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Dissipation kinetics and degradation products of cyantraniliprole in tomato plants and soil in the open field

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Abstract

Dissipation kinetics and transformation pathways of cyantraniliprole, as a new diamide class of insecticide, are very important, since the degradation products exhibited toxicological effects and may cause more environmental hazards than the parent product. The present study was carried out to explore the fate of cyantraniliprole in tomato plants and soil under open field conditions. The determination of residues was set on HPLC Diode-Array Detection and identification of degradation products by LCMS single quadrupole mass. The dissipation rate of cyantraniliprole was ascribed to first-order kinetics, where the rate of disappearance in tomato fruits was faster than in leaves and soil with half-lives determined to be 1.63, 5.25 and 5.92 days in tomatoes fruits, leaves and soil, respectively. The results showed that cyantraniliprole transformed into many degradation products and can be identified about 9 products. IN-J9Z38 which consider the major metabolite detected in all compartments. The detection of other degradation products varied within tomato fruits, leaves and soil. These results will help in management and establish the best scenario to minimize the adverse effects of residues and involved in risk assessment study.

***Keywords*:** Cyantraniliprole; Dissipation; Transformation products; Fate; Tomatoes; Soil.

1. Introduction

Once pesticides are applied in agricultural fields, the processes of their fate were begin due to natural environmental stresses including; temperature and sunlight [1]. However, the majority of them end up in the soil and the groundwater. In addition to being absorbed by the plant, pesticides migrate from the soil to water via surface runoff and downward movement and to the air by volatilization [2-3].

The physicochemical properties of, pesticides, soil, water and environmental factors greatly influence the pesticide degradation/transformation in the environment. It is probable that these transformed products are toxic or more toxic than the parent molecule [2-4]. Diamide has been presented as a new group of insecticides for pest management that is effective against a wide variety of insect pests in various commercial crops all over the world. Recently, its use has extended to include chemicals like flubendiamide, chlorantraniliprole and cyantraniliprole; nevertheless, some of these chemicals' metabolites are thought to be toxicologically significant and might cause environmental risks [5-6].

Due to its physicochemical characteristics, the second-generation anthranilic diamide insecticide cyantraniliprole (3-bromo-1-(3-chloro-2-pyridinyl)-N-[4-cyano-2-methyl-6[(methyl amino) carbonyl] phenyl]-1H-pyrazole-5-carboxamide) displays root systematicity and translaminar behavior, making it primarily employed in soil, seed treatment, and foliar application for pest control [7-8]. Cyantraniliprole has no cross-resistance with other pesticides and is very efficient against sucking pests such as aphids, trips, whiteflies, fruit flies, etc. [7-9]. It is a ryanodine receptor modulator (IRAC 2020) that causes uncontrollable muscular contraction, paralysis, and

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ultimately the death of insects by disrupting calcium ion concentration in muscle cells.

Cyantraniliprole is a comparatively persistent insecticide in the soil with a half-life of 16- 89 days. Previous studies showed cyantraniliprole liable to degradation into new compounds by influences via hydrolysis and photolysis impacts in soil and water at high pH and temperature. IN-J9Z38 was the primary photolysis and hydrolysis product [10-11]. Cyantraniliprole is a promising pesticide in Egypt, however, it may potentially be harmful to the environment. Additionally, excessive usage will cause more cyantraniliprole to be deposited in the soil and water environment. The majority of recent research mainly concentrates on its insecticidal effectiveness [12-13].

Therefore, it is important to have data dealing with the side effects of cyantraniliprole and its metabolites on the plant and soil. The dissipation of cyantraniliprole residues in tomatoes and soil simultaneously under prevailing conditions in Egypt has not been reported in the literature. To bridge the knowledge gap investigation was carried out to focus on the kinetics of cyantraniliprole degradation and dissipation in tomato plants and soil in open fields. In addition, an attempt was achieved to identify the associated degradation or transformation products. The obtained data will help in evaluating and understanding the fate of cyantraniliprole in tomato and soil under Egyptian field conditions.

2. Experimental

2.1. Pesticides and solvents

Cyantraniliprole standard (99.2 % purity), and formulation Benivia 10% OD were provided by DuPont company (USA). Chromatographic-grade solvents such as methanol and acetonitrile were purchased from Merck (Darmstadt, Germany). A Milli-Q Gradient System (Millipore Corporation, Billerica, MA, USA) was used to produce ultra-purified de-ionized water (DI). QuEChERS extraction tubes (citrate-buffered) containing 1 g of sodium chloride, 4 g of magnesium sulfate, 0.5 g of disodium citrate sesquihydrate, 1 g of trisodium citrate dehydrate, and dispersive (dSPE) solid-phase extraction tubes from Supelco, USA, were bought. These tubes contained 150 mg of magnesium sulfate and 25 mg of primary secondary amine (PSA).

