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# Dissipation of Chlorantraniliprole in Tomato Fruits and Soil

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**Abstract** The main objective of this study was to understand the residue and persistence behaviour of new insecticide chlorantraniliprole in tomato fruit and soil samples. Its residue was analyzed by HPLC and it dissipated in tomato fruit and soil following first order kinetics. The results showed half life ($t_{1/2}$) value of 3.30 and 3.66 days for chlorantraniliprole in tomato fruit and soil, respectively. According to maximum residue limit (MRL) the pre-harvest interval (PHI) of chlorantraniliprole on tomato was 8-days after the treatment.

**Keywords** Chlorantraniliprole · Residues · Tomato · Soil

Chlorantraniliprole [3-bromo-N-[4-chloro-2-methyl-6-[(methyl amino) carbonyl] phenyl]-1-(3-chloro-2-pyridinyl)-1H-pyrazole-5-caroxamide] is a recently introduced anthranilic diamide insecticide developed by Dupont Crop Protection in 2007. It is used as the active ingredient in many different formulations. This compound has a novel mode of action for synthetic insecticides called Ryanodine Receptor Activators (Cordova et al. 2006; Sattelle et al. 2008). The degradation of synthetic organic pesticides begins as soon as they are synthesized. Breakdown of the principle components may occur due to harsh environmental condition or chemical interaction (Sanz-Asensio et al. 1997). Therefore, dissipation studies for a given crop in the open field conditions of each growing area are necessary to test if the established pre-harvest interval (PHI) ensures that residues level are below the maximum residue limit (MRL). Tomato is considered to be an important crop and basic component of diet and is used almost daily in Egypt, raw, home-cooked or processed as a canned product, juice or paste (El-Nabarawy and Abou-Dania 1992). The objective of this study was to investigate the residual behavior and the dissipation rate of chlorantraniliprole in tomato fruits and soil (Fig. 1).

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## Materials and Methods

Analytical standard of chlorantraniliprole (purity ≥96%) was supplied by DuPont Crop Protection. A stock standard solution (100 mg/L) was prepared with methanol and stored at −20°C. Sonication was required to dissolve the standard. All solvent were HPLC grade and supplied by Alliance Bio, USA. Florisil (60–100 mesh) was pesticide residue grade (Sigma, USA) and activated in an oven at 130°C for 24 h. Prior to actual use in a column, it was cooled in a dessicator and subjected to appropriate deactivation with water (3% by weight to Florisil). Tomato plants (*lycopersicon esculentum*) were cultivated in plots consisting of eight rows. Plots were arranged in complete randomized block design at El-Hakimayia village, Miet-Gamer Province, El-Dkahlyia Governorate, Egypt, on 25 December 2010. Common agricultural and fertilization practices were used. Mature plants was sprayed by chlorantraniliprole 20%SC (Coragen) at the recommended rate of application i.e. 60 mL per feddan (1 feddan = 4,200 $m^2$). The amount of formulated pesticide required for 1 feddan was diluted in 200 mL of water applied to plants using knapsack sprayer motor. The control plots were left unsprayed. There was no rainfall at any time during the experimental period. The average daily temperature during the experiment was from 17 to 26°C. Sampling

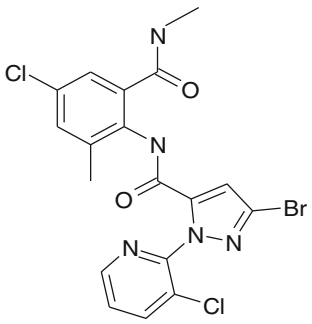


**Fig. 1** Structure of Chlorantraniliprole

was performed by randomly collecting from various places of the experimental plots according to the FAO/WHO (1986) recommendations. Three replicates were made and fruit samples were taken 2 h after pesticide application. After words, the fruits were collected randomly after 1, 3, 7, 10, 12, 15 and 21 days after application. Random samples of about 1 kg were collected from each plot and the samples were transferred immediately to the laboratory in an ice box. The samples were comminuted using the laboratory blender and representative homogenized (10 g) of each was then placed into 50 mL polyethylene tube and frozen at −20°C until analysis time (within 4 days of sampling). Representative samples of treated or untreated soil were collected from the surface of the plots to a depth of 10 cm after 2 h, 1, 3, 7, 10, 12, 15 and 21 days after plant treatment. Chlorantraniliprole was extracted from tomato fruit according to the method of Xu et al. (2010). Each sample was vortexed with 20 mL acetonitrile for 2 min. To this extract, 5 g sodium chloride was added and vortexed for another 1 min to obtained a separation of water and acetonitrile. The vortexed mixture was centrifuged at 3,800 rpm for 5 min. 10 mL of the clear upper acetonitrile phase was transferred to a spherical flask and evaporated to dryness in vacuum at 40°C water bath temperature. The dry residue in the flask was redissolved with 2 mL solvent (acetone/n-hexane = 2/8, v/v) for clean-up. 20 g of the soil sample was shaken mechanically with 100 mL of acetonitrile for 1 h in 500 mL stopper conical flask. The extract was carefully decanted and filtered through a clean pad of cotton. Known volume of extract was taken and evaporated to dryness. The dry residue in the flask was redissolved with 2 mL solvent (acetone/n-hexane = 2/8, v/v) for clean-up. The extracts were cleaned-up according to the method developed by Xu et al. (2010). The chromatographic column used for clean-up was packed from bottom to top with (1) absorbent cotton, (2) 1 cm high anhydrous sodium sulfate, (3) 2 g florisil, and (4) 1 cm high anhydrous sodium sulfate. The packed column was preconditioned with 5 mL solvent (acetone/n-hexane = 2/8, v/v). The redissolved extract was applied to the column. Then 5 mL of acetone/n-hexane (2/8, v/v) was used to separate interfering material and discarded. The elute obtained with the following 25 mL of acetone/n-hexane (2/8, v/v) was collected in spherical flask and then evaporated to dryness. The residue was redissolved with 1 mL methanol, and finally filtered by a 0.45 μm filter membrane for HPLC analysis. The rate of degradation (K) and half-life ($t_{1/2}$) values were obtained from the following equation of Gomaa and Belal (1975).

