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# Residue and Dissipation Dynamics of Lufenuron in Tomato Fruit Using QuEChERS Methodology

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**Abstract** One field experiment was conducted with lufenuron (Match® 5 % EC) on tomato crop during August 2011. The main objective was to understand the residue and dissipation behavior of insecticide lufenuron in tomato fruit samples. The dissipation behavior of lufenuron insecticide followed first-order rate kinetics at standard recommended dose application. The average initial deposit of lufenuron in tomato was observed to be 1.299 mg $kg^{-1}$at single application rate. This lufenuron residue dissipated to bellow LOQ of 0.03 mg $kg^{-1}$ 21 days after the treatment. Lufenuron residues were lost with pre-harvest intervals of 7 days, following application at the recommended dose by manufacture.

**Keywords** Tomato · Lufenuron · QuEChERS · Dissipation · Residue

Pesticides will continue to be used in the production of food and fiber. Thus, the use of pesticides during cultivation plays an important role in harvest quality and food protection. However, the presence of pesticide residues in food constitutes a possible risk to the consumer, because of their toxic effects to human health. Once a pesticide has been introduced into the environment, its chemical and physical properties determine its fate; where it goes and how long it persists. Each pesticide has its own unique set of properties. The degradation rate of a pesticide depends on the pesticides chemistry, as well as environmental factors, such as temperature, rainfall, and soil pH.

Lufenuron (RS)-1-[2,5-dichloro-4-(1,1,2,3,3,3-hexafluoropropoxy)phenyl]-3-(2,6 difluorobenzoyl) urea (Fig. 1), is a benzoylphenylurea insecticide whose mode of action is known to be the inhibition of chitin synthesis in the cuticle of insects (Tomlin 2000). It shows relatively low toxicity to mammals since the activity is highly specific to immature insect at the molting stage.

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 vegetable in Egypt. Tomato is considered to be an important crop and basic component of 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 diseases at all stages of its development. The crop is often applied with chemical pesticides to offer protection from sever damage. Very limited data have been reported concerning the dissipation of benzoylphenylurea insecticides in agricultural products (Aplada-Sarlis et al. 1999; Tsiropoulos et al. 1999; Khay et al. 2008) and, as a result, no published data are available concerning the fate of lufenuron in tomato. Therefore, the aims of the present study were to evaluate the dissipation of lufenuron residues as a function of time and to calculate the PHIs on treated tomato.

## Materials and Methods

Lufenuron analytical standard and the formulation (5 % EC) were kindly supplied by Syngenta (Cairo, Egypt). All

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organic solvent were HPLC grade and supplied by Merck Ltd. Deionized water was prepared by a Milli-Q water purification system. Primary secondary amine (PSA, 40 μm Bondesil) was purchased from Supelco (Supelco, Bellefonte, USA). Anhydrous magnesium sulfate was of analytical grade and purchased from Merck Ltd. Sodium chloride was analytical grade and purchased from El Naser pharmaceutical chemical Com. (Egypt). Anhydrous magnesium sulfate and Sodium chloride were activated by heating at 250°C for 4 h in the oven before use and kept in desiccators.

A high-performance liquid chromatography (Agilent 1100 HPLC system, USA), with quaternary pump, manual injector (Rheodyne), thermostat compartment for the column and photodiode array detector was used. Zorbax XDB $C_{18}$ (250 × 4.6 mm, 5 μm film thicknesses) was used as an analytical column for lufenuron.

Tomato plants 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 2 August 2011. Common agricultural and fertilization practices were used. No insecticide sprays were applied to the test plots prior to or during this experiment. Mature plants were sprayed by commercial formulation of lufenuron (Match® 5 % EC) at the recommended dose (20 mL/20 L) using knapsack sprayer motor. The spray solution was prepared in accordance with the manufacture recommendation. 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 25 to 39°C.

Sampling 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 0, 1, 3, 7, 10 and 15 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 (15 g) of each was then placed into 50 mL polyethylene tube. Samples were extracted and cleaned up immediately after sampling using QuEChERS methodology (Anastassiades et al. 2003). 15 mL of acetonitrile was added into each tube. The samples were well shaken using a vortex mixer at maximum speed. Afterwards, 6 g of anhydrous magnesium sulfate and 1.5 g of sodium chloride were added, then extract by shaking vigorously on vortex for 5 min and centrifuged for 10 min at 4,000 rpm. An aliquot of 4 mL was transferred from the supernatant to a new clean 15 mL centrifuge tube containing 100 mg PSA and 600 mg anhydrous magnesium sulfate. The samples were again vortexed for 3 min and then centrifuged for 10 min at 4,000 rpm. An aliquot of 2 mL was concentrated to dryness. The residue was redissolved in 2 mL of methanol and filtered through a 0.2 μm PTFE filter (Millipore, USA) prior to HPLC.

An aliquot (20 μL) of the final extract was injected into the HPLC with photodiode array detector as described by Gamon et al. (1998) with the following modifications: The mobile phase was methanol: water (80/20 v/v) at a flow rate of 0.8 mL/min. Detection wavelength for detection of lufenuron was set at 245 nm. The retention time of lufenuron was about 11.1 min. Residues were estimated by comparison of peak area of standards with that of the unknown or spiked samples run under identical conditions.

