Chlorantraniliprole Behaviour in Tomatoes under Climatic Changes of Temperature and Humidity

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Abstract: To evaluate the fate variation of chlorantraniliprole with climatic changes of the air temperature and the relative humidity in tomato fruits, the decline rate of chlorantraniliprole residues was investigated in winter and summer seasons, for three consecutive years under field condition. Residues of chlorantraniliprole were determined by high performance liquid chromatography with photodiode array detector (HPLC-DAD). Chlorantraniliprole was sprayed on tomato at recommended dosage. Samples of tomato were collected at one hour, 1, 3, 5, 7, 10 and 15 days after treatment. The decline rates of chlorantraniliprole were described using first-order kinetics. The results indicated that, the half–lives of chlorantraniliprole in tomatoes and the pre-harvest interval (PHI) changed significantly in some cases among winter and summer seasons, and in other cases in the same season in different years of the trial. The least half–life and PHI were 2.441 and 6 d in summer season of 2014, respectively, while the longest were 2.988 and 7.400 d in winter season of 2012, respectively. Also, a negative correlation coefficient was observed with the air temperature and both half–life times and PHIs, while it was a positive in the case of the relative humidity. It was concluded that PHIs may be significantly varied from season to season or from year to year. This work would be helpful to safe use of this insecticide.

Keywords: Chlorantraniliprole; pre-harvest interval (PHI); climatic changes; residue; tomato; half–life time

1. Introduction:

Climate change influences the risk of pesticides leaching, since higher temperatures and increased rainfall lead to contrasting effects on pesticide leaching (Palikhe 2007and Steffens *et al*., 2014). The warming is important, though its intensity has varied from decade to decade, from region to region and from season to season, and been mainly caused by greenhouse gases (Crosson, 1997). Temperature has a direct and an indirect influences on the persistence of pesticides in the plants (Bedos, 2002 and Tepper, 2012). Climate change refers to any change in climate overtime, whether due to natural variability or as a result of human activity (McCarthy *et al*., 2001 and Parry *et al*., 2007). Climate change has become a global issue in recent times manifesting in variations of different climate parameters including cloud cover, precipitation, temperature ranges, sea levels and vapour pressure. The variations in climate parameters affect different sectors of the economy, such as agriculture, health, water resources, energy, etc. (Ogbo *et al*., 2013).

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Tomato is one of the most popular vegetables in Egypt. Annual tomato production in the country is estimated to be seven million metric tones and area under cultivation about 221 thousand hectares which represent about 34 % of the average area of vegetables in Egypt. The tomato is considered to be an important crop and basic component of the diet and is used almost daily in Egypt. It is consumed in raw form as salad, home-cooked or processed as a sauce, juice or paste. The tomato crop is frequently infested by a number of insects at all stages of its development (Malhat, 2013). The crop is often applied with chemical pesticides to offer protection from severe damage.

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 (Fig. 1). 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*. 2006and 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).

The dissipation of chlorantraniliprole has already been studied in rice, corn and tomato crop ecosystems at varied levels of field doses under different edaphoclimatic conditions by adopting unique analytical methods (Dong et al. 2011; Xu *et al*. 2010; Malhat 2012and Malhat *et al.* 2012).

The present study was carried out to evaluate the variation of temperature and humidity in three different winter and summers on chlorantraniliprole dissipation and its PHI in tomatoes, in Etai El-Baroad, El-Beheira, Egypt, and to recommend and enhance safe usage of the insecticide to the growers.

