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Dissipation and Residue of Acetamiprid in Watermelon and Soil in the Open Field

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Abstract Residue dynamics of acetamiprid in watermelon and soil was studied in this paper utilizing liquid chromatography with tandem mass spectrometry (LC–MS/MS). The LODs for acetamiprid in whole watermelon, melon flesh and soil were 0.002 mg/kg. The fortified recoveries ranged from 73.7 % to 107.5 % with relative standard deviations (RSDs) of 1.7 %–5.9 %. Acetamiprid dissipated in watermelon and soil with the half-life 3.12–3.92 days and 1.18–1.46 days in two locations Beijing and Shandong provinces, respectively. In the terminal residue experiment, no higher residue than 0.01 mg/kg in melon flesh and 0.3 mg/kg in whole watermelon and soil were detected.

Keywords Acetamiprid · Dissipation · Watermelon · Soil

Watermelon is one of the most common crops in the warmer regions of the world. It is utilized for the production of juices, nectars and fruit cocktails, etc., and the by-product of pickle, preserve, pectin, etc. (Wani et al. 2008) Diseases and insects relevant to watermelon cultivation include powdery mildew, fusarium wilt, anthracnose, damping-off, bacterial spot, and Tetranychus urticae, Aphis gossypii, and Spodoptera exigua. (Park et al. 2010a) In order to increase watermelon production and to improve its quality, fungicides and insecticides need to be used to control diseases and pests. Acetamiprid, ((E)-N^1-[(6-chloro-3-pyridyl) methyl]-N^2-cyano-N^1-methylacetamidine), is the fastest-growing class of neonicotinoid insecticides developed by Nippon Soda Co. Ltd., for soil and foliar applications. (Anonymous 1998) Because of its efficiency in controlling pests such as aphids, whiteflies, jassids, thrips, leafminer, beetles, leaf hopper, bugs and borers, acetamiprid can also be applied in watermelon for harvests.

To the best of our knowledge and available literatures, analytical procedures for the quantitative analysis of acetamiprid have been determined by using HPLC (Obana et al. 2002), GC (Zhang et al. 2002), GC–MS (Mateu-Sanchez et al. 2003), LC–MS (Obana et al. 2003; Radisic et al. 2009), colorimetric method (Xu et al. 2011). These methods have contributed greatly to the rapid and simple detection of acetamiprid in agricultural samples.

To evaluate the deleterious effects of acetamiprid in crops and to ensure the consumers safety, residue dynamics of acetamiprid in environment such as in soil (Gupta and Gajbhiye 2007) and in crops okra (Singh and Kulshrestha 2005), mustard plant (Pramanik et al. 2006), chili (Sanyal et al. 2008), tea (Gupta and Shanker 2008) and zucchini (Park et al. 2010b) have been investigated. However, the residue dynamic of acetamiprid on watermelon in the field conditions has never been investigated.

In this article, a method based on QuEChERS to analyze acetamiprid in watermelon and soil by LC–MS/MS was established. The residue and dissipation dynamics behavior of acetamiprid in watermelon and soil were investigated.

Materials and Methods

The analytical standard for acetamiprid (99.9 % purity) and the acetamiprid formulation (70 %, water dispersible

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granules) were obtained from Ningbo Sinochem Chemical Company Limited. Acetonitrile (MeCN) of HPLC grade was purchased from Fisher Scientific (USA). Sodium chloride (NaCl) of analytical reagent grade was obtained from the Beijing Chemical Reagent Company (Beijing, PR China). Redistilled water was purified with a Milli-Q system (Millipore, USA). Bondesil primary secondary amine (PSA, 40–60 μm) was purchased from Agela Technologies, Tianjin, China.

The field trials, including the dissipation experiments and residue experiments, were conducted in major watermelon production regions in China at two different locations: Beijing (north of China, warm and semi-humid continental monsoon climate), Ji'nan (Shandong province, east of China, warm temperate climate). Field experiments were carried out from June 10 to July 13, 2011 in Beijing and from June 4 to July 4, 2011 in Ji'nan, Shandong province.

There were 7 treatments including 6 acetamiprid treatments and 1 control treatment. Each experimental plot was 30 m^2 and each treatment had three replications. No pesticide was used during the whole period of watermelon growth in the control treatment. A buffer area of 30 m^2 was used to separate the plots of different treatments. A 30 m^2 control plot without any application of acetamiprid was conducted simultaneity.

