50 ± 0.009
1.00	91.25 ± 0.005	92.62 ± 0.015

*Average of three replicate analyses ± SD.

described the recovery of imidacloprid residues in grape berries was in the range of 89.5–91.2% and in soil it was 89.5–92.6%. Initial residue deposit of imidacloprid on grapes was found to be 0.74 and 1.26 mg kg^{-1} from treatment at recommended and double recommended doses of 80 and 160 g a.i. ha^{-1}, respectively (Table 2). Dissipation of imidacloprid residues in grapes was very fast in the initial stages. Thereafter, rate of dissipation was slow and after 1 month 80–83.7% of the residues had dissipated. Further dissipation was very slow, only about 12% residues dissipated in the last 1 month. Residues remained on the fruits up to 60 days but at a low level of 0.056 and 0.108 mg kg^{-1} from treatment at the recommended and double the recommended dose, respectively. Residues of imidacloprid on grapes dissipated with the half-life of 16.6 days from both the treatments.

Maximum residue limit of imidacloprid on grapes is fixed at 1.0 mg kg^{-1} both by Codex Alimentarius Commission (Anonymous, 2004) and European Union (Anonymous, 2009). Considering this value the safe pre-harvest interval of imidacloprid on grapes is 2 days only. But for calculation of pre-harvest interval the LOQ of 0.05 mg kg^{-1} was considered. Based on the persistence study and LOQ of 0.05 mg kg^{-1}, the pre-harvest interval was worked out to be 60 and 71 days, following application at the recommended and double the recommended doses, respectively. The residues of imidacloprid were also estimated in grape berries at harvest. Residues from both the treatments of 80 and 160 g a.i. ha^{-1} were below the quantifiable limit of 0.05 mg kg^{-1} on grape berries at harvest (105 days after the last spray). The residue levels in soil (under canopy) collected at harvest were below the quantifiable limit of 0.05 mg kg^{-1} from both the treatments.

Arora *et al.* (2009) studied the persistence of imidacloprid on grape leaves and have evaluated only the harvest time residues on grape berries. They have reported that at harvest, i.e. 86 days after the last spray application, residues in grape berries were below determination limit of 0.05 mg kg^{-1} which is in agreement with the results obtained in our study. In grape leaves, the residues dissipated at the half-life of 2.35 and 2.97 days. Imidacloprid seems to persist for a longer period of time on fruits, but degrades faster when applied to vegetable crops. Dubey *et al.* (2006) reported that when applied as drench treatment to apple tree basin imidacloprid was detected in the fruits up to 20 days and in soil beyond 40 days. Hassan *et al.* (2005) reported that brinjal fruit was fit for consumption even after 3 days of spray application of imidacloprid. Ishii *et al.* (1994) studied the residue behavior of imidacloprid in rice and cucumber and reported that the pesticide possesses systemic properties and is translocated to the aerial parts quickly but has quite low persistence in plants. A study on the dissipation of imidacloprid in Orthodox tea and its transfer from made tea to infusion required a waiting period of 7 days after pesticide

Table 2 Dissipation of imidacloprid residues in grape berries and soil

	Imidacloprid residues recovered (mg kg^{-1})*		
	Treatment		
Days after spray	Untreated control	Confidor 200 SL at 80 g a.i. ha^{-1}	Confidor 200 SL at 160 g a.i. ha^{-1}
0	BDL	0.740	1.260
1	BDL	0.601 (18.8)	1.022 (18.9)
3	BDL	0.542 (26.8)	0.841 (33.2)
6	BDL	0.420 (43.24)	0.730 (42.0)
10	BDL	0.341 (53.9)	0.621 (50.7)
15	BDL	0.260 (64.8)	0.512 (59.36)
20	BDL	0.245 (66.9)	0.420 (66.7)
25	BDL	0.201 (72.8)	0.316 (74.9)
30	BDL	0.148 (80.0)	0.205 (83.7)
40	BDL	0.102 (86.2)	0.152 (87.9)
50	BDL	0.074 (90.0)	0.122 (90.3)
60	BDL	0.056 (92.4)	0.108 (91.4)
105(at harvest)	BDL	BDL	BDL
Soil at harvest	BDL	BDL	BDL

*Average residues of triplicate laboratory samples taken from a composite field sample.
Figures in the parenthesis are the percent dissipation of residues.
Limit of quantification (LOQ) – 0.05 mg kg^{-1}.
Below detectable limit (BDL) < 0.05 mg kg^{-1}.

application at a recommended dose for tea (Gupta *et al*., 2008). In the present study imidacloprid could not be detected beyond 60 days when applied at the recommended dose. The results from this study make imidacloprid an ideal insecticide that can be safely used on grapevines, at the stage of the crop and dose mentioned.

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