2.2. Standard preparation

A stock solution of cyantraniliprole (1000 mg L^{-1}) was prepared in acetonitrile by weighing approximately 0.1008 g into a 100 mL volumetric flask, the pure solvent solutions required for preparing a standard curve (0.05, 0.1, 0.5, 1.0, 5.0, 10.0 and 100 mg L^{-1}) were prepared from the stock solution by serial dilution. All standard solutions were stored in a refrigerator at 4°C.

2.3. Field experiment

To study the degradation kinetics of cyantraniliprole in tomatoes, and soil, a supervised field experiment was conducted from March – to June 2021 at the Faculty of Agriculture, Cairo University, Giza Governorate in Egypt. Tomato seedlings (variety: 023) were planted in soil in rows. The distance between each plant was 50 cm, as well as the distance between rows was 75 cm. The plot is divided into 30 rows, rows length 7 m. Regular monitoring of the environmental conditions was regularly followed in order to know any extreme conditions that might influence the results. The average temperature of the experiment was between 27°C to 38°C, while the relative humidity was between 50-80%. The crop was sprayed by manual Knapsack sprayer 20-liter capacity once with cyantraniliprole formulation Benevia 10% OD, the recommended dose of cyantraniliprole for tomato agricultural application is 75 ml $100L^{-1}$. Field maintenance and crop cultivation were carried out in accordance with regionally customary agricultural methods.

There were no erratic weather conditions or rainfall. The characterization of soil texture was classified as clay composed of clay (89.5%) sand (1.5%), and silt (9.0%). The organic matter was 1.9% containing 138 mg kg^{-1} nitrogen, 8.34 mg kg^{-1} available phosphorus, 183 mg kg^{-1} available potassium, soil pH in a 1:2.5 (soil: water) was 8.6 and electrical conductivity was 2.92 dS m^{-1}.

2.4. Sampling of tomatoes and soil

For residue estimation and stability, the samples were collected from the tomatoes (fruit and leaves), surface soil, (around the root zone 0–15 cm depth). Samples collected from fruits were at the red ripening stage. The leaves were also at the mature stage, and were taken on 0 (2 h after application), 1, 3, 5, 7, 10, and 14 days after the application, and were collected randomly to ensure reliable and representative sampling. Parallelly untreated (blank) samples were collected from the field, and the samples were packed in polythene bags and immediately brought to the laboratory for processing.

2.5. Sample preparation, extraction and clean up procedure

The citrate-buffered QuEChERS method was used for the extraction of cyantraniliprole [14]. One kg of tomato fruits was weighted and chopped in the blender, also 100 g of leaves were chopped in the blender, after samples were homogenized, from the representative samples 10 g from fruits and 5 g from leaves in triplicate were transferred with accuracy in a

50 mL centrifuge tube. Also, 10 grams were accurately weighed from homogenized soil samples into a 50 mL PTFE centrifuge tube .

Ten milliliters of acetonitrile were added to each tube, followed by vigorous shaking using a mechanical shaker for 10 minutes. After being vortexed, the tubes were soaked in water for 10 minutes. Posteriorly, the QuEChERS extraction method was applied by using an extraction tube containing 1 g of sodium chloride, 4 g of magnesium sulfate, 1 g of trisodium citrate dihydrate, and 0.5 g of disodium citrate sesquihydrate was added to each tube and re-shaken for 1 minute. The tubes were centrifugation at 4000 rpm for 5 minutes, 1 mL of the supernatant was transferred to a dSPE clean-up. dSPE-tube normally consists of 25 mg of PSA and 150 mg of magnesium sulfate. The tubes were agitated using vortex for 1 minute and centrifuged at 5000 rpm for 5 minutes. The resulting supernatants were filtered through a 0.22 µm Nylon syringe filter into an auto sampler vial for injection [15-16].

2.6. Instrumentation

Estimation of cyantraniliprole was performed on an Agilent HPLC 1260 Infinity ii Diode-Array Detection (DAD) according to Parvatamma et al. [17] and Malhat et al. [18] with some modifications. The system consists of a quaternary gradient solvent pump to control the flow rate of the mobile phase and an auto-sampler for automatic injection, HPLC separation was performed on a Zorbax Eclipse Plus C_{18} (4.6×250 mm, 5 µm) column. The mobile phase consisted of solvents in a mixture of Milli-Q water containing 0.1 mL of 1 M formic acid, methanol, and acetonitrile in the ratio of 10:70:20 at a flow rate of 0.70 mL min^{-1}. Column thermostat temperature was controlled at 35 °C during analysis, 20 µL was injected by auto-sampler injection, and the absorption was read at 265 nm.