To investigate the dissipation dynamics of acetamiprid in watermelon and soil, formulation of acetamiprid (WDG, 70 %) was dissolved in water and sprayed with JACTO-HD400 internal pump backpack sprayer at an active constituent dose of 63 g a.i./ha (1.5 times of the recommended high dosage) on the surface of watermelon and the bare soil with no plants. It was applied once when the watermelon is half big of the harvest. The volume of water for each experimental plot (30 m^2) is 1800 mL. Representative watermelon and soil samples were collected randomly from each plot at 2 h (calculated as the original concentration), 1, 2, 3, 5, 7, 10, 14, 21 and 30 (only for soil) days after spraying.

For the ultimate residue experiment in watermelon and soil, formulation acetamiprid 70 % WDG was applied at a low dosage of 42 g a.i./ha (recommended high dosage) for 2 and 3 times and a high dosage of 63 g a.i./ha (1.5 time of recommended high dosage) for 2 and 3 times, respectively. The re-treatment interval was 7 days and the pre-harvest interval was 5, 7, 10 and 14 days.

About 2,000 g soil sample was randomly sampled to a depth of 0–15 cm in each plot using the Leyuan soil sampling drill (i.d. 35 mm × height 20 cm) at 12 different spots. The soil samples were sifted through a 1 mm sieve and then mixed well and 200 g soil samples were stored in airtight plastic bag. About 6 normal watermelons were randomly sampled in each plot. The watermelon samples are cut into four petals, two of the opposite angels were taken. The whole watermelon and melon flesh were cut into small pieces and comminuted with a blender (Philips, China). Subsample 200 g whole watermelon and melon flesh samples were put in the plastic box, separately. Samples were placed in a deep freezer at −18°C for analysis within 2 months.

Sample of 10 g the blending soil, melon flesh or whole watermelon was weighed into a 50 mL centrifuge tube, and then 5 mL water (soil only), 10 mL acetonitrile and 3 g NaCl were added and extracted with a vortex mixer for 2 min. The centrifuge tube was centrifuged for 5 min at 3,800 rpm. Dispersive solid phase extraction (DSPE) was utilized for sample cleanup. Supernatant acetonitrile layer 1 mL was transferred into a 2 mL centrifuge tube containing 50 mg PSA. The centrifuge tube was centrifuged for 5 min at 10,000 rpm after vortexed for 30 s. The supernatant liquid was filtered by a 0.22 μm nylon membrane filter and then analyzed by HPLC–MS/MS.

Acetamiprid was determined by Agilent 1200 HPLC series (Agilent technologies, USA) consisting of a G1322A degasser, a G1311A quaternary pump, a G1316A TCC, a G1329A ALS and a 3.5 μm Eclipse Plus C18 (2.1 mm × 50 mm) column (Agilent technologies, USA). The mobile phase was acetonitrile–water containing 0.1 % formic acid (9/1, V/V) and the injection volume was 5 μL. The column temperature was maintained at 30°C with a flow rate of 0.30 mL/min.

The effluent from the LC system was introduced into an Agilent 6410B triple-quadrupole mass spectrometer (Agilent technologies, USA), equipped with an electrospray ionization interface, operating in the positive ion mode (ESI+). The source parameters were: capillary current 8 nA; desolvation gas flow 10.0 L/min; desolvation gas temperature 350°C; nebulizer gas (N_2) pressure

Table 1 Acetamiprid quantification and confirmation parameters using LC–MS/MS

Compound	Molar mass	Fragmentor (V)	Precursor ion	Product ion	Collision energy (V)	Quantification/ confirmation
Acetamiprid	222.68	80	223.1	126.0	15.0	Quantification
				56.0	15.0	Confirmation

35.0 psi; capillary voltage 4,000 V. The MRM was conducted with a dwell time of 200 ms. The MRM was applied and the parameters were listed in Table 1.

For instrument control, mass hunter workstation software data acquisition for triple quad B. 02. 01 (B 2043.12) and qualitative analysis version B.03.01/build 3.1.346.0 were used for data acquisition and processing.

Results and Discussion

To evaluate the linearity and sensibility of the analytical method, a series of matrix standard solutions (0.005, 0.01, 0.02, 0.05, 0.1, 0.2, 0.5 mg/L) were diluted by matrix extract. The calibration curves showed good linearity with typical correlation coefficient (R^2) between 0.997 and 1. It was used to calculate the concentration of acetamiprid residues in whole watermelon, melon flesh and soil.The LOD value was 0.002 mg/L and the LOQ value was established as 0.005 mg/kg, respectively.