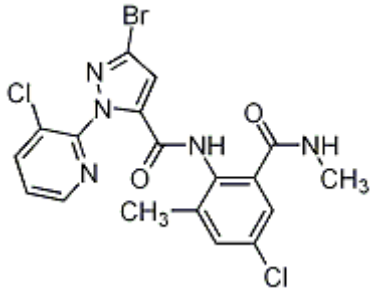

Fig. 1. Chemical structure of chlorantraniliprole

2. Materials and Methods

2.1. Reagent and chemicals

Chlorantraniliprole reference standard (purity ≥96%) was supplied by DuPont Crop Protection. All organic solvents used in this study were of HPLC grade and purchased from Scharlau (Barcelona, Spain). The suitability of solvents was ensured by running reagent blank along with actual analysis. Sodium chloride of analytical grade was obtained from El Naser Pharmaceutical Chemicals Co. (Cairo, Egypt). Anhydrous magnesium sulfate of analytical grade, purchased from Merck (Germany), was activated by heating at 400°C for 4 h in muffle furnace, then cooled and kept in a desiccator before use. Primary secondary amine (PSA, 40 µm Bondesil) was obtained from Supelco (Bellefonte, PA).

2.2. Preparation of standard solutions

The stock solution containing 1,000 µg /ml of the analyte was prepared using acetonitrile as solvent. The standard solutions used for fortification of the matrices and instrument calibration purposes were prepared by serial dilution. All standard solutions were stored at 4°C before use. The standard calibration curve of chlorantraniliprole was constructed by plotting analyte concentrations versus peak area.

2.3. Field experiment design

The experiment was conducted in Etai El-Baroad Agricultural Research Station, El-Beheira, Egypt, in winter and summer seasons, for three consecutive years. Tomato seedling [(*Solanum lycopersicum* Mill.) cv. Malika] was planted in each winter season, on October 2nd in 2011, 2012 and 2013, and on March 15th in 2012, 2013 and 2014 in each summer seasons. The experiments were designed in the following ways: plot size, 7 x 6 m; plot to plot distance, 1.5m; plant to plant distance, 0.4 m for row to row distance 1 m. Treatment plots were arranged in a randomized complete block design with three replicates. Irrigation and fertilization were made according to the crop schedule. The plots had not been treated with chlorantraniliprole in the past. To ensure the reliability of the experimental results, the field trials were previously investigated to be free of the pesticide. Treatments were carried out using a knapsack sprayer motor. Chlorantraniliprole(Coragen 20 %SC)was the commercial formulation applied at the dose recommended by the manufacturer (60 mL per feddan). The spray volume taken was 200 L/ feddan (one feddan = 0.42 ha). Untreated control tomatoes were sprayed with the same amount of water. chlorantraniliprole was sprayed on December 4th in each year in winter seasons, and on June

30th in each summer seasons of the experiment. Tomato samples were collected one hour, 1, 3, 5, 7, 10 and 15 days after each treatment. Immediately after picking, the samples were put into polyethylene bags and transported to the laboratory in an ice box, where they were chopped and thoroughly mixed. Samples were kept deep in frozen (-20 °C) until analysis. Control samples were obtained from the control plots. During the trials, the average minimum/maximum daily air temperatures and the average relative humidity (of days after chlorantraniliprole spraying) were obtained from Meteorological Station of Etai El-Baroad. There was no rainfall at any time during the experimental period.

2.4. Analytical methods

2.4.1. Sample extraction

The samples were comminuted using the laboratory blender and representative homogenized (10 g) of each was then placed into 50 ml polyethylene tube. Chlorantraniliprole was extracted from tomato fruit according to the method of Xu et al. (2010). Samples were extracted and cleaned up as follow: 20 ml of 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 acetonitrile for clean-up. An aliquot of the extract (2.0 mL) was transferred to a 5 mL centrifuge tube with 0.3 g anhydrous $MgSO_4$, 0.05 g PSA, 50 mg C18 and Graphitized carbon black (GCB) 0.005 g GCB. After shaking vigorously on vortex for 30 s, the tube was centrifuged at 10,000 rpm for 2 min. An aliquot of 2 ml was filtered through a 0.2 µm PTFE filter (Millipore, USA). The sample was then ready for the final analysis in the LC system.

