



Clothianidin dissipation in tomato and soil, and distribution in tomato peel and flesh

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ABSTRACT

Clothianidin, a new neonicotinoid insecticide, was systematically evaluated. An analytical method using gas chromatography with electron capture detection was developed. Recoveries were between 92% and 102%, with relative standard deviations from 3% to 5% at three fortified levels. The decrease of clothianidin in tomato and soil samples under field conditions at Beijing, Shandong, and Anhui were determined. The dissipation rates of clothianidin fit first-order kinetics. Its half-lives ranged from 6.7 to 12.7 days in soil, and 7.0 to 11.9 days in tomato. On the suggested pre-harvest interval of 7 days, the distribution of clothianidin in tomato peel and flesh was studied. Most residues were found on the peel. Hence, removing the tomato peel before consumption is advisable. The stability of clothianidin fortified at 0.3 or 3 mg/kg in frozen green and red ripe tomatoes was also determined. The half-life mainly depended on the spiked levels of this pesticide.

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1. Introduction

Clothianidin, (*E*)-1-(2-chloro-1,3-thiazol-5-yl-methyl)-3-methyl-2-nitroguanidine, is a neonicotinoid insecticide. It had been discovered by the Agro Division of the Sumitomo Chemical Co., Ltd. (formerly Takeda Chemical Industries, Ltd.), and was co-developed with Bayer Crop Science (Uneme, 2011). This pesticide is highly effective in controlling hemipterous insects as well as coleopterous, thysanopterous, and certain lepidopterous pests (Chen, Huang, Wong, & Li, 2005). Water-soluble granules of 16% and 0.5% clothianidin formulations are used in rice, melon, pear, mango, tomato, cucumber, leafy vegetables, and tea plantations in Taiwan (Chen, Wang, Li, & Gong, 2009). Uneme (2011) has reported the physical, chemical, biological, and toxicological (i.e., mammalian and environmental toxicities) properties of clothianidin.

There is a body of literature on clothianidin. Its structural features and synthesis have been studied by Uneme (2011). Its agonistic action on nicotinic acetylcholine receptors (nAChRs) and effects on the dopaminergic system of rat striatum have been examined by de Oliveira, Nunes, Barbosa, Pallares, and Faro (2010) by *in vivo* brain microdialysis. Its effects on nAChRs expressed on cercal afferent/giant interneuron synapses and dorsal unpaired median neurons have been explored by Thany (2009). However, studies on the

residue and dissipation of clothianidin are limited. Hou, Cai, Zhang, & Wan, (2010) and Xie et al., (2009) have developed analytical methods for the determination of several neonicotinoid insecticides, including clothianidin, in vegetable, fruit, and tea. The former has used high performance liquid chromatography (HPLC) with diode-array detection (DAD). The latter has used HPLC with tandem mass spectrometry (MS/MS). Chen, Huang, Wong, & Li, (2005) has analyzed clothianidin and its four metabolites in rice by HPLC. Drozdzyński (2008) has determined clothianidin residues in inflorescences of common horse chestnut using HPLC–MS/MS (Drozdzyński, Folkman, & Gnusowski, 2008). Chen, Wang, Gong, Li, and Zhao (2008) and Chen, Wang, Li, and Gong, (2009) have analyzed clothianidin dissipation in *Brassica chinensis* by HPLC.

Clothianidin is used in tomato, one of the most widely produced vegetables, for protection against *Besimtia tabaci*. However, to the best of our knowledge, there are few studies on clothianidin dissipation in tomato using analytical methods. Tomato fruits gradually ripen and are usually harvested weekly. In practice, tomatoes are harvested in two different physiological stages, namely, the green and red tomato stages, depending on the time interval between harvesting and consumption. Green ripe tomatoes can be consumed 4–6 days after harvesting. Red ones can be immediately consumed (Omirou, Vryzas, Papadopoulou-Mourkidou, & Economou, 2009).

In Japan, Korea, and the USA, the maximum residue limits (MRLs) are 3, 1, and 0.05 mg/kg, respectively. The pre-harvest

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interval (PHI) for clothianidin is 1 day suggested by Japan. In China, the suggested PHI is 7 days, and there is no suggested MRL.

