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Dissipation and Residue of Thiacloprid in Cabbage and Soil

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Abstract Residue dynamics of thiacloprid in cabbage and soil was studied in this paper utilizing liquid chromatography with tandem mass spectrometry (LC–MS/MS). The field trial was conducted in two sites: Beijing, China and Hubei, China. Thiacloprid dissipated rapidly with the half-life 1.3–1.6 days in cabbage and 2.1–3.1 days in soil. In the terminal residue experiment, no higher residue than 0.06 mg/kg in cabbage and 0.16 mg/kg in soil was detected, which was far below either EU MRL (0.2 mg/kg) or Japan MRL (1 mg/kg).

Keywords Thiacloprid · Dissipation · Cabbage · Soil

Thiacloprid (Jeschke et al. 2001) is a neonicotinoid insecticide developed jointly by Bayer AG in Germany, Nihon Bayer Agrochem in Japan and Bayer Corporation in USA as the second member of Bayer's chloronicotintyl family. Thiacloprid (Tomlin 2006) is a potent agonist of insect nicotinic acetylcholine receptors and disturbs synaptic signal transmissions. It has a broad spectrum of activity against not only sucking insects but also chewing insects (Elbert et al. 2001).

As the member of the biggest selling insecticide class worldwide (Liu et al. 2010), it is necessary to find out the residue dynamic characteristic of thiacloprid in fruits, vegetables and environment. Omirou et al. (2009) has studied the dissipation rate of thiacloprid in greenhouse tomato with a half-life of 1.9 days. There was no higher residue than EU MRLs (0.5 mg/kg) 2 days after normal dose and 7 days after double dose. Saimandir et al. (2009) reported the half-life 11.1–11.6 days of thiacloprid in eggplant. Dubey et al. (2008) reported the half-life 3.8–4.6 days and around 3.3 days of thiacloprid in apple and tea respectively. Yu et al. (2007) reported the half-life 0.7–1.2 days of thiacloprid in medical herbs (marjoram, thyme and camomile) using the biexponential model and the half-life 3.5 and 3.6 days in soil using the first-order function and biexponential model respectively. Krohn (2001) investigated the environmental behavior and obtained the half-life in soil 9–27 days in northern and southern Europe and 12–20 days in aquatic environment. However, the residue dynamic study was never conducted on brassica vegetables.

This study was intended to investigate the residue and dissipation in cabbage and soil and provide some reference for safe application.

Materials and Methods

The balance (1602MP8-1, readability 0.1 mg) was from Sartorius AG, Germany; JY2002 balance was from Shanghai precision & scientific instrument Co., Ltd., China; TDL-40B centrifuge was from Shanghai Anting Scientific Instrument Factory, China; Centrifuge 3K15 was from SIGMA Laborzentrifugen GmbH, Germany; QL-861 vortex mixer was purchased from Haimen Qilinbeier instrument manufactural Co., Ltd., Jiangsu, China; Nylon membrane filter (0.22 μm) was purchased from Beijing Ruifengtongchuang Analysis Instrument Co., Ltd., China; HR2004 blender was from Philips, China.

Acetonitrile was HPLC grade and purchased from Fisher Scientific, USA. Sodium chloride is AR and

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purchased from Sinopharm Chemical Reagent Co., Ltd, China. Bondesil primary secondary amine (PSA, 40–60 μm) is purchased from Agela Technologies, Tianjin, China. Water was purified with Aquapro ABW-6000-U water purifier (Chongqing, China). The analytical standard for thiacloprid is supplied by Dikma Technologies Inc. with 99.5% purity.

Thiacloprid 50% water dispersible granule (WG) was supplied by Shanxi WRQ crops protect Co., Ltd, China.

Experiments were conducted in 2010 at two sites: Beijing, China and Hubei Province, China. Beijing is in northern China and has temperate monsoon climate. Hubei is in central China and has subtropical monsoon climate.

The dissipation trials of cabbage and soil were conducted in separate plots, and the soil dissipation plot didn't plant any cabbage. Each trial includes 3 plots and each plot was 15 m^2, the application dosage was 28 g/ha which was twice of recommended maximum dose and applied once when cabbage was at the folding stage. The cabbage and soil samples were collected 2 h and 1, 2, 3, 5, 7, 10, 14, 21 days after the application of thiacloprid.

The terminal residue plots were 45 m^2 for each and applied with 14 and 21 g/ha which was 1 time and 1.5 times of recommended maximum dosage. For each treatment the formulation was applied 3 and 4 times which were recommended numbers of application and 1 time more when cabbage was at the folding stage, and re-treatment interval was 7 days which was recommended minimum re-treatment interval. The cabbage and soil samples were collected 5, 7, 10 days after the last application of thiacloprid.

