Bull Environ Contam Toxicol (2012) 89:664–668
DOI 10.1007/s00128-012-0594-y

Residues and Dissipation Dynamics of Fosthiazate in Tomato and Soil

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Received: 15 November 2011 / Accepted: 1 March 2012 / Published online: 14 March 2012

Abstract Residue dynamics of fosthiazate in tomato and soil was studied in this paper utilizing liquid chromatography with tandem mass spectrometry (LC–MS/MS). The field trial was conducted in three sites: Beijing, Liaoning, Hubei in China. Fosthiazate dissipated with the half-life 0.75–2.6 days in tomato or tomato plants and 2.5–11.6 days in soil. In the terminal residue experiment, no higher residue than 0.023 mg kg^{-1} in tomato and 0.27 mg kg^{-1} in soil was detected. Residues of fosthiazte in tomato were far below Japan maximum residue levels (0.2 mg kg^{-1}).

Keywords Fosthiazate · Dissipation · Tomato · Soil

Tomato (*Lycopersicon esculentum Mill.*) is one of the most important vegetable crops grown throughout the world for consumption in various forms. A number of viral, bacterial, fungal and nematode pathogens attack tomato and cause bad economic consequences. Root–knot nematodes (*Meloidogyne species*), reniform nematodes (*Rotylenchulus reniformis*), cyst nematode (*Globodera rostochiensis*) are known to attack tomato in many different parts of the world. So far, Ferrari et al. (2008) studied that fosthiazate, as pre-planting application, appears the most convenient treatment against root-knot nematodes in tomato and muskmelon.

Fosthiazate [(*RS*)-*S*-*sec*-butyl-*O*-ethyl 2-oxo-1,3-thiazolidin-3-yl-phosphonothioate)] is a member of nonfumigant organophosphate nematicide, which has been on the market in Japan since 1990's, and because of its efficiency in controlling root-knot nematodes, it has been widely used in Europe as well as in Asia and Latin America (Toki and Imai 1994). Achieved with fosthiazate, it also has systemic activity against various species of insects and mites on the foliar part (Koyanagi et al. 1998). Much of the research for nematode control with fosthiazate has conducted on various crops such as potato, peanuts, cotton, tobacco and so on (Kimpinski et al. 1997; Lawrence and McLean 1995; Minton et al. 1993; Rich et al. 1994; Woods et al. 1999). Studies in field plots have shown that fosthiazate treatments provided the best percent nematode control by the comparison to commonly used nonfumigant (excepting oxamyl) and fumigant nematicides (Giannakou et al. 2005; Ingham et al. 2000; Melton et al. 1994).

A lot of information is available regarding the efficacy of fosthiazate in applications, only a few studies have examined the leaching, degradation and adsorption of fosthiazate in soil under simulated field conditions. It had been reported that the soil pH significantly influences the degradation of fosthiazate and the soil organic matter content mainly controlled the adsorption of fosthiazate mobile in the soil (Karpouzas et al. 2007; Pantelelis et al. 2006; Qin et al. 2004). Qin et al.(2004) first reported laboratory degradation and adsorption studies of fosthiazate with half-life ($t_{1/2}$) values ranging from 17.7 to 46.8 days and the low values of the Freundich adsorption coefficients (K_f) ranging 0.1 to 1.2 mL/g in three contrasting soil. Tsiropoulos et al. (2005) reported analytical procedures for the quantitative analysis of fosthiazate residues employing techniques by using high performance-liquid chromatography (HPLC). Lin et al. (2007) developed a method to separate the four stereoisomers of fosthiazate by using HPLC and the stereoselective toxicity was evaluated by using AChE inhibition tests (in vitro) and D. magna acute toxicity tests (in vitro).

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In this study, a method based on QuEChERS was established to determine fosthiazate in tomato and soil by liquid chromatography with tandem mass spectrometry (LC–MS/MS), and the residues and dissipation of fosthiazate in tomato and soil in the open field were studied.

Materials and Methods

The analytical standard for fosthiazate (96.0 % purity) and the fosthiazate formulation (15 %, granular formulation) were obtained from Yifan Chemical Technology Limited, Zhejiang Province, China. The stock standard solution of fosthiazate was prepared at 100 mg/L in acetonitrile (MeCN). Working standard solutions were prepared by proper dilution with MeCN. 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) and octadecylsilane chemically bonded silica (C18, 40–60 μm) were purchased from Agela Technologies, Tianjin, China.