Clothianidin dissipation in tomato was investigated using an analytical method based on solid-phase extraction (SPE) cleanup and gas chromatography (GC) with electron capture detection (ECD). Confirmation by GC–MS was performed. This determination of clothianidin by GC was a pioneer endeavor. Clothianidin dissipation in tomato and soil in three sites (Anhui, Shandong, and Beijing) was determined. Clothianidin stability in frozen green and red ripe tomatoes spiked at different initial levels was evaluated. Clothianidin residue distribution in tomato flesh and peel was also detected on harvest day. These residue data may help the government generate guidelines for the proper and safe use of this pesticide.

2. Materials and methods

2.1. Chemicals and solvents

The clothianidin standard was purchased at 99.0% purity. The formulation used in the experiments was 50% water dispersible granule (WDG). Analytical grade ethyl acetate, acetone, petroleum ether (60–90 °C), sodium chloride were obtained from the Beijing Chemical Reagent Co., Ltd. Petroleum ether was distilled before use. HPLC grade acetonitrile and hexane were purchased from Dikma Technologies, Inc.

Clothianidin has a melting point of 176.8 °C and vapor pressure of 3.8×10^{-11} (20 °C). Its solubilities at 25 °C are 0.304 g/L (pH 4) and 0.340 g/L (pH 10) in water, 15.2 g/L in acetone, 6.26 g/L in methanol, as well as 2.03 g/L in ethyl acetate. Its partition coefficients (log Pow) are 0.893 (pH 4), 0.905 (pH 7), and 0.873 (pH 10). At room temperature, clothianidin is stable in an aqueous solution in the dark, but is unstable under daylight irradiation.

2.2. Field description

All field trials were conducted according to the “Guidelines on Pesticide Residue Trials” (NY/T 788-2004) issued by the Institute for the Control of Agrochemicals, Ministry of Agriculture, People’s Republic of China. The field trials were carried out in Beijing (116.25° E, 39.92° N), Anhui Province (Hefei, 117.16° E, 31.51° N), and Shandong Province (Qingdao, 120.19° E, 36.04° N), which were geographically separated. None of the farms had been treated with clothianidin in the past. Each experimental treatment consisted of three replicate plots and a control plot. The area of each plot was 15 m². The plots were 1 m apart from one another.

2.3. Experimental design of the dissipation study under field conditions

To study the dissipation of clothianidin in tomato and soil, clothianidin (50% WDG) was dissolved in water and applied to the tomato plots at a dosage of 120 g a.i./ha (2 times the recommended dosage). Representative samples were collected from each plot after spraying the insecticide on days 0 (2 h), 1, 3, 5, 7, 14, and 21. The soil samples were collected on days 0 (2 h), 1, 3, 5, 7, 14, 21, 30, 45, and 60 using a soil auger.

All samples were stored at –20 °C until further analysis.

2.4. Experimental design of the distribution study in tomato peel and flesh

To investigate the final residues of clothianidin in tomato flesh and peel, both the recommended dose (60 g a.i./ha sprayed 3 and 4 times) and 1.5 times the recommended dose (90 g a.i./ha sprayed 3

and 4 times) were applied to each plot. There was an interval of 7 days between each application. The tomato flesh and peel samples collected from the field 7 days after spraying were separated and analyzed according to the analytical steps detailed below.

2.5. Experimental design of the dissipation study in frozen green and red ripe tomato samples

To study clothianidin dissipation in green and red ripe tomatoes frozen at –20 °C, entire tomato samples were crushed. A certain working solution was added to obtain clothianidin concentrations of about 3 and 0.3 mg/kg. The samples were stored under –20 °C and analyzed after 0, 1, 3, 5, 7, 14, 21, 28, 45 days.

2.6. Sample preparation

2.6.1. Tomato samples

For the extraction, entire field tomato samples were thoroughly crushed using a blender. About 10 g of the minced tomato sample was weighed, placed in a 50 mL centrifuge tube, and extracted with 20 mL acetonitrile by ultrasonication for 10 min. About 5 g of sodium chloride was then added. The mixture was vigorously mixed manually for 1 min, and centrifuged at 3000 rpm for 5 min. A 10 mL aliquot of the upper layer was evaporated to near dryness using a vacuum rotary evaporator at 35 °C.

