Original Research Article

Dissipation dynamics and risk assessment of imidacloprid in grape berries using LC- MS for food safety

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ABSTRACT

Aim: The present study was taken up to assess the imidacloprid residue pattern in order to define strategies for improvement of quality and safetymainly healthfulness in grapes.

Place and duration of study: The present study was carried out in Tamil Nadu during the period 2020-2021.

Methodology: Dissipation studies were carried out in a farmer's field at Theni, India (9^{o} N latitude and 76^{o} E longitude and 375m above mean sea level) with all good agricultural practices**.** During this study Grapes (Muscat Hamburg variety) was grown and the commercial formulation of imidacloprid 17.8% SL was applied at recommended dose (53 a.i ha^{-1}) and double dose (106 a.i ha^{-1}) Two sprays were given with an interval of 10 dayby using a power operated sprayer as 500 L ha^{-1} spray fluid for dissipation study. The samples were processed by adopting modified QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) method

Results: The initial deposit imidacloprid in grape berries was 0.65 and 1.56 $^{\text{mg kg-1}}$ at the recommended dose (53 g a.i ha^{-1}) and double dose respectively (106 g a.i ha^{-1}). The insecticide exhibited a slower dissipation rate (Table 3) and reached below its quantification level (<0.01 $^{\text{mg kg-1}}$) in grape berries on 25th, 30th day at recommended and double doses respectively.

Conclusion: The toxicological dietary risk assessment data shows that risk quotient is less than one which confirms safer to consumers. Pre-harvest interval does not apply for imidacloprid at recommended dose as being grapes harvested on the day of application itself were found safe for consumption and PHI/ safe waiting period of 2 days is suggested for double dose for harvesting.

Keywords: Grapes, Imidacloprid, method validation, dissipation, risk assessment, food safety

1. INTRODUCTION

Grape (*Vitisvinifera*L.) is one of the most important non-climacteric fruit widely cultivated around the world in temperate zone which has acclimatized to tropical and subtropical agro-climatic conditions prevailing in the Indian sub-continent. Grape berries are consumed as both fresh and processed products and one of the richest fruits in carbohydrates (15-18 g per 100g) with a high caloric content (65 kcal), while the Glycaemic Index (GI) is quite low (in the range of 43-59). Commercial cultivation of grapes tends to attract various kinds of pests to the vineyards. In India as many as 60 species of insects and a few mites have been found damaging vines (1). Because of high incidence and damage from these pests, grape growers often use higher application rate of the insecticides with multiple sprayings at different crop growth stages, even up to harvest. Evidence showed that approximately 7 per cent of pesticides utilized in agriculture were applied in grapes (2). In most areas of Tamil Nadu (India), the grape crop is grown by implying a higher usage of chemical inputs (pesticides) without any knowledge on optimal safe usage. Pesticides applied during the fruit growth period can dissipate faster because of the growth dilution effect (3). However, when applied after fruit growth, they are likely to be carried over to fruits. Increased awareness in the public about pesticide residues in fruits and vegetables, as well as the potential health impacts, necessitates the use of effective pesticide residue removal procedures in the home.

Imidaclopridis one the highly used chemical formulation against thrips and it registered under (CIB&RC, 2021). Imidacloprid is having water solubility (610 mg L^{-1} at 20^oC) melting point (143^oC), Log K_{ow} (0.57) and vapour pressure (2×10^{-4} at 20^oC) (4). More over studies on the residue dynamics of pesticides in grapes are very less under Indian conditions and no studies from Tamil Nadu. Considering these conditions, the present study was taken up to assess the imidacloprid residue pattern in order to define strategies for improvement of quality in grapes and mainly healthfulness in grapes. Imidacloprid total residue includes both the parent compound and 6-chloronicotinic acid formed by photodegradation. The 6-CNA gained more attention posing threat for some pollinators, so along with parent compound, its metabolite, 6-CNA was also analysed.