For identification of cyantraniliprole and its metabolites, a screening on LCMS 1260 Infinity ii G6125B MSD (Agilent, USA) with a single quadrupole mass was used. Chromatographic separation for LC was carried out on a Waters Symmetry C_{18} column (4.6×75 mm, 3.5 µm, Ireland) at a 30 °C column temperature. The mobile phase is composed of deionized water 30% and methanol 70%, both containing 0.1% formic acid and 5 mM ammonium formate. The mobile phase flow rate was 0.3 mL min^{-1}. The injection volume was 5 µL, and the entire analytical running time was 20 minutes.

A high definition mass spectrometry was performed on a single quadrupole mass system detector and operated in Atmospheric Pressure Ionization-electrospray ionization (API-ES) positive mode was used for the MS detection with the following MS parameters: the interface voltage was 4.0 kV and the interface current was 5.2 Torr, nitrogen was used as both nebulizing and drying gas with pressure 35 psig and flow 13.0 L min^{-1}. The drying gas temperature was 350°C. Highly selective MS detection was achieved by selected ion monitoring (SIM) and scan mode [19].

For metabolite screening, one ml from the cyantraniliprole standard (1000 mg L^{-1}) was put in a petri-dish then evaporated at room temperature and through direct exposure to sunlight for 8 hours, after the exposure period ended, the dishes were washed with 100 ml of acetonitrile and transferred into a bottle for direct injection, then procedure SIM and Scan mode by LC-MS for cyantraniliprole before and after degradation, with a fragmented voltage of 200 v the quantitative ion was 473.01/442 *m/z* and the qualitative ion was 473.01/284 *m/z*. a full MS scan was initially conducted of cyantraniliprole before and after degradation under sunlight within a mass range of 100–1200 *m/z* for a standard with a fragmented voltage of 200 v, then an MS master scan was operated with a scan range of 150–500 *m/z* in the targeted mass inclusion filter containing all metabolite candidates of cyantraniliprole [20-21].

2.7. Method validation

Method validation ensures analysis credibility and the analytical method was performed in accordance with Selby et al. [9] and SANTE [22]. In this experiment, the analytical method for tomato fruits, and soil was validated in terms of the instrumentation, the accuracy of parameters, precision, linearity, and limits of detection (LOD) and quantification (LOQ). The accuracy of the method was determined by recovery tests, samples spiked with two concentration levels 0.1 and 0.5 mg kg^{-1} were used to determine the recovery percentages in tomato fruits and soil, and leaves spiked at concentration levels of 0.5 and 1 mg kg^{-1}. The linearity of the calibration curve was evaluated using the correlation coefficient (R^2) for the peak areas against the concentrations in the range of 0.05 to 100 mg L^{-1}; R^2 should be greater than 0.99. After using the aforementioned procedure to evaluate the fortified samples and control samples, recovery rates (%) were obtained by comparing the observed concentrations to the fortified concentrations. Relative standard deviation (RSD, %) of recoveries among replicates was used to assess the accuracy. Untreated control samples was also processed similarly [16].

2.8. Calculation of kinetic data

A first-order kinetic model was used to calculate the dissipation rate constant and dissipation half-life of cyantraniliprole in tomato fruits, leaves and soil. The plot of concentration versus time was subjected to exponential regression equation, given as follows: $C_t = C_0 \times e^{-kt}$

where C_t is the concentration at time t, C_0 is the highest concentration of total cyantraniliprole residue or the initial concentration, and k is the dissipation rate constant. In accordance with the equation obtained from the field data, the biological half-life in days (DT_{50}) was calculated from the following equation [23-25]: $DT_{50} = \ln(2)/k = 0.693/k$

3. Results and Discussion

3.1. Optimization and validation of the residue analysis method

The suggested technique involved extraction using acetonitrile and buffered citrate in tomato and soil. The analysis of cyantraniliprole residues in tomato fruits, leaves, and soil was set using HPLC-DAD. Since the identification of the cyantraniliprole and metabolite on LCMS single quadrupole mass in tomato fruits, leaves and soil came next, it was crucial to purify the extract as much as possible.