$$\text{Rate of degradation (K)} = 2.303 \times \text{slope} \quad (1)$$

$$\text{Half} - \text{life } (t_{1/2}) = 0.693/\text{K} \quad (2)$$

HPLC analysis was performed with an Agilent 1100 HPLC system (USA), with photodiode array detector. The chromatographic column was $C_8$ Zorbax SB (250 × 4.6 mm, 5 μm film thickness). Flow rate of mobile phase (Methanol/water = 95/5 v/v) was 0.8 mL/min. and injection volume was 20 μL. Detection wavelength for detection of chlorantraniliprole was set at 260 nm. The retention time of chlorantraniliprole was about 4.9 min. Control tomato and soil samples were fortified with a standard solution of chlorantraniliprole at three levels. Final concentration of chlorantraniliprole in control samples were 0.05, 0.1 and 0.5 μg. Extraction of control samples was performed as mentioned earlier. Results of recovery study are shown in Table 1. Data were statistically evaluated by one-way analysis of variance (ANOVA). All statistical analysis was done using the statistical package for social sciences (SPSS 16.0) program.

**Table 1** Recoveries and relative standard deviations for chlorantraniliprole in tomato ruit and soil at various fortification level

| Fortified level | Tomato fruit | | Soil | |
|---|---|---|---|---|
| (mg/kg) (n[a] = 3) | Recovery | RSD | Recovery | RSD |
| 0.05 | 104 | 5.4 | 98 | 7.8 |
| 0.1 | 99 | 6.8 | 96 | 5.2 |
| 0.5 | 98 | 3.3 | 95 | 6.2 |

[a] Number of replicates

## Results and Discussion

The dissipation trends of chlorantraniliprole in tomato fruit were shown in Table 2. Chlorantraniliprole dissipated rapidly after application. The concentration of chlorantraniliprole 2 h after treatment was 2.308 mg/kg. The residues amount decreased to 1.71 2 mg/kg, in tomato fruit within the first 24 h after application. Following that period, chlorantraniliprole residues in/on tomato fruit decreased to 0.996, 0.620, 0.390, 0.115 and 0.10 mg/kg, at 3, 7, 10, 12 and 15 days after treatment, respectively. Samples taken 21 days after treatment contained no detectable amount of

**Table 2** Dissipation of chlorantraniliprole residues (mg $kg^{-1}$ ± SD[a]) in/on tomato fruit and soil

| Time (days) | Tomato fruit | | Soil | |
|---|---|---|---|---|
| | Residue level (mean ± SD) | Dissipation % | Residue level (mean ± SD) | Dissipation % |
| Zero | 2.308 ± 0.151 | 0.00 | 4.555 ± 0.445 | 0.00 |
| 1 | 1.712 ± 0.154 | 25.82 | 3.193 ± 0.217 | 29.90 |
| 3 | 0.996 ± 0.148 | 56.84 | 2.215 ± 0.024 | 51.37 |
| 7 | 0.620 ± 0.071 | 73.13 | 1.710 ± 0.339 | 62.45 |
| 10 | 0.390 ± 0.056 | 83.10 | 0.986 ± 0.049 | 78.35 |
| 12 | 0.115 ± 0.020 | 95.01 | 0.593 ± 0.059 | 86.98 |
| 15 | 0.100 ± 0.001 | 95.66 | 0.165 ± 0.011 | 96.37 |
| 21 | ND[b] | – | ND | – |
| MRL | 0.3 | | – | |
| k ($days^{-1}$) | 0.209 | | 0.189 | |
| $t_{1/2}$ (days) | 3.30 | | 3.66 | |

[a] n = 2

[b] Not detectable

chlorantraniliprole (below the quantification limit 0.03 mg/kg) in tomato fruit. The dissipation rate of tomato fruit exhibited a first order kinetics. The half-life of chlorantraniliprole calculated in tomato fruit treated at recommended dose was 3.30-day (Table 2). The dissipation of the pesticide residues in/on crops depends on environmental condition, type of application, plant species, dosage, and interval between application, the relation between the treated surface and its weight and living state of the plant surface, in addition to harvest time (Khay et al. 2008; Cabras et al. 1990). While the FAO/WHO has not established maximum residue limits (MRLs) for chlorantraniliprole, European Union MRL for chlorantraniliprole in tomato is 0.6 mg/kg. It can thus be concluded that the preharvest interval (PHI) of chlorantraniliprole on tomato was 8-days after the last treatment. The results showed that the dissipation was also fast in the soil, although the concentration level of chlorantraniliprole in soil higher than in the tomato fruit. The half-life of chlorantraniliprole calculated in soil under the treated plant was 3.6-days.

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