2. MATERIAL AND METHODS

2.1. Chemical and reagents

The analytical standard of imidacloprid (98.3%) and 6-chloronicotinic acid (98.9%) were purchased from Sigma Aldrich, Bangalore, India. The HPLC grade ethyl acetate (≥ 99.7%), acetonitrile (≥ 97%), hexane (≥ 95% purity) were procured from Sisco Research Laboratories, Mumbai, India. Analytical grade sodium chloride (≥ 99% purity) procured by Merck, Mumbai, India and anhydrous magnesium sulphate (≥ 99% purity) were supplied by Himedia Laboratories, Mumbai, India. Anhydrous sodium citrate dibasic sesquihydrate (≥ 99% purity) was supplied by Sigma Aldrich, Bangalore, India. Anhydrous tri-sodium citrate dihydrate (≥ 99% purity) procured by Merck, Mumbai, India. Primary secondary amine (PSA, 40 μm), graphitised carbon black (GCB) were obtained from Agilent Technologies (Palo Alto, CA, USA). Formic acid (≥ 99% purity) was supplied by Fisher Scientific Limited (Czech Republic). The commercial formulation of imidacloprid 17.8% SL (TATAMIDA) was purchased locally in pesticide dealer shop at Coimbatore, Tamil Nadu, India.

2.2 Preparation of standard solutions

The imidacloprid stock solution (400 mg/L) was prepared in HPLC grade acetonitrile by weighing approximately 10.18 mg of the analytical standard into a calibrated Glass A volumetric flask (25 mL). The secondary stock solution (40 mg/L) was prepared from the stock solution in 25 mL volume by transferring 2.5 mL. The calibration and spiking standard solutions were prepared in the range of 0.01- 0.1 mg/L from the secondary stock solution by serial dilution process. All the standard solutions were stored in deep freezer at -20^{o}C until use. The matrix matched standard solutions of 0.01, 0.025, 0.05, 0.075 and 0.1 mg/L were prepared with different grape matrices viz., immature grapes, mature grapes, juice, squash and raisin separately.

2.3. Methods

2.3.1. Field experiment details

Dissipation study was carried out in a farmer's field at Theni, India (9^{o} N latitude and 76^{o} E longitude and 375m above mean sea level) with all good agricultural practices. The plot size was 50m^{2} area that had no application of imidacloprid prior to taking up the study and treatments were made up of three replicated plots. During this study Grapes (Muscat Hamburg variety) was grown and the commercial formulation of imidacloprid 17.8% SL was applied at recommended dose (53 a.i ha^{-1}) and double dose (106 a.i ha^{-1}) as per Central Insecticide Board and Registration Committee (5) during grape berries initiation stage (45 days) after flowering. Two sprays were given with an interval of 10 days by using a power operated sprayer as 500 L ha^{-1} spray fluid for dissipation study.During field trial, a total rainfall of 116 mm was received with 28.16^{o}C and 19.16^{o}C as maximum, minimum temperatures respectively. A relative humidity of 78.16% was recorded for the entire trial period.

2.3.2. Sample collection and preparation

The grape berries were picked from vines at random from each replication just after spraying 0 (2hrs), 1, 3, 5, 7, 10, 15, 20, 25, 30, 35 days and harvest time samples and brought to the laboratory for further processing. Samples were homogenised by using a high-volume blade homogeniser and stored at -40^{o}C temperature. For decontamination study samples were treated with simple household methods.

2.3.3.Extraction and clean-up for dissipation studies

The samples were processed by adopting modified QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) method (6). A representative sample of 10 g was transferred into a 50 ml centrifuge tube and mixed using a vortexer for one minute after adding 10 ml of acetonitrile. About 4 g of anhydrous MgSO4 and 1g of NaCl were subsequently added and again shaken well by vortexer, then centrifuged at 6000 rpm for 10 minutes. After centrifuging, 6 mL of supernatant aliquot was transferred into a 15 ml centrifuge tube containing 100 mg Primary Secondary Amine (PSA), 600 mg anhydrous magnesium sulphate (MgSO4) and 10 mg Graphitized Carbon Black (GCB). The mixture was vortexed for half minute and then centrifuged for 10 minutes at 3000 rpm. Finally, 1 mL was taken and filtered directly by using 0.2 µm membrane syringe filter and transferred into 1.0 mL LCMS autosampler vials for analysis of imidacloprid and its metabolite 6-chlornicotinic acid residues.