A 30 m^2 control plot without any application of thiacloprid was conducted simultaneously.

The cabbage samples were cut into small pieces and comminuted with a blender. The soil samples were sifted through a 1 mm sieve and then mixed well. All the samples were stored in a −20°C freezer bef analysis.

A 10 g cabbage or soil sample was weighted into a 50 ml centrifuge tube, and added with 5 mL water (soil only), 10 ml acetonitrile and 3 g NaCl, and then extracted with a vortex mixer for 2 min. The centrifuge tube was centrifuged for 5 min at 3,500 rpm.

Dispersive solid phase extraction (DSPE) was utilized for sample cleanup. An aliquot of supernatant MeCN 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 vortexing for 30 s. The supernatant liquid was filtered by a 0.22 μm nylon membrane filter and then analyzed by LC–MS/MS.

The chromatographic separation was achieved using an 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 × 50 mm) column (Agilent technologies, USA). The mobile phase was MeCN-water containing 0.1% formic acid (8/2, V/V) and the injection volume was 5 μL. The column temperature was maintained at 30°C with a flow rate of 0.15 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: desolvation gas temperature 350°C; desolvation gas flow 10.0 L/min; nebulizer gas (N_2) pressure 35.0 psi; capillary voltage 4,000 V. The Multiple reaction monitoring (MRM) was applied and the parameters were listed in Table 1.

Masshunter 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.

The external standard method was chosen for the determination of thiacloprid. All the samples were compared to matrix standard solution which was diluted by blank matrix extract without the detection of thiacloprid instead of standard solution in solvent (acetonitrile) to eliminate the matrix effect.

Results and Discussion

To evaluate the linear and sensibility of the analytical method, a series of matrix standard solutions (0.001, 0.002, 0.005, 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1 mg/L) were diluted by matrix extract. The calibration curve of cabbage were drawn with correlation coefficient $R^2 = 0.9978$ from 0.01 to 1 mg/L. The calibration curve of soil were drawn with correlation coefficient $R^2 = 0.9996$ from 0.002 to 1 mg/L. Both of the calibration curves have good linearity. The limits of detection (LOD) in cabbage and soil were 0.01 and 0.002 mg/L respectively.

To evaluate the accuracy and precision, a fortified recovery experiment was done. The fortified levels were 0.01, 0.05 and 0.2 mg/kg with 6 duplicates. The results were listed in Table 2. The fortified recoveries ranged from 76.1% to 108.8%, and relative standard deviation (RSD) ranged from 7.2% to 10.9%, 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 cabbage and soil was fitted with first order kinetics as seen in Figs 1 and 2. The dissipation equation of cabbage were $C = 0.5262e^{-0.521t}$ with the half-life of 1.3 days in Beijing and $C = 1.9922e^{-0.447t}$ with the half-life of 1.6 days in Hubei. The dissipation equation of soil were $C = 0.1114e^{-0.33t}$ with the half-life of 2.1 days in Beijing

Table 1 The multiple reaction monitoring parameters for thiacloprid

Compound	Precursor ion	Fragmentor (V)	Production	Collision energy (V)	Dwell time (ms)	Quantification/ Qualitation
Thiacloprid	252.9	105	125.9	29	150	Quantification
			90.0	54	150	Qualitation
			98.9	60	150	
			185.9	16	150	

Table 2 Fortified recoveries of thiacloprid in cabbage and soil samples

Matrix	Fortified level (mg/kg)	Average fortified recoveries (%)	RSD (%)
Cabbage	0.01	108.8	10.9
	0.05	106.3	8.9
	0.2	86.2	7.2
Soil	0.01	92.8	10.1
	0.05	89.5	7.3
	0.2	76.1	7.8