2.4.2. Liquid chromatographic analysis

HPLC analysis was performed with an Agilent 1100 HPLC system (USA), with quaternary pump, manual injector (Rheodyne), thermostat compartment for the column and photodiode array detector. The chromatographic column was C_{18} Zorbax XDE (250 mm x 4.6 mm x 5 µm). The column was kept at room temperature. The flow rate of the mobile phase (methanol /water = 95/5 v/v)) was 0.8 ml/min, and injection volume was 20 µl. The wavelength for detection of chlorantraniliprole was set at 260 nm. The retention time of chlorantraniliprole was 4.9 min. Residues were estimated by comparison of peak areas of standards with that of the unknown or spiked sample run under identical conditions

2.4.3. Validation study

The method was subjected to the validation study before its application to determining the insecticide chlorantraniliprole residues in the samples. Recovery assays were carried out on samples of untreated tomato which were spiked with the target compound at three concentration levels in five replicates (Table 1). The method precision parameters in terms of average recovery and relative standard deviation were calculated and assessed according to the European Union guidelines (SANCO/12495/2011). The linearity of the chromatographic response was evaluated over the range between 0.01 and 2 mg kg^{-1} at five concentration levels.

2.5. Half-life calculation

Half-life time ($t_{1/2}$) of chlorantraniliprole was calculated mathematically according to Moye *et al.* (1987). The dissipation kinetics of chlorantraniliprole residues were determined by plotting residue against elapsed time after application, and equation of best curve fit with maximum coefficients of determination (R^2) was determined. For dissipation of targeted insecticide in tomato, exponential relationship was found to be applicable corresponding to the general first-order kinetics equation:

$$C_t = C_0 e^{-kt,}$$

Where C_t represents the concentration of the pesticide residue at the time of t, C_0 represents the initial deposits after application and k is the constant rate of pesticide disappearance per day. From this equation, the dissipation half-life periods ($t_{1/2} = ln\ (2)/k$) of the insecticide.

2.6. Statistical analysis

Data were subjected to analysis of variance (ANOVA) followed by least significant difference (CoStat Statistical Software, 1990).

Results

3.1. Linearity, recovery and detection limits

To ensure quality of the insecticide residue results, the method performance characteristics were generated and evaluated before real tomato samples were analysed. The average recovery and relative standard deviation (RSD) data of chlorantraniliprole from spiked samples are detailed in Table 1. As seen, the recoveries were in the range between 98.9% and 100.1% with associated RSDs not exceeding 7%. These results are considered to be highly satisfactory for the purpose of pesticide residue analysis and they are compliant with the European Union criteria which stipulate the average recoveries in the range 70-120% with corresponding RSD less or equal 20% (SANCO/12495/2011). The limit of quantification (LOQ) of the method was defined as the lowest spiking level for which the validation criteria were satisfied and it was equal 0.01 mg kg^{-1}. Excellent linearity with the coefficient of determination (R^2) > 0.99 was achieved for the studied insecticide when using standard in the extract of tomato matrix (matrix-matched standard).

Table 1. Recovery and relative standard deviation (RSD) percentages of chlorantraniliprole in tomato at three fortification levels

Fortified level (mg kg^{-1}) (n*=5)	Recovery (%)	RSD (%)
0.01	100.1	**7**
0.05	98.9	**8**
0.1	99.3	**5.3**

*** number of replicates**

3.2. Decline of chlorantraniliprole residues in tomato fruits

In general, the results showed that the residue of chlorantraniliprole in tomato fruits was varied significantly not only between winter and summer seasons but also in some cases between winter and winter seasons or between summer and summer seasons (when compared with the corresponding days after insecticide spraying). In winter seasons, data indicated that chlorantraniliprole residues were the lowest in year 2013, while they were highest in 2012, followed by 2011. The residues ranged from 2 to 0.030 mg kg-1. It is clear that, they varied significantly after seven days of spraying through all years of the experiment. In summer seasons, chlorantraniliprole residues were the lowest in year 2014, while they were highest in 2012, followed by 2013. The residues ranged from 1.917 to 0.029 mg kg-1. The results also revealed that the chlorantraniliprole residues were significantly lower in summer seasons than in winter seasons. The half life calculated of chlorantraniliprole was significantly changed through years of the study whether in winter or summer seasons. The half-life ranged from 2.988 d in winter 2012 to 2.441 d in summer 2014. As well as the pre-harvest intervals (PHIs) were significantly different during seasons of the trial. They were longer in winter seasons (ranged from 7.4 to 7.1 d) than in summer seasons (ranged from 6.5 to 6 d) (Table 2).