2.3.4. LC-MS instrument

The detection and estimation of residues was done by using Shimadzu 2020 series LCMS equipped with SPD-M20A (Diode array detector) and reverse phase C18 (Eclipse plus- Agilent) column has 250mm length x 4.6 mm id x 5 µ particle size which is placed in a column oven, at 40˚C. Mobile phase used for estimation was LiChrosolv grade acetonitrile with 0.1 % formic acid and ultra-pure water with 0.1 % formic acid in the ratio of 50:50. The LCMS pump was operated at 55 kgf/cm^2 pressure in a binary mode so as to discharge the mobile phase in the above mentioned ratio at a constant flow rate of 0.4 mL/min. The imidacloprid residues were detected at the wavelength of and the retention time of which, at the above-mentioned operating condition was 7.74. Shimadzu lab solutions software was used to analyse the chromatograms and further calculations based on obtained peak areas in the chromatograms.The method used to determine the residues of imidacloprid in grape matrices was developed and validated as per SANTE guidelines (7) and evaluated with parameters viz., recovery, repeatability, linearity, limit of detection, limit of quantification, sensitivity, trueness, precision and matrix effect. The recovery study was carried out with five levels of fortifications (0.01, 0.025, 0.05, 0.075 and 0.1 $^{\text{mg kg-1}}$) and repeatability was ascertained by calculating the relative standard deviation of respective recoveries. The linearity was checked by developing the calibration curve with imidacloprid standard solutions in the range between 0.005 – 0.1 $^{\text{mg kg-1}}$. The sensitivity of the developed method was evaluated by arriving the limit of detection by spiking the imidacloprid with selected matrices at the lowest concentration level meeting the analytical method requirements. The precision of the present method was performed in terms of repeatability (Relative Standard Deviation) for each spiked levels of 0.01, 0.025, 0.05, 0.075 and 0.1 $^{\text{mg kg-1}}$ of both the matrices.Matrix effect (ME) was evaluated by comparing the response obtained from solvent standards and matrix matched standards. The ME was evaluated using

$$\text{ME (\%)} = \frac{\text{Peak area of matrix standard} - \text{peak area of solvent standard}}{\text{Peak area of matrix standard}} \times 100$$

2.3.5. Statistical analysis

The imidacloprid residue was calculated by using

$$\text{Residue } (^{\text{mg kg-1}}) = \frac{A1\times C\times I1\times F}{A2\times W\times I2}$$

Where, A_1 = Peak area of the sample, A_2 = Peak area of the standard, I_1 = Injected volume of standard (μL), I_2 = Injected volume of sample (μL), C = Concentration of standard solution (mg/L), F = Final volume of the sample (mL) and W= weight of the sample (kg). The imidacloprid residue data thus obtained from the field experiments were subjected to first-order dissipation kinetics equation $Ct = Coe^{-kt}$, where, Ct is the pesticide concentration ($^{\text{mg kg-1}}$) at time t (day), C_o is the apparent initial concentration ($^{\text{mg kg-1}}$), k is the dissipation rate constant (8). The half-life of imidacloprid was determined as DT_{50} = ln2/k (9).

The maximum residue limit (MRL) has been published by European pesticide database for imidacloprid in grapes was 1.0 $^{\text{mg kg-1}}$ (10) and pre-harvest interval (PHI) of imidacloprid was calculated usingPHI = [InC_0=InMRL]/k

2.3.6. Dietary risk assessment

The estimated daily intake (EDI) of imidacloprid residue was calculated by multiplying the highest residue concentration ($^{\text{mg kg-1}}$) with the food consumption rate (kg/ day) divided by the mean body weight of an adult. The long-term risk assessment of intakes compared to pesticide toxicological data were performed by calculating the risk quotient (RQ), dividing the EDI by the relevant acceptable daily intake (ADI) expressed in $^{\text{mg kg-1}}$ body weight (bw)/day. ADI value of imidacloprid is considered to be 0.06 $^{\text{mg kg-1}}$bw/day (11). The average body weight and recommended vegetable consumption of an Indian adult are considered to be 55 kg (12) and 300 g/day (13) respectively. The acceptable risk for long term human dietary intake of imidacloprid is confirmed when RQ is less than 1 and if RQ is more than 1 it is an unacceptable risk(Table.7).