For the cleanup, a Florisil SPE cartridge (1000 mg, 6 mL; Agela Technologies Inc.) was used. The cartridge was first conditioned with 5 mL each of acetone and petroleum ether. The concentrated extracts were thrice washed with 5 mL of petroleum ether/acetone (8:2, v/v), and transferred to the cartridge. The washings were discarded. The cartridge was eluted with 10 mL of petroleum ether/acetone (6:4, v/v). The eluent was collected, evaporated to near dryness using a vacuum rotary evaporator at 30 °C, and evaporated to complete dryness under a gentle nitrogen stream. The residue was dissolved in 2.5 mL of petroleum ether/acetone (8:2, v/v) for GC–ECD analysis.

2.6.2. Soil samples

Soil samples were prepared by removing large stones. About 10 g of a sample was weighed and placed in a 50 mL centrifuge tube. Subsequently, 5 mL of distilled water and 20 mL of ethyl acetate were added. Extraction was performed by ultrasonication for 20 min. About 5 g of sodium chloride was added, and the mixture was vigorously shaken for 1 min. Centrifugation at 3000 rpm for 5 min followed. A 10 mL aliquot of the upper layer was evaporated to near dryness using a vacuum rotary evaporator at 30 °C. Evaporation to complete dryness was performed under a nitrogen stream. The residue was dissolved in 2.5 mL of petroleum ether/acetone (8:2, v/v) for GC–ECD analysis.

2.7. Instrumental analyses

Clothianidin was determined using an Agilent 7890A GC equipped with an ECD and an HP-5 (30 m × 0.32 mm × 0.25 μm) capillary column. The injector was operated at 270 °C, and the injection volume was 2 μL. The oven temperature was programmed to ramp from 100 °C for 5 min, was raised to 150 °C at 10 °C/min, and then raised to 260 °C at 30 °C/min for 5 min. Nitrogen was used as the carrier gas at a flow rate of 2 mL/min. The detector was operated at 300 °C. The approximate retention time of clothianidin was 11.135 min.

An Agilent 6890N-5973 MS under electroionization mode was used to confirm clothianidin. A DB-1 chromatographic column (30 m × 0.25 mm × 0.25 μm) supplied by Agilent Technologies was employed. Helium was used as the carrier gas at 1 mL/min. The

column temperature was maintained at 100 °C for 1 min, then programmed at 10 °C/min to 150 °C, and then raised to 280 °C at 20 °C/min for 2 min. The injector port was maintained at 270 °C, and 2 mL of the sample was injected in the pulsed splitless mode. The electron impact ionization mode was used at an ionizing energy of 70 eV. The ion source temperature was 230 °C. The MS quad temperature was 150 °C. The solvent delay was 5 min.

2.8. Data and statistical analyses

The dissipation dynamics and half-life of clothianidin were determined by the first-order kinetic equations $C_t = C_0 e^{-kt}$ and $t_{1/2} = \ln 2/k$, respectively. C_t is the clothianidin concentration at time t , C_0 is the initial concentration, k is the rate constant, and $t_{1/2}$ is the half-life (Li, Qiu, & Wu, 2008).

3. Results and discussion

3.1. Method validation

Clothianidin has previously been determined by HPLC coupled with different detectors such as UV (Chen et al., 2009), DAD (Hou, Cai, Zhang, & Wan, 2010), or MS/MS (Xie et al., 2009). In the present study, clothianidin was analyzed by GC–ECD, which was the first time to determine it by GC, and this method had several advantages: (1) limit of quantitation (LOQ) was 0.01 mg/kg in tomato and soil, defined as the minimum fortified level of recovery, which was achieved by MS/MS in other studies; (2) this method was rugged despite of its ease. It can remove impurities of tomato and soil samples efficiently, and there was no interferences at the elute time of clothianidin (typical GC–ECD chromatograms were shown in Fig. 1). Consequently, the method was sensitive, selective and easy to master.