3.3 Climatic change of temperature and humidity

The averages of air temperatures and the relative humidities were fluctuated, during the days after spraying of chlorantraniliprole in tested seasons. In winter seasons, the mean air temperatures ranged from 19.06 (in 2012) to 21.0 ºC (in 2013), while the relative humidity ranged from 82.2 (in 2011) to 63.3 % (in 2012). Whereas, in summer seasons, the mean air temperatures ranged from 34.3 ºC (in 2012) to 38.3 ºC (in 2014), while the relative humidity ranged from 73.9 (in 2012) to 66.07 % (in 2014) (Table 3).

3.4 Correlation coefficient between the air temperature or relative humidity and chlorantraniliprole half lives or pre-harvest intervals (PHI) of tomato fruits

The correlation coefficient was a negative between the averages of air temperatures (of the days after chlorantraniliprole spraying of each season in the experiment) and both the half-life times of chlorantraniliprole and PHIs, with values of -0.619 and -0.973, respectively. However, it was a positive between the averages of relative humidities and both the half-life times of

chlorantraniliprole and PHIs, with values of 0.245 and 0.350, respectively (Table 4).

3. Discussion:

The influence of the climatic changes on pesticide behaviour is extremely complex, because not only do they affect most of the chemical and plant factors, but they also interact with each other. Current best estimates of changes in climate indicate an increase in global mean annual temperatures of 1^{o}C by 2025 and 3 ^{o}C by the end of the next century (Palikhe 2007). In the present work, it was examined the relation between the climate changes of the air temperature and the relative humidity on the fate of chlorantraniliprole and pre-harvest intervals of tomato fruits (PHIs). The results clearly indicated that the residues of chlorantraniliprole in tomato fruits (when compared with the corresponding days after insecticide spraying) changed significantly from winter season to the summer season and through the same season in some years of the trial. Despite the residues of chlorantraniliprole were the higher in winter and summer seasons of 2012, the lowest residues were in 2013 for winter seasons and in 2014 for the summer seasons. Consequently, the half-life time of chlorantraniliprole in tomato fruits decreased significantly to the shortest in summer season of 2014, and it was the longest in winter season of 2012. Also the pre-harvest intervals of tomato fruits (PHIs) reduced significantly to the shortest period in summer season of 2014, and it was the longest in the winter of 2012. On the other hand, the average recorded of the air temperature through the days after chlorantraniliprole spraying was the highest in summer season of 2014, and the lowest in winter season of 2012.

Furthermore the correlation coefficient was a negative between the averages of air temperatures of the days after chlorantraniliprole sparying and the half life times of chlorantraniliprole or PHIs. Whereas, it was a positive between the averages of the relative humidities and the half life times of chlorantraniliprole or PHIs. In a previous study,(Tepper 2012) found that the temperature has a direct influence on the uptake of pesticides and on the rate at which pesticides volatilise from plant surfaces. It also has an indirect influence on the evaporation of the aqueous component of pesticide droplets. Also, higher temperature increases volatilisation rates and promotes the transfer of vapours into the atmosphere from plants. Volatilisation may represent a major dissipation pathway for pesticides applied to crops. It accounts for up to 90% of the applied dose in some cases (Bedos, 2002). Also, the rate at which spray droplets evaporate is determined by the amount of water vapour that the air can absorb. The absorption potential is dictated by the amount of water vapour already in the air and the temperature of the air. Relative humidity is the ratio of the actual amount of water vapour in the air to the amount it could hold when saturated. The air's capacity to hold water vapour increases as air temperature increases. At 30ºC, the capacity is more than three times that at 10ºC; consequently, while the amount of water vapour in the air may be static, the relative humidity decreases as temperature increases. A better indicator of the rate at which pesticide droplets evaporate is Delta T. Delta T is the difference between the wet and dry bulb temperatures. It combines the effects of temperature and relative humidity (Tepper, 2012). Otherwise, the residue pattern of chlorantraniliprole in tomatoes under different treatments have followed a trend in which shorter harvest intervals led to higher residue level. While the FAO/WHO (2013) has not established maximum residue limits (MRLs) for chlorantraniliprole, European Union MRL for chlorantraniliprole in tomato is 0.6 mg/kg. These results suggested that it is safe to harvest 7days after spreying in summer season or 8 days in the winter season when applying the recommended dose of chlorantraniliprole. In light of the present findings, weather variability and climate change in the air temperature and relative humidity affect the persistence of the pesticide and its PHI. These issues should be seriously considered when to recommend and promote safe usage of pesticide to the growers.