SIM and Scan positive mode spectrums of cyantraniliprole before and after degradation under the sunlight of standard solution were screened, several metabolites candidates are identified by MS fragmentation of the compound through NIST library and previous reports [16,20-21,26-27], and these metabolites were matched with those found in the samples of tomato fruits, leaves, and soil. The calibration equations, recoveries, RSDs, R^2 values, LOD and LOQ of cyantraniliprole were listed in this study as follows: The calibration range was linear from 0.05 to 10 mg L^{-1} giving a linear calibration curve with R^2 value of 0.9998 (fig. 1), with an RSDr (n=5) (repeatability) of 1.13% - 6.21%.

For recoveries of cyantraniliprole in different matrices for tomato fruits, leaves and soil, at two spiking concentrations, the accuracy and precision ranged from 85.35% to 95.17%, as shown in table (1). These results were determined from three samples, each of which performed five replicate analyses on the same day by a single analyst. Satisfactory results of the repeatability method were obtained with (RSDr = 3.56 – 6.26 %). The LOD is the lowest amount of cyantraniliprole that was spiked into blank samples to elicit a signal that was three times more intense than the noise [17,21,28]. The LOD was was determined to be 0.01 mg L^{-1} with an RSD of 5.78%. The lowest fortification level that provides a recovery percentage of 80–120 with an RSD of less than 20% is the LOQ of the procedure. LOQ in tomato fruit and the soil was 0.05 mg kg^{-1}, while it was 0.1 mg kg^{-1} in leaves. This falls within the EU's MRL of 1 mg kg^{-1} for cyantraniliprole in tomatoes.

Table 1. Validation results of cyantraniliprole.

Parameters		Values
Range (mg l^{-1})		0.05 - 10
Linearity (R^2)		0.9998
Equation of calibration curve		y = 184.863x + 46.093
LOD in acetonitrile (mg l^{-1})		0.01
LOQ fruits (mg kg^{-1})		0.05
LOQ leaves (mg kg^{-1})		0.1
LOQ soil (mg kg^{-1})		0.05
Spiking level (mg kg^{-1}) (% recovery ± RSDr, n = 5)		
Fruits	0.1	93.2 ± 5.48
	0.5	91.4 ± 4.97
Leaves	0.5	92.7 ± 6.26
	1	95.1 ± 4.62
Soil	0.1	89.4 ± 3.56
	0.5	85.3 ± 3.85

3.1. Dissipation kinetic of cyantraniliprole in tomatoes and soil

Tolerance levels differ from country to country, and from crop to crop as well as from time to time. Therefore, dissipation behavior is of great importance for constructing dissipation curves under different climatic and cultivation conditions. The experiment was carried out to quantify the residue levels. Quantitative determination of residues levels was interpreted from the standard curve of the active ingredient for cyantraniliprole. The control sample was free from any residues, table (2) showed the residue levels of cyantraniliprole in the field experiment, also, figure (S1) clarifies the dissipation curves of cyantraniliprole detected in various treatments presented in tomato fruits, leaves and soil.

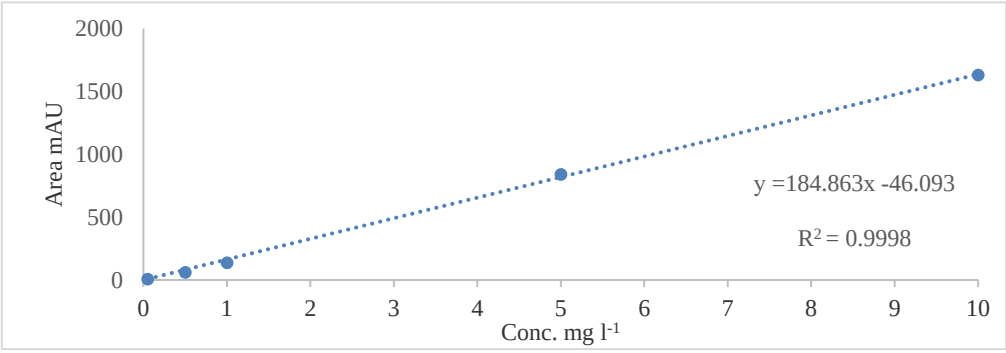

Fig. 1. Representative calibration curve of cyantraniliprole.

Table 2. Residue dissipation pattern of cyantraniliprole in tomato fruits, leaves and soil.