The field trials, including the dissipation and residue experiments, were carried out in major tomato production regions in China at three different locations: Beijing (north of China, warm and semihumid continental monsoon climate), Xingcheng (Liaoning province, northeast of China, warm and semihumid coastal monsoon climate) and Xiantao (Hubei province, middle of China, the subtropics monsoon climate) from April to June in 2011. There were 5 treatments including 4 fosthiazate treatments and 1 control treatment. Each experiment plot was 15 m^2 and each treatment replicated three plots. No pesticide was used during the whole growth period of tomato in the control treatment. The buffer area was used to separate the plots with different treatments.

To investigate the dissipation of fosthiazate in tomato and soil, fosthiazate (15 %, granular formulation) mixed together with soil and scattered evenly into the groove when tomato was transplanted, and 45 m^2 soil and tomato for fosthiazate dissipation at dosage of 4,500 g a.i.ha^{-1} (1.5 times of the high recommended dosage of the pesticide producer). Representative soil samples and tomato plant or tomato samples were collected from three replicate plots on 0, 1, 2, 3, 5, 7, 10, 14, 21, 30 and 45 days after fosthiazate application for dissipation experiment. For the ultimate residue experiment, fosthiazate (15 %, granular formulation) was mixed together with soil and scattered evenly into the groove at low dosage of 3,000 g a.i.ha^{-1} (recommended high dosage) and high dosage of 4,500 g a.i.ha^{-1} (1.5 times of the recommended high dosage) one time when tomato was transplanted. Tomatoes and soil were sampled at the first harvest time for residue experiment. About 1,000 g soil sample was randomly sampled to a depth of 0–10 cm in each plot using the Leyuan soil sampling drill (i.d. 35 mm × height 20 cm) at 12 different spots. Six tomato plants or tomatoes were collected randomly from each plot. Tomato samples were cut into small pieces and comminuted with a blender (Philips, China). The soil samples were sifted through 1 mm sieve and then mixed well. Both tomato and soil samples were stored at −18°C until analyzed.

The blended tomato, tomato plant or soil sample 10 g was weighed 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 3,800 rpm. 1 mL of the supernatant ACN layer was transferred from the upper layer into 2 mL centrifuge tube containing 150 mg PSA and 150 mg C18, and then vortexed 30 s and centrifuged at 10,000 rpm. The upper layer was filtered into autosampler vial with 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 um Eclipse Plus C18 (2.1 mm × 50 mm) column (Agilent technologies, USA). The mobile phase was ACN 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 0.2 mL min^{-1}.

The effluent from the LC system was introduced into an Agilent 6410B triple-quadrupole mass spectrometer (Agilent technologies, USA), equipped with an electro-spray ionization interface, operating in the positive ion mode (ESI+). The source parameters were: capillary current 8 nA; desolvation gas flow 10.0 L min^{-1}; desolvation gas temperature 350°C; nebulizer gas (N_2) pressure 35.0 psi. The multiple reaction monitoring (MRM) was conducted with a dwell time of 200 ms. For instrument control, 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 parameters of LC–MS/MS for fosthiazate analysis were shown in Table 1.

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

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

Compound	Molar mass	Fragmentor (V)	Precursor ion	Product ion	Collision energy (V)	Dwell time (ms)	Quantification/ confirmation
Fosthiazate	283.3	90	306.0	204.2	15.0	200	Quantification
				250.0	10.0	200	Confirmation

Results and Discussion

The linear calibration curve was obtained for fosthiazate by plotting the average peak area against the concentration. The range of the 8 points calibration curves varied from 0.001 to 0.2 mg kg^{-1} in tomato, tomato plant and soil matrices. The calibration curves showed good linearity with typical correlation coefficient (R^2) between 0.9976 and 0.9996. It was used to calculate the concentration of fosthiazate residues in tomato, tomato plant and soil. The LOD value is 0.001 mg kg^{-1} and the LOQ value is 0.002 mg kg^{-1}, respectively.