Table 2 Average recovery and RSD of acetamiprid in three matrices spiked at three different levels

Sample types	Fortification levels (mg/kg)	Recovery (%)	RSD (%)
Soil	0.05	93.6 ± 1.9	2.1
	0.1	83.7 ± 3.1	3.7
	0.5	89.0 ± 1.5	1.7
Whole watermelon	0.05	79.6 ± 3.6	4.5
	0.1	107.5 ± 2.4	2.2
	0.5	73.7 ± 2.6	3.6
Melon flesh	0.05	86.9 ± 1.7	1.9
	0.1	87.0 ± 3.7	4.2
	0.5	77.3 ± 4.5	5.9

To evaluate the accuracy and precision, soil, melon flesh or whole watermelon sample were spiked at 0.05, 0.1 and 0.5 mg/kg levels with five replicates. The results were listed in Table 2. The fortified recoveries ranged from 73.7 % to 107.5 %, and relative standard deviation (RSD)

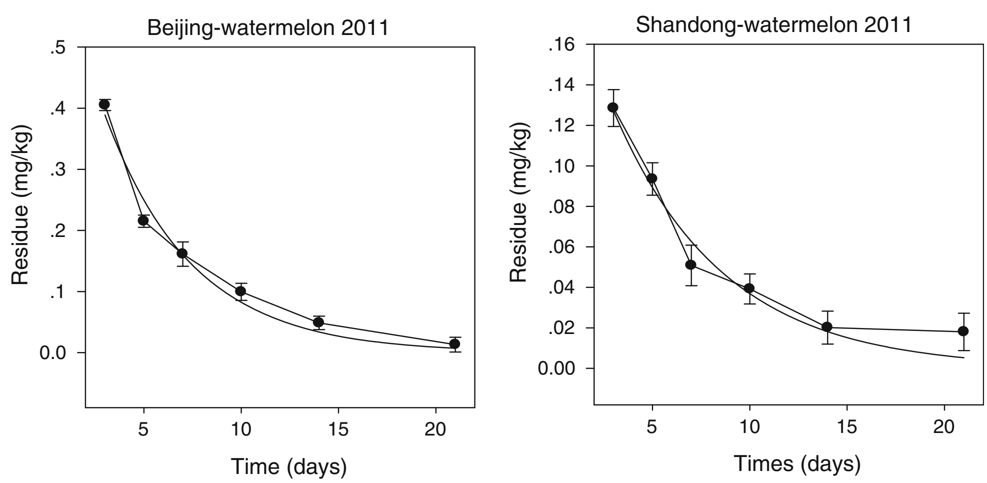

Fig. 1 Dissipation of acetamiprid residue on watermelon in Beijing and Shandong in 2011

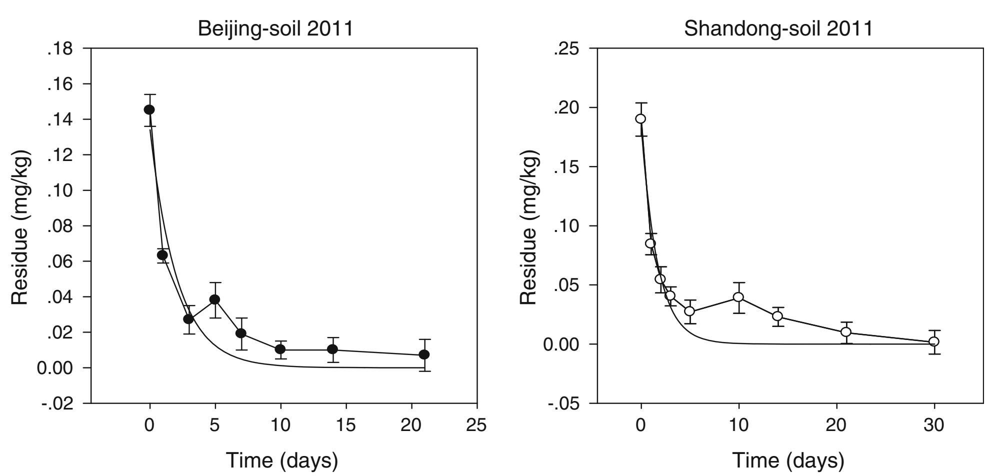

Fig. 2 Dissipation of acetamiprid residue on soil in Beijing and Shandong in 2011