Time after application (days)	Fruits		Leaves		Soil	
	Residues mg kg^{-1} ±SD	Dissipation %	Residues mg kg^{-1} ±SD	Dissipation %	Residues mg kg^{-1} ±SD	Dissipation %
Initial	4.696± 0.048	0	3.571 ± 0.158	0	7.136 ± 0.037	0
1	3.154 ± 0.088	32.83	2.233 ± 0.161	37.47	5.731 ± 0.047	19.70
3	1.266 ± 0.034	73.03	2.297 ± 0.269	35.68	4.776 ± 0.045	33.07
5	0.759 ± 0.014	83.84	2.147 ± 0.142	39.88	3.926 ± 0.038	44.98
7	0.356 ± 0.041	92.42	1.176 ± 0.202	67.07	1.769 ± 0.007	75.22
10	0.136 ± 0.007	97.10	0.808 ± 0.105	77.37	0.726 ± 0.032	89.83
14	LOQ<	---	LOQ<	---	0.426 ± 0.005	94.04
Dynamic equations	y = 3.5699x – 0.425		y = 3.0201x – 0.132		y = 12.631x – 0.117	
Correlation coefficient	0.79		0.91		0.93	
Half-life (d)	1.63		5.25		5.92	

Initial = 2 hours after application

Concerning the control sample, results explore the samples are free from any detected residues. The treated sample cyantraniliprole concentrations decreased steadily with time. After the application, the initial deposits in tomato fruits were 4.696 mg kg^{-1}, then decreased to 0.136 mg kg^{-1} on the 10th day, where the percentage dissipation reached 97.10%, while at the 14th day level of residue was less than LOQ. Dissipation of cyantraniliprole from tomato fruits followed first-order dissipation kinetics with a correlation coefficient of determination (R^2 > 0.79). The calculated half-live of cyantraniliprole in tomato fruits was 1.63 days.

Similarly, the initial residues in leaves degraded from 3.571 to 0.808 mg kg^{-1} on the 10th day and was less than LOQ on the 14th day, where the dissipation rate was 77.37% on the 10th day of application, The dissipation with time was described mathematically by a kinetic-first order, and the regression coefficient (R^2 > 0.91), with a half-life value of 5.25 days.

In soil, the initial residue of cyantraniliprole was 7.136 mg kg^{-1}, the residues gradually declined with time reaching 0.426 mg kg^{-1} after 14 days from application, which represent a 94% loss of the initial deposit. Also, Dissipation data are in accordance with the first-order kinetic equation (R^2 > 0.93) and yielded a half-life value of 5.92 days.

The results indicated that the residue levels in leaves increased with time elapsed compared with the residue levels in fruits and soil. This may be due to respiration from leaves which lose water through stomata on the surface (evapotranspiration), this creates a driving force for water and soluble compounds to flow into the leaf tissues. However, fruits lack stomata, and this is not accompanied by a new flow of the soluble compound in it [6,21,29-30].

Soil results showed rapid degradation of the cyantraniliprole may be explained by the high pH for soil which was 8.6, where Sharma et al. [26-27] reported that cyantraniliprole and chlorantraniliprole are vulnerable to hydrolytic degradation at alkaline pH. This clearly was due to the higher pH of natural water. Faster hydrolytic degradation of cyantraniliprole in alkaline water, especially when compared with chlorantraniliprole.

Numerous studies have looked at how cyantraniliprole residue dissipates in various crops. In many research, it was shown that crops dissipate residues more quickly than soils. It was found that the half-life determined in several field crops was between 1 and 12 days, although it was between 2 and 22 days in different soils [16,33-35]. This is because of the various environmental conditions from one country and region to another, as well as the recent climatic changes that played a significant role in varying the fate of pesticides, necessitating a re-evaluation of the behavior and disappearance of the pesticide in the various components of the environment. Furthermore, in different experimental sites, particularly during the crop-growing season, soil characteristics and other climatic factors, such as temperature, moisture, sunlight and rainfall, vary. It's also possible that a number of crop development variables led to the half-life' dissipation [16,31]. Data revealed that the mean half-life of cyantraniliprole in tomatoes fruits, leaves and soil was 1.63, 5.25, and 5.92 days respectively, which were similar to the reported half-life by [32-35].

3.3. Degradation of cyantraniliprole in tomato and soil and its transformation mechanism

Due to the lack of providing reference standards of degradation products for cyantraniliprole, and to overcome this situation a high-level concentration from the cyantraniliprole standard (1000 mg L^{-1}) was exposed to sunlight for 8 hours. To identify the degradation products by using LCMS. Also, these degradation products were confirmed at based on the framework proposed by Huynh et al. [20-21], which mainly depends upon the MS fragment ions to elucidate the proposed chemical structure for each

fragment. Consequently, the cyantraniliprole standard was exposed to sunlight in order to obtain the available degradable products. Components and the convergence of retention time of these products and some of the data obtained for fragment ions were taken into consideration to identify the degradable products in biotic system and compare their retention times as well as the accurate *m/z* were compared to those which have the same fragment ion. This information was compared to degradable products in the tomato fruits, leaves, and soil samples to identify their degradation products in the samples.