3. RESULTS AND DISCUSSION

The analytical method adopted to estimate the residue of imidacloprid and its metabolite 6-chloronicotinic acid in immature and mature grape berries was validated by deducing recovery percentage, Relative Standard Deviation (RSD)and linearity. The recoveries of imidacloprid and its metabolite 6-chloronicotinic acid in immature, mature grapes, grape juice, squash and raisin were in accordance with SANTE guidelines and fall within the range of 70-120% for recovery (Table 1, 2,3&4) and less than20% for RSD (7). The method linearity ranged from 0.005 to 0.1 mg/L concentration for both the matrices(Table. 5).The correlation coefficient of imidacloprid and 6-chloronicotinic acid, both for solvent and matrix-matched calibration standards was greater than 0.99 and the linear regression equation was y = 1E + 06x + 680.41 and y = 3E + 06x + 9393.95 for standards imidacloprid and 6-chloronicotinic acid respectively. The LOD and LOQ were 0.005 and 0.01 $^{\text{mg kg-1}}$ respectively. The proposed LOQ (0.01 $^{\text{mg kg-1}}$) of the method was below maximum residue limit (MRL) value fixed by EU Pesticide database (1.0 $^{\text{mg kg-1}}$).

The precision of the analytical method in terms of RSDs was in the range of 0.17 to 12.33.

3.1. Dissipation of imidacloprid residues in grape berries

The initial deposit imidacloprid in grape berries was 0.65 and 1.56 $^{\text{mg kg-1}}$ at the recommended dose (53 g a.i ha^{-1}) and double dose respectively (106 g a.i ha^{-1}). The insecticide exhibited a slower dissipation rate (Fig.1 &Table. 6) and reached below its quantification level (<0.01 $^{\text{mg kg-1}}$) in grape berries on 25th, 30th day at recommended and double doses respectively and this was due to systemic nature of imidacloprid in plant systems where rapid translocation of residues into internal parts of berries(14). The present findings are more or less similar to results of studies in grapes where imidacloprid residues reached to BDL with half-lives of 2.21 and 2.94 days (15) and 2.35 and 2.97 days (16). A study was conducted with spirotetramat + imidacloprid where imidacloprid was degraded by 10th day to BDL with half live of 5.07 days (17). However, higher half-life (16.6 days) was reported for imidacloprid in grapes (18) due to variation in insecticide formulation, dosage and environmental factors. The present findings are more or less in agreement with studies other than grapes where imidacloprid was dissipated to BDL on 15th day in sweet orange (19), 10th day in kinnow mandarin (20), 10th day in pomegranate (21).

Table 1. Recovery percentage of imidacloprid residues in immature grapes

Spiked level (µg g^{-1})	Recovery (%)							Mean recovery (%) * ± SD	RSD (%)
	R1	R2	R3	R4	R5	R6	R7		
0.01	106.09	115.45	117.24	112.38	91.80	101.24	106.18	107.19 ± 8.86	8.26
0.025	84.80	86.69	80.00	87.82	87.71	94.46	94.13	87.94 ± 5.09	5.78
0.05	85.90	86.70	90.80	91.34	93.12	91.90	94.17	90.64 ± 3.24	3.57
0.075	101.34	97.57	101.90	99.76	98.63	94.91	103.36	99.64 ± 2.87	2.88
0.1	102.27	102.50	104.17	100.74	105.37	102.50	104.17	103.10 ± 1.55	1.50

***Mean of seven replications, SD- Standard Deviation, RSD- Relative Standard Deviation**

Table 2. Recovery percentage of imidacloprid residues in mature grapes

Spiked level (µg g^{-1})	Recovery (%)							Mean recovery (%) * ± SD	RSD (%)
	R1	R2	R3	R4	R5	R6	R7		

0.01	100.41	109.73	116.17	102.10	105.90	112.05	104.68	107.29 ± 5.63	5.25
0.025	105.11	117.40	101.42	109.45	101.47	100.68	110.95	106.64 ± 6.25	5.86
0.05	86.98	88.08	88.64	94.64	88.81	89.53	91.39	89.72 ± 2.56	2.85
0.075	109.12	104.64	102.31	91.45	104.93	87.45	97.75	99.66 ± 7.84	7.87
0.1	90.45	91.44	85.51	95.00	91.44	85.51	95.00	90.62 ± 3.91	4.32

*Mean of seven replications, SD- Standard Deviation, RSD- Relative Standard Deviation