Table 3 The terminal residues of acetamiprid in soil, whole watermelon, melon flesh in Beijing and Shandong in 2011

Dosage (g a.i./ha)		Low dosage (42)								High dosage (63)							
Numbers of application		2				3				2				3			
PHI (days)		5	7	10	14	5	7	10	14	5	7	10	14	5	7	10	14
Residue (mg/kg)																	
Beijing	Soil	0.038	0.007	0.011	0.006	0.003	0.005	0.003	0.003	0.005	0.004	0.006	0.005	0.006	0.003	0.007	0.002
Shandong		0.046	0.002	0.017	0.008	0.024	0.001	0.019	0.027	0.162	0.002	0.020	0.021	0.028	0.003	0.006	0.004
Beijing	Whole watermelon	ND	ND	ND	ND	0.003	ND	ND	ND	ND	ND	ND	ND	0.016	0.006	0.002	ND
Shandong		0.027	0.014	0.009	0.006	0.016	0.003	0.009	0.004	0.054	0.010	0.010	ND	0.085	0.012	0.010	0.004
Beijing	Melon flesh	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Shandong		0.007	0.007	0.006	0.004	0.006	0.002	0.002	ND	0.022	0.019	ND	ND	0.010	0.004	0.003	0.002

ND not detected, lower than limit of detection (LOD)

ranged from 1.7 % to 5.9 %, which means a satisfactory accuracy and precision.

The dissipation samples were analyzed, and drawn in scatter plot with several outliers removed. The dissipation curve of watermelon and soil was fitted with first order kinetics as shown in Figs. 1 and 2. The dissipation equation of acetamiprid in watermelon were $C = 0.7570e^{-0.2221t}$ with the half-life of 3.12 days in Beijing and $C = 0.2162e^{-0.1769t}$ with the half-life of 3.92 days in Shandong. The dissipation equation of acetamiprid in soil were $C = 0.1341e^{-0.4759t}$ with the half-life of 1.46 days in Beijing and $C = 0.1825e^{-0.5896t}$ with the half-life of 1.18 days in Shandong. The half-life values of acetamiprid on watermelon and soil were similar in two sites. The result indicates that acetamiprid dissipates rapidly in soil than in watermelon and will not enrich in watermelon or soil.

According to relevant reports, the half-life values of acetamiprid were 2.3 days in okra (Singh and Kulshrestha 2005), 1.02–1.59 days in mustard plant (Pramanik et al. 2006), 2.24–4.84 days in chili (Sanyal et al. 2008), 1.82–2.33 days in green tea shoots and 1.84–2.25 days in made tea for both dry and wet seasons (Gupta and Shanker 2008). Thus, the half-life value of acetamiprid is affected by the kind of crop. Suman et al. (2007) reported that the half-life values of acetamiprid in soil under laboratory conditions varied from 15.7–17.4 days under field capacity, 19.2–29.8 days under the submerged condition and 125.4–150.5 days under dry condition. Acetamiprid dissipation rate was found to be faster in the field condition and slower in air-dry soil.

The terminal residue samples were analyzed, and the result was listed in Table 3. The concentration level of acetamiprid in watermelon and soil could be detected after application of acetamiprid at 42 g a.i./ha (recommended high dosage) and high dosage 63 g a.i./ha (1.5 times the recommended high dosage) at two locations. Maximum residue limit (MRL) of acetamiprid in watermelon is provisionally established by the European Union (EU) at 0.01 mg/kg and by Japan at 0.3 mg/kg. The terminal residues of acetamiprid in whole watermelon and melon flesh were below the MRL of EU at 14 days after the treatments. The terminal residues of acetamiprid on the day of all preharvest intervals in whole watermelon, melon flesh and soil, were all below the MRL of Japan in two locations.

Overall, the methods used for extraction, clean-up and estimation of residues were found to be satisfactory qualitatively as well as quantitatively. Acetamiprid dissipated with the half-life 3.12–3.92 days in watermelon and 1.18–1.46 days in soil in two different locations that were located in the north and east of China. According to the terminal residue results, this study expounded that aetamiprid will not enrich in watermelon or soil. The present finding suggests that acetamiprid could be used in watermelon safely with recommended dosage. This work would be also helpful to provide guidance on the proper and safe application of acetamiprid in agricultural products and environment.

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