In this study, sample was prepared with a modified QuEChERS method. Acetonitrile was selected as the extraction solvent and then cleaned up with PSA and C_{18}. Recovery plays a significant role in method validation procedure for trace level analyte quantitation from matrix. The fortified levels were 0.002, 0.02 and 0.1 mg kg^{-1} with 5 duplicates. Blank analyses were performed in order to check interference from the matrix. Then the samples were extracted and cleaned up as pre the procedure given above. The method give good recovery of fosthiazate residue ranged 95.8 %–108.5 % in tomato, tomato plant and soil. The precision results of the method in terms of the relative standard deviations (RSD) ranged from 1.2 to 11.8. The results were listed in Table 2.

The results demonstrated that the approach established was suitability and repeatability for the determination of fosthiazate residue in tomato, tomato plant and soil. The method is suitable for three (low, medium and high) concentration levels and considered adequate for other concentrations within linear range, which showed satisfactory results during the method validation.

Table 2 Fortification and recovery of fosthiazate in tomato and soil samples

Sample types	Fortification levels (mg kg^{-1})	Recovery (%)	RSD (%)
Tomato	0.002	95.8 ± 1.9	2.0
	0.02	99.2 ± 1.4	1.4
	0.1	98.7 ± 1.2	1.2
Soil	0.002	97.7 ± 4.2	4.3
	0.02	97.6 ± 4.8	4.9
	0.1	96.6 ± 1.7	1.8
Tomato plant	0.002	97.1 ± 11.4	11.8
	0.02	96.5 ± 5.1	5.3
	0.1	108.5 ± 3.8	3.5

Three different locations were chosen to study dissipation of fosthiazate residues in tomato and soil. Granular nematicide fosthiazate was applied in soil when tomato seedlings were transplanted. First sampling was carried out 23 days in Beijing, 23 days in Liaoning and 46 days in Hubei after the tomato seedlings transplanting and the residues were calculated as the initial concentration for fosthiazate dissipation in tomato plant or tomato. Tomato plants were sampled in Beijing and tomatoes were sampled in Liaoning and Hubei.

The results of dissipation data in tomato or tomato plant are shown in Fig. 1. The initial residues in tomato plant were 12 mg/kg in Beijing and 1.3 mg/kg in Liaoning tomato samples. The initial concentration in tomato plant is higher than that in tomato, and the fosthiazate uptake in tomato plant reached the peak concentration after 23 days application. The dissipation dynamics of fosthiazate in tomato plant or tomato could be described by the following first-order kinetics equation: $C = 0.1152e^{-0.9232t}$ (Hubei), $C = 1.1896e^{-0.2699t}$ (Liaoning) and $C = 11.6039e^{-0.9139t}$ (Beijing), respectively. The dissipation half-lives (DT_{50}) for fosthiazate in tomato or tomato plant were 0.75, 2.6 and 0.76 days in Hubei, Liaoning and Beijing, respectively. The climates of the three experiment locations and sampling time are different, but the dissipation half-lives (DT_{50}) for fosthiazate in tomato or tomato plant were from 0.75 to 2.6 days. It could be concluded that the dissipation of fosthiazate in tomato or tomato plant is not affected by the weather very much.

For dissipation in soil, samples were collected after fosthiazate applied in soil immediately. Because of granular formulation, the peak residues were detected after 7 days application in Hubei and Liaoning, 20 days application in Beijing and the residues were calculated as the initial concentration for fosthiazate dissipation in soil. The results of dissipation data in soil are shown in Fig. 2. The dissipation dynamics of fosthiazate in soil could be described by the following first-order kinetics equation: $C = 0.9631e^{-0.2754t}$ (Hubei), $C = 25.3171e^{-0.0595t}$ (Liaoning) and $C = 7.5057e^{-0.1325t}$ (Beijing), respectively. The dissipation half-lives (DT_{50}) for fosthiazate in soil

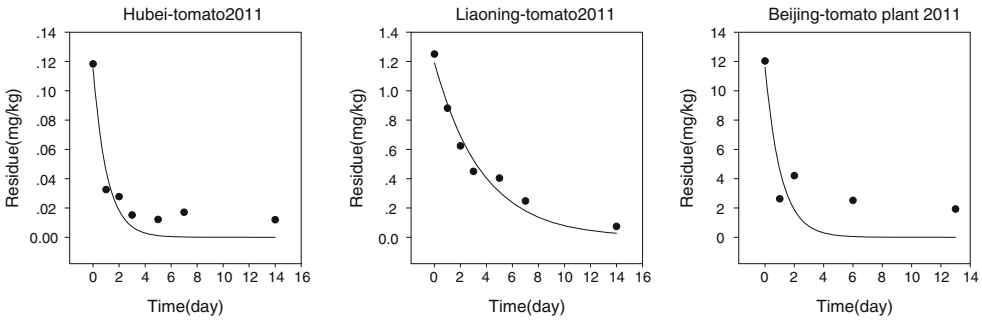

Fig. 1 Dissipation of fosthiazate in tomato or tomato plant in Hubei, Liaoning and Beijing in 2011