In this study, a total of 9 degradation products were detected and identified in the different samples (Fig. 2). The potential degradation products, and their formulas, chemical structures, mass spectra, and retention time are presented in table (3).

For example, cyantraniliprole was detected at 2.65 min with the molecular ion $[M + H]^+$ of m/z 473.7 (fig. S2), and MS fragmentation of the molecular ion yielded several characteristic product ions, including m/z, 284.0 and 442.0.

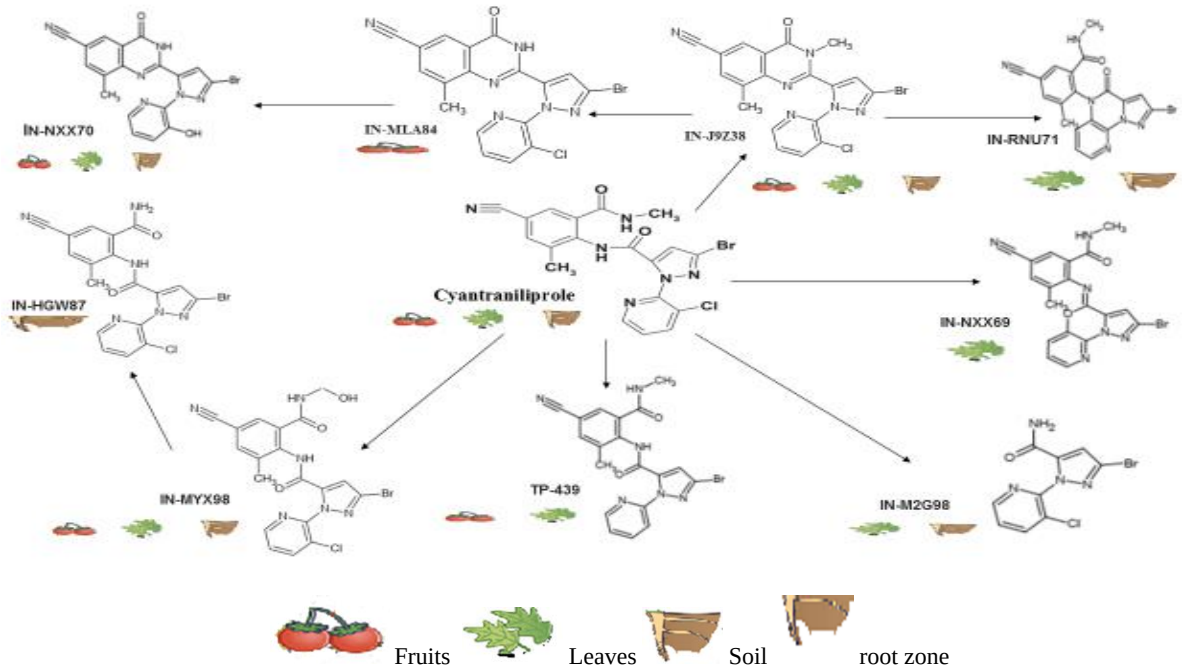

Fig. 2. Degradation products of cyantraniliprole in tomato fruits, leaves and soil.

Table 3. Mass-spectra data and formulas of cyantraniliprole degradation products.

Name	formula	RT (min)[a]	Molecular weight[b]	characteristic ions (m/z)[c]	Abundance level			Confidence level[d]
					Fruits	Leaves	Soil	
Cyantraniliprole	C19H14BrClN6O2	2.65	473.7	284, 442	+	+	+	1
IN-J9Z38	C19H12BrClN6O	4.87	455.7	350, 361, 419	+	+	+	2
IN-MLA84	C18H10BrClN6O	3.46	441.7	312, 405	+	-	-	2
IN-NXX70	C18H11BrN6O2	3.68	423.1	289, 299, 327	+	+	+	2
IN-RNU71	C19H13BrN6O2	2.76	437.1	301, 406	-	+	+	2
IN-MYX98	C19H14BrClN6O3	2.25	489.1	284, 302	+	+	+	2
IN-HGW87	C18H12BrClN6O2	2.51	458.9	284, 442	-	-	+	2
IN-NXX69	C19H13BrN6O2	3.77	437.0	405	-	+	-	2
IN-M2G98	C9H6BrClN4O	0.987	300.1	177, 205	-	+	+	2
TP439	C19H15BrN6O2	1.43	439.1	250, 408	+	+	-	3

[a] retention time of cyantraniliprole and degradation products on the LC-MS
[b] the accurate masses (*m/z*) were obtained according to [16,20-21,26-27]
[c] the characteristic ions acquire using LC-MS in both SIM and Scan mode
(+): detected, (-): not detected
[d] the confidence level 1: reference standard, level 2 characteristic ions observed according to [20-21,26-27], level 3 characteristic ion observed according to [20,27].