The recovery experiment was spiked at three levels (shown in Table 1). The mean recoveries from five replicates of fortified samples for tomato and soil were within the range of 92–102%. The relative standard deviations (RSDs) were between 3% and 5%. All recoveries and RSD values were acceptable. The response was linear within the range of 0.01–4.0 mg/L ($y = 29,680x + 297.37$, $R^2 = 0.9993$).

The identity of clothianidin residues was confirmed by GC–MS in the scan mode (m/z 50–500). Under the above described GC–MS

Table 1
Fortified recoveries of clothianidin in tomato and soil ($n = 5$).

Matrix	Spiked level (mg/kg)	Average recovery (%)	RSD(%)
Tomato	0.01	97	3
	0.3	92	4
	3	97	4
Soil	0.01	94	3
	0.3	98	5
	3	102	5

conditions, the retention time of clothianidin was 8.36 min. The characteristic ions were 132, 134, 187, and 189, as shown in Fig. 2.

3.2. Clothianidin dissipation in tomato and soil under open conditions

Table 2 shows the dissipation equation, determination coefficient, and half-lives of clothianidin in tomato and soil in the Beijing, Shandong, and Anhui sites. Clothianidin residues in tomato and soil were observed to have a gradual dissipation with time.

3.2.1. In soil samples

The initial clothianidin concentration in the soil from Beijing was 4.53 mg/kg, and the residues decreased to 1.20 mg/kg 30 days after application. This result indicated that 74% of the pesticide dissipated. The initial clothianidin concentrations in the soils from Shandong and Anhui were 10.05 and 10.92 mg/kg, respectively. The residues decreased to 3.28 and 0.70 mg/kg 21 days after application, indicating that 67% and 94% of clothianidin dissipated in Shandong and Anhui, respectively. The half-life of clothianidin in the Beijing soil (12.7 days) was similar with the half-life in the Shandong soil (12.6 days). The half-life in the Anhui soil (6.7 days) was much shorter.

The behavior of clothianidin in soil is governed by a variety of complex dynamic physical, chemical, and biological processes. Such processes include sorption–desorption, volatilization, chemical and biological degradation, uptake by plants, run-off, as well as leaching (Fang & Qiu, 2002). Differences in dissipation rates in various environments are influenced by many factors, such as weather (rain and temperature), soil character (pH, microorganisms, and organic matter), as well as application period of pesticide.

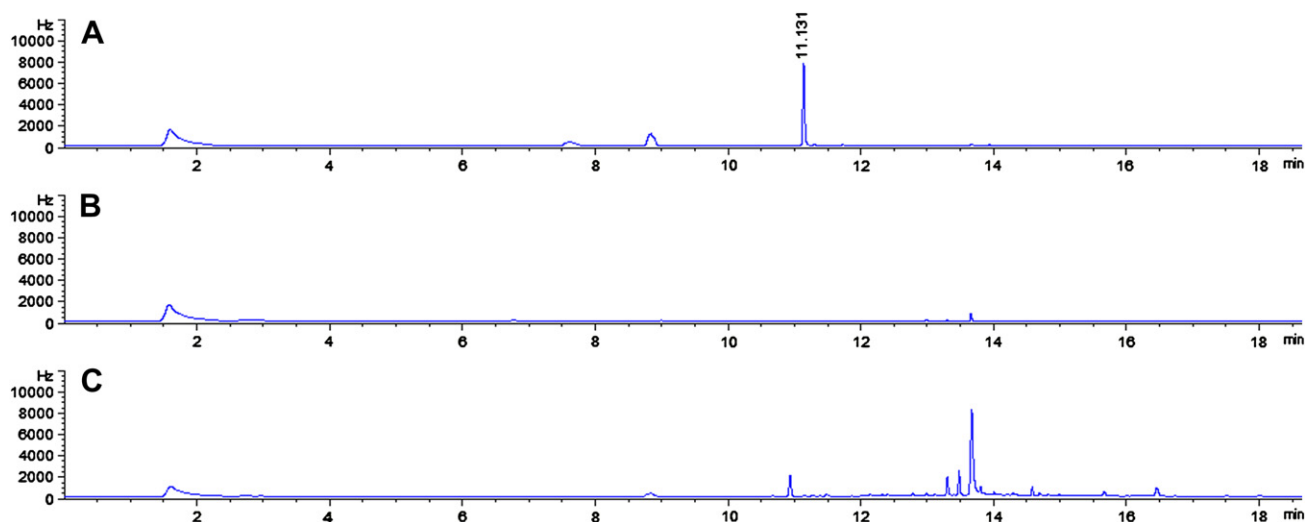


Fig. 1. The chromatogram of (A) standard clothianidin at 1.0 mg/kg; (B) control tomato sample; (C) control soil sample.