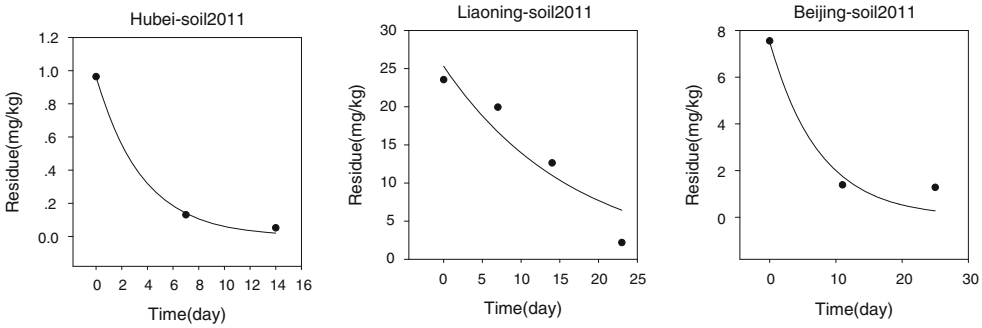

Fig. 2 Dissipation of fosthiazate in soil in Hubei, Liaoning and Beijing in 2011

Table 3 Residues of fosthizate in tomato and soil at Beijing, Liaoning and Hubei in 2011

Locations	Dosage (g a.i.ha^{-1})	Times of application	Preharvest of the first harvesting (days)	Average residues (mg kg^{-1})	
				Tomato	Soil
Liaoning	3,000	1	63	ND[a]	0.012
	4,500	1	63	ND	0.058
Beijing	3,000	1	52	ND	0.19
	4,500	1	52	ND	0.27
Hubei	3,000	1	60	0.012	0.055
	4,500	1	60	0.023	0.086

[a] Not detected, lower than limit of detection (LOD)

were 2.5, 5.2 and 11.6 days in Hubei, Liaoning and Beijing, respectively. The soil pH of three locations are 6.6 (Hubei), 6.9 (Liaoning), 7.6 (Beijing) and are all about 7, so here the soil pH is not the important factor to determine the DT50. Because of the field experiments in Beijing was carried in the greenhouse, so the dissipation of fosthiazate in soil of Beijing is slower than Hubei's and Liaoning's. According to the actual soil organic matter content, we can see the result is reasonable.

The concentration level of fosthiazate in tomato and soil could be detected after application of fosthiazate at 3,000 g a.i.ha^{-1} (recommended high dosage) and high dosage 4,500 g a.i.ha^{-1} (1.5 times the recommended high dosage) at three locations. The residues of fosthiazate (Table 3) in tomatoes were all below 0.023 mg kg^{-1} 52 days after the treatments and the residues in soil were positive correlated with the dosage.

The methods used for extraction, clean-up and estimation of residues were found to be satisfy qualification as well as quantitation. Fosthiazate dissipated slower in soil than in tomato in three different locations which were located in northern and middle China. According to the United States Department of Agriculture, Foreign Agricultural Service, Pesticide MRL Database, the MRL (maximum residue limit) of fosthiazate for tomato is 0.02 mg kg^{-1} in EU, 0.2 mg kg^{-1} in Japan. The residues of fosthiazate in tomato and soil reached below the MRL of Japan when harvesting at the tested dosages.

The present study suggests that fosthiazate could be used in tomato safely with recommended dosage. There is no MRL of fosthiazate for tomato to be legislated publicly in China (http://www.mrldatabase.com).This work would be also helpful for the China government to establish the

MRL of fosthiazate in tomato and to provide guidance on the proper and safe use of this nematicide.

Acknowledgments This study was sponsored by Yifan Chemical Technology Limited (Zhejiang Province, China) and the Institute for the Control of Agrochemicals, Ministry of Agriculture of the People's Republic of China.

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