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Table 2. Residues of chlorantraniliprole in tomato fruits

Time after application (Day)	Residues of Chlorantraniliprole in tomato fruits (mg kg^{-1})						
	Seasons						
	Winter			Summer			L.S.D
	Years						
	2011	2012	2013	2012	2013	2014	
	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	
Z	2.000^{ab}±0.041	2.119^{a}±0.039	2.012^{ab}±0.041	1.917^{bc}±0.043	1.911^{bc}±0.043	1.850^{c}±0.045	0.241
1	1.448^{b}±0.038	1.716^{a}±0.032	1.409^{b}±0.039	1.209^{c}±0.046	1.140^{cd}±0.049	1.010^{d}±0.055	0.162
3	1.017^{b}±0.020	1.114^{a}±0.019	0.960^{c}±0.022	0.979^{c}±0.021	0.797^{d}±0.026	0.783^{d}±0.026	0.061
5	0.809^{b}±0.023	0.976^{a}±0.019	0.770^{bc}±0.024	0.748^{c}±0.025	0.509^{d}±0.037	0.534^{d}±0.035	0.055
7	0.462^{b}±0.009	0.510^{a}±0.008	0.373^{c}±0.012	0.239^{d}±0.018	0.222^{d}±0.019	0.102^{e}±0.042	0.013
10	0.134^{b}±0.007	0.201^{a}±0.005	0.129^{c}±0.007	0.095^{d}±0.010	0.074^{f}±0.013	0.079^{e}±0.012	0.003
15	0.046^{b}±0.016	0.069^{a}±0.011	0.030^{e}±0.024	0.041^{c}±0.018	0.036^{d}±0.020	0.029^{e}±0.025	0.002
HL(Day)	**2.718^{ab}±0.033**	**2.988^{a}±0.030**	**2.484^{bc}±0.037**	**2.596^{bc}±0.035**	**2.539^{bc}±0.036**	**2.441^{c}±0.037**	**0.266**
PHI(Day)	**7.200^{ab}±0.013**	**7.400^{a}±0.013**	**7.100^{b}±0.014**	**6.500^{c}±0.015**	**6.100^{d}±0.016**	**6.000^{d}±0.016**	**0.281**

Z: one hours after the insecticide application (zero time).
HL: Half-life time ($t_{1/2}$)
PHI: Pre-harvest interval
ND: Not detected.
Values within the same row having the same letters are non-significant, p<0.05.
SD: Standard deviation

Table 3. The mean air temperatures (ºC) and relative humidities (%) for days after spraying of chlorantraniliprole

Year	Seasons			
	Winter		Summer	
	Temperature mean±SD	Humidity mean±SD	Temperature mean±SD	Humidity mean±SD
2011	20.37±0.5	82.2±4	-	-
2012	19.06±2.0	63.3±7.1	34.3±1.1	73.9±3.0
2013	21.0±1.0	78.2±6.0	37.22±1.2	65.4±3.9
2014	-	-	38.3±3.0	66.07±7.4

SD: Standard deviation

Table 4. Correlation coefficient between averages of air temperatures or relative humidities (for the days after spraying) and chlorantraniliprole half lives or pre-harvest intervals of tomato fruits (PHI) during six seasons of the experiment.

Climatic parameter	Correlation coefficient	
	HL	PHI
Temperature	-0.636	-0.985
Humidity	0.233	0.362

HL: Half-life time ($t_{1/2}$)
PHI: Pre-harvest interval

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