The degradation product at *m/z* 455.7 was detected in all samples at a retention time of 4.87 min with MS characteristic revealing major product ions at *m/z* 350.3, 361.1 and 418.9 (fig. S3). This degradation product was identified as IN-J9Z38 which consider the main degradation product of cyantraniliprole in other plants species and soil [16,20-21,26-27].

This product is a result of metabolism, hydrolysis, and photodegradation, and was found at a high level during the dissipation of cyantraniliprole. Figure (3) showed that major metabolite IN-J9Z38 was detected in fruit samples till 14-day post-treatment. Also, it is clear from the data in fig. (3) that the peak area for metabolite increased with time elapsed post-treatment while the parent compound decreased until the non-detectable level.

The polarity of IN-J9Z38 is less than the cyantraniliprole product and was found more persist in soil than the parent compound [3,20]. The presence of IN-J9Z38 in pollinator-attractive matrices (such as pollen and nectar) warrants additional research due to its possible toxicity to honeybees when administered orally, and its toxicological effects in addition to cyantraniliprole should also be carefully taken into account [20,36]. Lee et al. [14] reported that residue levels of the metabolite IN-J9Z38 in proso millet grain gradually increased with the duration leading up to harvest over 30 days, where cyantraniliprole may be transformed or metabolized into IN-J9Z38 during cultivation. This is entirely consistent with what we found. Our observation of this transformation product sparks interest because, nevertheless, other research has shown little or trace amounts of IN-J9Z38 residues in tomatoes, Chinese cabbage, cucumbers, rice and soil [8,31-33]. Results indicated the abundance of major metabolite IN-J9Z38 in tomato fruits which almost consumed freshly and this consider an indirect exposure that may be exhibited adverse effects on non-target species.

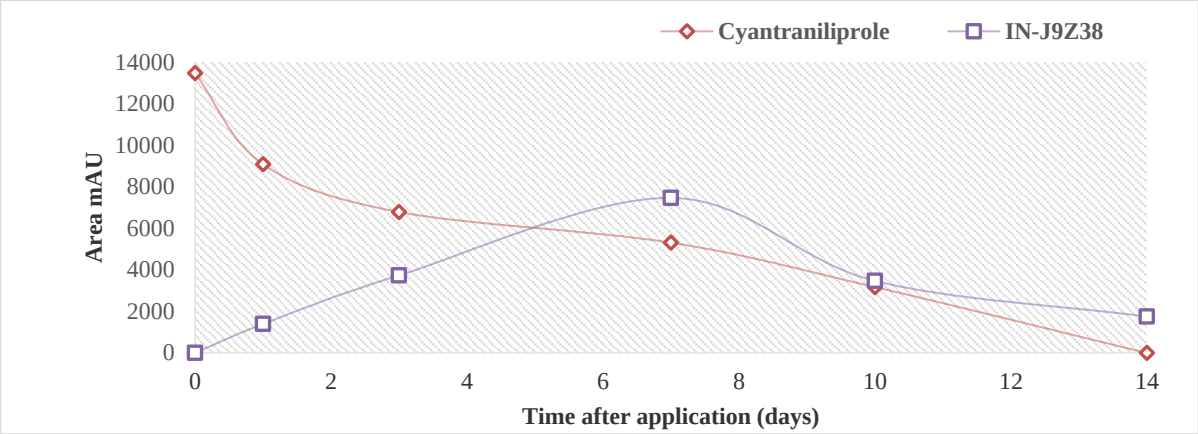

Fig. 3. Relative abundances of cyantraniliprole and metabolite IN-J9Z38 detected in tomato fruits after application.

In the artificial soil, Zhang et al. [11] found that cyantraniliprole degraded more quickly than its major metabolite IN-J9Z38. Furthermore, according to the results of the toxicity test, cyantraniliprole and IN-J9Z38 can cause oxidative stress in earthworms at a dose of 5.0 mg kg^{-1}, which eventually leads to cellular damage. Additionally, cyantraniliprole caused more oxidative damage than IN-J9Z38. Although cyantraniliprole degraded more quickly in the artificial soil than its primary metabolite IN-J9Z38, it nonetheless posed a greater risk to earthworms. Xiao et al. [37] reported that cyantraniliprole under high temperatures was photolyzed to IN-J9Z38, and the transformation rate may reach 98%. They also found that the toxicity of IN-J9Z38 was 4.66 folds that of the parent compound in large fleas.