Table 3. Recovery percentage of 6-chloronicotinic acid residues in immature grapes

Spiked level (µg g^{-1})	**Recovery (%)**							**Mean recovery (%) * ± SD**	**RSD (%)**
	R1	**R2**	**R3**	**R4**	**R5**	**R6**	**R7**		
0.01	84.06	94.58	90.21	97.02	81.48	87.50	75.93	87.25 ± 7.41	8.50
0.025	98.92	108.89	107.22	103.17	95.40	104.05	95.26	101.84 ± 5.46	5.36
0.05	113.32	110.58	106.42	101.68	112.47	109.01	112.02	109.36 ± 4.12	3.77
0.075	116.55	114.83	119.33	119.20	119.12	110.78	111.86	115.95 ± 3.58	3.09
0.1	114.46	113.51	116.76	111.45	116.49	116.76	111.45	114.41 ± 2.37	2.07

*Mean of seven replicates, SD- Standard Deviation, RSD- Relative Standard Deviation

Table 4. Recovery percentage of 6-chloronicotinic acid residues in mature grapes

Spiked level (µg g^{-1})	Recovery (%)							Mean recovery (%) * ± SD	RSD (%)
	R1	R2	R3	R4	R5	R6	R7		

0.01	78.76	92.88	89.27	79.10	76.50	94.92	87.57	85.57 ± 7.41	8.66
0.025	83.48	85.60	72.23	75.71	78.64	81.90	73.58	78.73 ± 5.13	6.51
0.05	96.72	94.33	88.45	94.46	88.38	92.84	93.60	92.68 ± 3.15	3.40
0.075	92.22	86.42	85.02	90.62	91.22	89.13	83.28	88.27 ± 3.40	3.85
0.1	88.28	90.37	92.25	96.29	89.45	91.04	93.24	91.56 ± 2.66	2.91

***Mean of seven replicates, SD- Standard Deviation, RSD- Relative Standard Deviation**

Table 5. Linearity parameters and matrix effect for imidacloprid and 6-CNA residues in different grape matrices

Pesticides	Matrix	Calibration range (mg/L)	Regression equation	Correlation coefficient (R^2)	Matrix effect (%)
Imidacloprid	Solvent	0.005-0.1	y = 1E+06x + 5254.1	0.9999	-
	Immature grapes	0.005-0.1	y = 2E+06x - 2285.5	0.9921	4.32
	Mature grapes	0.005-0.1	y = 840790x - 773.9	0.9959	5.61
	Juice	0.005-0.1	y = 3E+06x + 2285.8	0.9998	5.09
	Squash	0.005-0.1	y = 3E+06x + 125.78	0.9997	6.17
	Raisin	0.005-0.1	y = 4E+06x - 232.39	0.9997	6.40
6-chloroniconitic acid	Solvent	0.005-0.1	y = 3E+06x - 3815.8	0.9998	-
	Immature grapes	0.005-0.1	y = 148936x - 97.683	0.9996	5.44
	Mature grapes	0.005-0.1	y = 83366x - 172.24	0.9967	2.56
	Juice	0.005-0.1	y = 4E+06x + 923.27	0.9999	4.40
	Squash	0.005-0.1	y = 5E+06x - 1525.9	0.9999	5.16
	Raisin	0.005-0.1	y = 3E+06x - 421.39	0.9999	3.67

Table 6. Persistence and dissipation of imidacloprid 17.8 % SL residues in/on grapes (mg kg^{-1})

Residues (mg kg^{-1})												
Imidacloprid @ 53 g a.i ha^{-1}							Imidacloprid @ 106 g a.i ha^{-1}					
Days after treatment	R1	R2	R3	Mean± SD	RSD (%)	Dissipation (%)	R1	R2	R3	Mean ± S D	RSD (%)	Dissipation (%)
0 (2hrs)	0.65	0.72	0.68	0.68 ± 0.03	4.98	-	1.60	1.52	1.56	1.56 ± 0.04	2.37	-
1	0.44	0.47	0.50	0.47 ± 0.03	5.99	30.88	1.08	1.06	1.06	1.07 ± 0.01	1.33	31.41
3	0.46	0.41	0.42	0.43 ± 0.02	5.51	36.76	0.74	0.74	0.73	0.74 ± 0.01	1.14	52.56
5	0.36	0.33	0.41	0.37 ± 0.04	11.11	45.58	0.71	0.69	0.69	0.70 ± 0.01	1.80	55.12
7	0.24	0.23	0.19	0.22 ± 0.03	13.36	67.64	0.44	0.42	0.42	0.43 ± 0.01	2.90	72.43