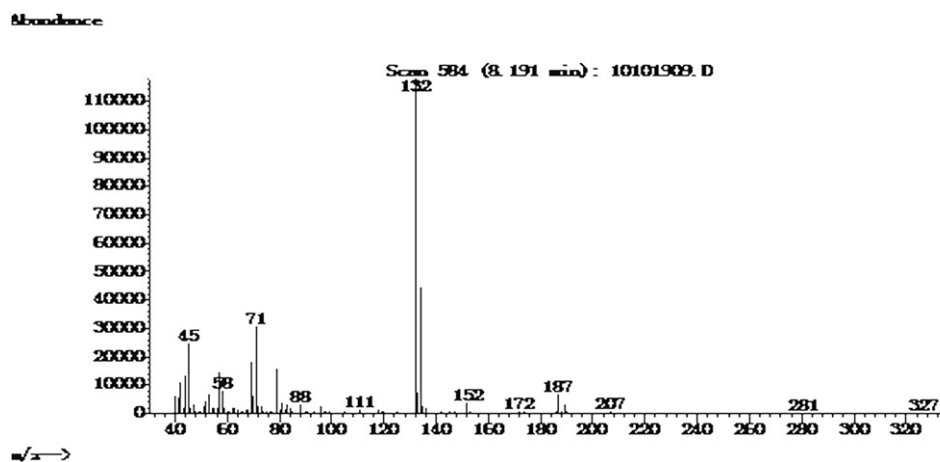


Fig. 2. The MS spectrum of a standard solution of clothianidin at 6 mg/kg (under electron impact ionization mode, m/z 50–500).

Table 2
Regression equation, correlation coefficient and half-life of clothianidin in tomato and soil.

Sample	Sample location	Regression equation	Correlation coefficient	Half-life (day)
Soil	Beijing	$y = 4.9618 e^{-0.0546x}$	0.9058	12.7
	Shandong	$y = 10.815 e^{-0.0551x}$	0.9360	12.6
	Anhui	$y = 7.6992 e^{-0.1028x}$	0.9215	6.7
Tomato	Beijing	$y = 0.1247 e^{-0.0989x}$	0.9048	7.0
	Shandong	$y = 0.0383 e^{-0.09x}$	0.9013	7.7
	Anhui	$y = 0.3351 e^{-0.0583x}$	0.9262	11.9

In the present study, samples were collected in Beijing and Shandong, which are in northern China, and in Anhui, which is in the south. The geographical difference led to significant variances in many aspects (e.g., humidity, rain, sunshine, and so on). These factors influenced the dissipation of clothianidin.

3.2.2. In tomato samples

In the tomato samples from Beijing, Shandong, and Anhui, the initial concentrations were 0.17, 0.05, and 0.43 mg/kg, respectively. The differences were probably due to the varied tomato sizes upon clothianidin application. At Beijing and Anhui, the residues were below 0.01 mg/kg 30 and 21 days after clothianidin application. In Shandong, 86% clothianidin residue dissipated at 30 days. The half-lives were 7.0, 7.7, and 11.9 days in Beijing, Shandong, and Anhui, respectively. Obviously, the half-lives in Beijing and Shandong were nearly the same, and the half-life in Anhui was much longer. The half-lives were not similar with that previously reported for clothianidin in cabbage (1–2 days) by Chen, Wang, Gong, Li, and Zhao (2008).

Under field conditions, the dissipation of pesticides is affected by various environmental factors, such as volatilization, wash-off, and photodegradation. In agricultural fields, the growth dilution of treated plants may play a significant role in the diminution of pesticides in crop plants (Huang et al., 2010). The growth rate also played a certain role in clothianidin dissipation in the current study. The different growth rates of the tomatoes from the three locations resulted in different half-lives. Photodegradation may have also played a significant role. Annual sunshine hours (ASHs) significantly affect the photodegradation rate of pesticides in an open environment (Li, Ma, Li, Qin, & Wu, 2011). The physical–chemical properties showed as above that at room temperature, clothianidin is unstable under daylight irradiation in an aqueous solution. The ASHs in three sites were different because of the different latitudes and weather conditions, which may lead to the different dissipation of clothianidin.