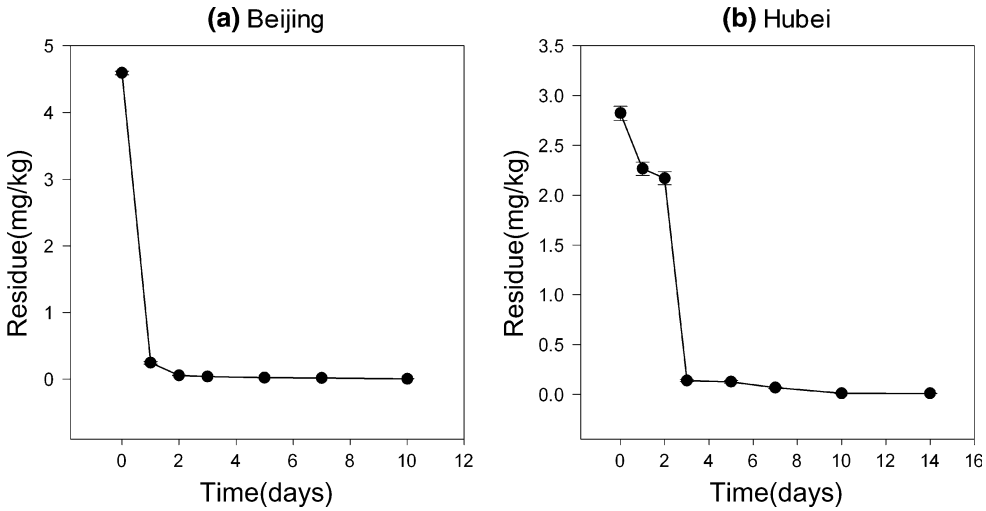

Fig. 1 Dissipation of thiacloprid residue on cabbage

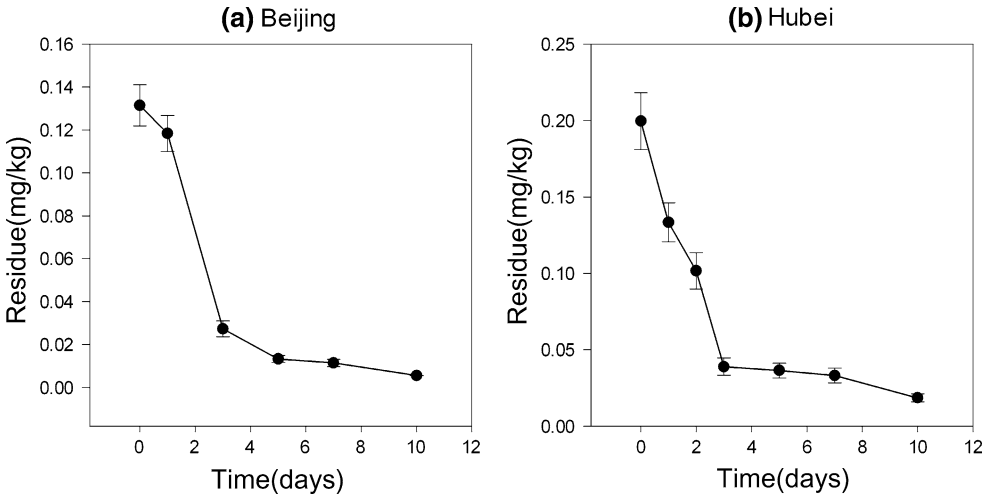

Fig. 2 Dissipation of thiacloprid residue on soil

Table 3 The terminal residues of thiacloprid in cabbage and soil in Beijing and Hubei

Application rate (g/ha)	Numbers of application	Preharvest interval (days)	Residue (mg/kg)			
			Cabbage		Soil	
			Beijing	Hubei	Beijing	Hubei
Low 14	3	10	0.012	ND	<LOQ	0.018
		7	0.021	0.034	<LOQ	0.024
		5	0.012	0.027	<LOQ	0.027
	4	10	ND	0.016	<LOQ	0.020
		7	0.018	0.025	<LOQ	0.035
		5	0.015	0.046	<LOQ	0.041
High 21	3	10	ND	0.010	ND	0.054
		7	0.021	0.025	<LOQ	0.039
		5	0.011	0.059	<LOQ	0.053
	4	10	ND	0.017	<LOQ	0.054
		7	0.030	0.032	0.014	0.15
		5	ND	0.062	0.013	0.16

ND not detected, below LOD

and $C = 0.1445e^{-0.226t}$ with the half-life of 3.1 days in Hubei. The half-life on cabbage and soil was similar in two sites. The result indicates that thiacloprid dissipates rapidly in cabbage and soil and will not enrich in cabbage or soil.

The terminal residue samples were analysed, and the result was listed in Table 3. Maximum residues limits (MRLs) of thiacloprid in cabbage have been set by several countries or organizations. European Union (Europe Commission 2010a) and Japan (The Japan Food Chemical Research Foundation 2010b) declared the MRL of thiacloprid in cabbage was 0.2 and 1 mg/kg respectively as both the residue definition was the parent compound itself. All the residues in cabbage were lower than 0.062 mg/kg which was far below either EU MRL or Japan MRL, and there was no higher residue than 0.16 mg/kg in soil, which means it's perfectly safe for thiacloprid using in cabbage field even as 1.5 times of recommended maximum rate and 1 time more than recommended numbers of application. It may also indicate more strict MRL should be established in China.

Overall, thiacloprid dissipated rapidly with the half-life 1.3–1.6 days in cabbage and 2.1–3.1 days in soil. According to the terminal residue results, no higher residue than 0.062 mg/kg in cabbage and 0.16 mg/kg in soil was detected, which was far below either EU MRL or Japan MRL.

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