10	0.11	0.10	0.12	0.11 ± 0.01	7.94	83.82	0.24	0.26	0.27	0.26 ± 0.01	4.80	83.33
15	0.04	0.05	0.05	0.05 ± 0.01	7.33	92.64	0.11	0.10	0.12	0.11 ± 0.01	9.22	92.94
20	0.02	0.01	0.02	0.02 ± 0.01	7.72	97.05	0.07	0.06	0.06	0.06 ± 0.01	8.93	96.15
25	BDL	BDL	BDL	BDL	-	-	0.03	0.03	0.03	0.03 ± 0.01	3.00	98.07
Harvest	-	-	-	ND	-	-	-	-	-	ND	-	-
Kinetic equation	Y= 0.0762x + 2.8424						Y= 0.0676x + 3.1213					
R^2 value	0.988						0.993					
Half-life	3.95 days						4.45 days					
PHI	-						1.79 days					

ND- Not Detected, BDL- Below Detectable Level (0.01 mg kg^{-1}), PHI- Pre-Harvest Interval, SD- Standard deviation

Table 7. Dietary risk assessment of imidacloprid in grape berries at 53 g a.i ha^{-1} and 106 g a.i ha^{-1}

53 g a.i ha^{-1}						106 g a.i ha^{-1}					
Days after treatment	Imidacloprid residues* (mg kg^{-1})	Dietary risk assessment				Days after treatment	Imidacloprid residues* (mg kg^{-1})	Dietary risk assessment			
		Male (65kg)		Female (55kg)				Male (65kg)		Female (55kg)	
		EDI (mg kg^{-1}/ bw/day)	Risk quotient (RQ)	EDI (mg kg^{-1}/ bw/day)	Risk quotient (RQ)			EDI (mg kg^{-1}/ bw/day)	Risk quotient (RQ)	EDI (mg kg^{-1}/ bw/day)	Risk quotient (RQ)
0 (2hrs)	0.68	0.001569	0.0262	0.00185	0.0309	0 (2hrs)	1.56	0.003600	0.0600	0.00425	0.0709
1	0.47	0.001085	0.0181	0.00128	0.0214	1	1.07	0.002469	0.0412	0.00292	0.0486
3	0.43	0.000992	0.0165	0.00117	0.0195	3	0.74	0.001708	0.0285	0.00202	0.0336
5	0.37	0.000854	0.0142	0.00101	0.0168	5	0.70	0.001615	0.0269	0.00191	0.0318
7	0.22	0.000508	0.0085	0.00060	0.0100	7	0.43	0.000992	0.0165	0.00117	0.0195
10	0.11	0.000254	0.0042	0.00030	0.0050	10	0.26	0.000600	0.0100	0.00071	0.0118
15	0.05	0.000115	0.0019	0.00014	0.0023	15	0.11	0.000254	0.0042	0.00030	0.0050
20	0.02	0.000046	0.0008	0.00005	0.0009	20	0.06	0.000138	0.0023	0.00016	0.0027
25	BDL	-	-	-	-	25	0.03	0.000069	0.0012	0.00008	0.0014
30	BDL	-	-	-	-	30	BDL	-	-	-	-

EDI-Estimated Daily Intake, BDL- Below Detectable Level, * Mean of three replications

4. Conclusion

The present study confirms that residues of imidacloprid in grapes were below LOQ after treatment irrespective of doses. We conclude that reduction of pesticide residue depends on not only the behaviour and physiochemical properties of the pesticides and also climatic conditions prevailed during experimental study, The toxicological dietary risk assessment data shows that risk quotient is less than one which confirms safer to consumers. Pre-harvest interval does not apply for imidacloprid at recommended dose being as grapes harvested on the day of application itself were found safe for consumption and PHI/ safe waiting period of 2 days is suggested for double dose for harvesting.

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Fig.1 Dissipation curve of imidacloprid 17.8 SL in grapes