In Beijing and Shandong, the half-life of clothianidin was shorter in tomato than in soil. However, in Anhui, the decrease in clothianidin was interestingly more rapid in soil than in tomato. The dissipation study of a pesticide is an important part for full evaluation of it. These data would be helpful for the proper and safe use of this pesticide.

3.3. Final residues of clothianidin in tomato flesh and peel

As aforementioned, the residue levels of clothianidin in tomato peel and flesh were determined on the suggested PHI in China. Clothianidin was applied 3 and 4 times at the recommended dosage and at 1.5 times the recommended dosage. The results shown in Table 3 revealed that most clothianidin was in tomato peel. For example, when 60 g a.i./ha was thrice applied, the residue in peel was 5.11 times that in flesh. Under other conditions, the ratio was more than 5. In other words, more than 80% of clothianidin was in tomato peel on harvest day. The above results can be attributed to the low log Pow values of clothianidin (0.893 at pH 4, 0.905 at pH 7, and 0.873 at pH 10). These values may indicate that clothianidin was difficult to dissolve in an organic phase and hence penetrated the peel into the flesh. Therefore, the peel must be removed before consumption.

Table 3
The final residues of clothianidin on tomato flesh and peel.

Days after spraying	Number of times sprayed	Dosage (g a.i./ha)	Residue on flesh (mg/kg)	Residue on peel (mg/kg)	$C_{\text{peel}}/C_{\text{flesh}}$
7	3	60	0.027 ± 0.001	0.138 ± 0.022	5.11
	4	60	0.035 ± 0.001	0.186 ± 0.043	5.31
	3	90	0.037 ± 0.005	0.197 ± 0.073	5.32
	4	90	0.028 ± 0.001	0.186 ± 0.047	6.64

Table 4
Regression equation, correlation coefficient and half-life of clothianidin in tomato and soil.

Concentration of clothianidin (mg/kg)	Sample type	Regression equation	Correlation coefficient	Half-life (day)
0.3	Green tomato	$y = 0.3174 e^{-0.0445x}$	0.8991	15.6
	Ripe tomato	$y = 0.3258 e^{-0.0412x}$	0.8625	16.8
3	Green tomato	$y = 2.2767 e^{-0.0206x}$	0.9419	33.6
	Ripe tomato	$y = 2.2246 e^{-0.0169x}$	0.9052	41.0

The weight of the peel is about 1–2% of a whole tomato. Consequently, the residues for whole tomatoes are well below the MRLs set by USA (0.05 mg/kg), Korea (1 mg/kg), and Japan (3 mg/kg).

3.4. Stability

Table 4 shows the dissipation of clothianidin in minced green and red ripe tomato samples during storage. The residues of clothianidin gradually decreased with storage time, and the dissipation had the same trend at the same fortified level. However, the corresponding pH values were different (4.51 for green and 4.14 for red). At 3 mg/kg clothianidin concentration, the average half-life in green and red ripe tomatoes was 37.3 days. At 0.3 mg/kg, the average half-life was 16.2 days.

Clothianidin in the tomato samples were comparatively unstable, especially at low concentrations. Therefore, whole tomatoes should be sampled, stored, and transferred in future field studies. Treated tomato samples should also not be stored for a long time even under frozen conditions. Analyses should be done as soon as possible.

4. Conclusions

The dissipation rate of clothianidin in tomato and soil samples were evaluated under field conditions, and the residues in tomato peel and flesh were determined. The dissipation rates at three sites, namely, Beijing, Anhui, and Shandong were different. The half-lives in Beijing and Shandong were similar, and they were different from that in Anhui. The final residues on harvest day were higher in tomato peel than in flesh. The stability of clothianidin in green and red ripe tomatoes under frozen condition depended on the clothianidin concentration. A higher clothianidin level resulted in a longer half-life.

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