IN-J9Z38 also transformed into other's degradation products called IN-RNU71, IN-MLA84, and IN-NXX70. IN-RNU71 was found as a result of photodegradation in leaves and surface soil and not detected in fruits samples at a retention time of 2.76 min with MS characteristic product ions at *m/z* 301.01 and 406.1 (fig. S4), while, IN-NXX70 was set in all samples, at retention time 3.68 min and MS fragmentation ions at *m/z* 289.1, 299.3 and 327.5 (fig. S5), as a result of photodegradation and hydrolysis process. IN-MLA84 was detected in fruits samples, with a retention time was set at 3.46 min, and MS characteristic ions at *m/z* 311.6 and 405.0 (fig. S6) as a result of photodegradation and metabolism [26].

Other major degradation products were detected from transformation of cyantraniliprole such as IN-MYX98, IN-NXX69, IN-M2G98, and TP 439. IN-MYX98 was found as a result of metabolism, photodegradation, and hydrolysis in fruits, leaves, surface, and root zone in soil samples, at a retention time of 2.25 min with MS characteristic ions at *m/z* 284.6 and 302.0 (fig. S7). IN-MYX98 was

transformed by the hydrolysis process into another product IN-HGW87, which is found only in the root zone soil sample at a retention time of 2.51 min (fig. S8) with MS characteristic ions at *m/z* 283.9 and 442.0.

IN-NXX69 was detected at a retention time of 3.77 min with MS characteristic ions at *m/z* 405.1 (fig. S9) from the photodegradation process in leaves samples and not detected in fruit or soil samples, while IN-M2G98 was detected in all samples except fruit samples, as a result of photodegradation and hydrolysis process, and was set soon from the injection as a retention time of 0.987 min and MS characteristic ions at *m/z* 177.5 and 205.3 (fig. S10), whilst the TP 439 as called in literature [20-21] was detected at the retention time of 1.43 min and MS characteristic ions at *m/z* 250.3 and 408.4 (fig. S11) in all sample except the soil sample as a result of photodegradation and metabolism [26-27].

3.4. Transformation pathways of cyantraniliprole

Based on our results and other previous reports [20-21,26-27], the degradation products pathways involved in the transformation of cyantraniliprole in tomato fruits, leaves and soil, are shown in fig. (2) and figure (S12 a, b).

We propose that once applications of cyantraniliprole the process of transformation pathways is begun, and the major following product is IN-J9Z38 as a result of cyantraniliprole predominantly underwent ring closure, it was obviously a result of cyclization with concomitant loss of water [27]. Errede et al. [38] reported that the presence of water facilitated cyclodehydration. The main product IN-J9Z38 was followed by N-demethylation leading to the formation of IN-MLA84. Additionally, IN-J9Z38 was dechlorinated and hydroxylated on the pyridine ring to form IN-RNU71 and IN-NXX70, respectively. Thus, IN-J9Z38 is considered a key intermediate for several subsequent transformation reactions. Also, the formation of IN-NXX70 was composed of dechlorinated from the form IN-MLA84.

Other pathways transformation, the hydroxylated of cyantraniliprole at the *N*-methyl group led to product IN-MYX98, which transformed by dealkylated composed to IN-HGW87, the free amide of parent cyantraniliprole [20].

On the other side, the break-down of cyantraniliprole in the carboxamidebridge between the phenyl and pyridine rings led to the formation of IN-M2G98, which could be composed of the parent cyantraniliprole or other degradation product [21]. Further degradations of cyantraniliprole were observed during dechlorination followed by hydroxylation leading to the formation of IN-NXX69 [20-21]. Finally, the formation of TP439, where the number 439 refers to the molecular weight. Dechlorinating from the pyridine ring of cyantraniliprole transform to TP439 [26].

4. Conclusion

The dissipation kinetics and transformation pathways of cyantraniliprole in tomatoes, and soil, showed that the residues amount and the degradation products are varied. The dissipation rate of cyantraniliprole in tomatoes fruits was faster than in soil, also there were more degradation products in leaves, and soil, than in fruits sample. In addition, the high dose rate that used, where it considers much than used over the many countries. The major transformation of cyantraniliprole was IN-J9Z38 that is considered a toxicologically significant compound in the environment. Many reports showed that the environmental persistence of IN-J9Z38 was higher than cyantraniliprole and has a higher risk than its parent compound. It is hoped that decision-makers and owners of producing companies will evaluate the pesticides and degradation products, and determine risk levels of degradation products besides the active ingredient before it is allowed to be registered. The present study could help to understand the fate of cyantraniliprole in some environmental components, and more research is needed to identifying the other degradation products of cyantraniliprole.

5. Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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