Untreated tomato samples were homogenized before begin spiked with lufenuron. Recovery assays were performed in the 0.1–1.0 mg $kg^{-1}$ range. The samples were processed according to the above procedure. At each fortification level, five replicates were analysed. Statistical analyses were done using the Statistical Package for Social Sciences (SPSS 10.0).

## Results and Discussion

A standard calibration curve of lufenuron was constructed by plotting analyte concentration against peak area. The detector response was linear in the range of analysed lufenuron by the given method with correlation coefficients >0.999. Blank tomato samples were used to establish the detection (LOD) and quantification (LOQ) limits for lufenuron by HPLC. The LOD and LOQ were determined as the sample concentration of lufenuron at signal to noise ratio of 3:1 and 10:1, respectively. The LOD and LOQ were estimated to be 0.01 and 0.03 mg $kg^{-1}$, respectively. Recovery results are shown in Table 1. The recoveries

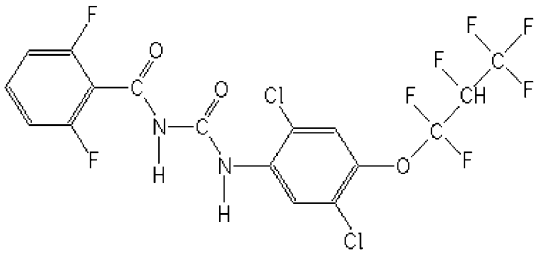


**Fig. 1** Molecular structure of lufenuron

**Table 1** Recoveries and relative standard deviations for lufenuron in tomato at various fortification level

| Fortified level (mg $kg^{-1}$) ($n^a = 5$) | Recovery | RSD |
|---|---|---|
| 0.10 | 87.1 | 5.3 |
| 0.50 | 85.7 | 3.4 |
| 1.00 | 94.3 | 7.5 |

[a] number of replicates

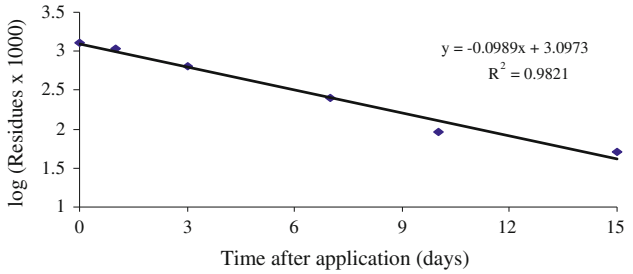


**Fig. 2** Semi-logarithm graph showing dissipation kinetics of lufenuron on tomato fruit

obtained from tomato ranged from 85.7 % to 94.3 %. The relative standard deviation (RSD) was <7.5 %. These results demonstrate the good performance of the method.

The dissipation results of lufenuron in tomato were shown in Fig. 2. The average residue of lufenuron recorded was 1.299 mg $kg^{-1}$ immediately following application of the recommended dosage. The lufenuron residues were decreased with the time. The residues were dissipated to an extent of 16.78 % after 1 day showing residues of 1.081 ± 0.13 mg $kg^{-1}$. Following that period, the residual amount of lufenuron dissipated by 51.42%, 80.60 %, 92.84 % and 96.07 % after 3, 7, 10 and 15 days after spraying, with average deposits of 0.631 ± 0.07, 0.252 ± 0.09, 0.093 ± 0.01 and 0.051 ± 0.01 mg $kg^{-1}$, respectively. Finally, the residue of lufenuron in tomato was bellow 0.03 mg $kg^{-1}$ 21 days after the treatment. The dissipation of the pesticide in/on crops depends on the climatic condition, type of application, plant species, dosage, the interval between application, and harvest (Khay et al. 2008). Half-life value ($t_{1/2}$) for degradation of lufenuron on tomato fruits was calculated as per Hoskin (1961) and observed to be 3.043 days, at the recommended dosage. While the FAO/WHO has not established MRLs for lufenuron, European Union MRL for lufenuron in tomato was 0.5 mg $kg^{-1}$. Residues of lufenuron on tomato fruits were less than its MRL value after 7 days of its application at the recommended dosage.

## References

Anastassiades M, Lehotay SJ, Štajnbaher D, Schenck F (2003) Fast and easy multiresidue method employing extraction/partitioning and "dispersive soild-phase extraction" for the determination of pesticide residues in produce. J AOAC Int 86:412–431

Aplada-Sarlis P, Miliadis GE, Tsiropoulos NG (1999) Dissipation of teflubenzuron and triflumuron residues in field sprayed and coldstored pears. J Agric Food Chem 47:2926–2929

FAO/WHO (1986) Recommended methods of sampling for determination of pesticide residues, vol. VIII, 2nd edn, pt VI

Gamon M, Saez A, Pelegri R, Peris I, De la Cuadra JG, Coscolla R (1998) Liquid chromatographic determination of five benzoylurea insecticides in fruit and vegetables. J AOAC Int 81: 1037–1042

Hoskin M (1961) Mathematical treatments of the rate of loss of pesticide residues. FAO P1 Prot Bull 9:163–168

Khay S, Choi J, Abd El-Aty A, Mamun M, Park B, Goudah H, Shim J (2008) Dissipation behavior of lufenuron, benzoylphenylurea insecticide, in/on Chinese cabbage applied by foliar spraying under greenhouse condition. Bull Environ Contam Toxicol 81: 369–372

Tomlin CDS (2000) The pesticide manual, 12th edn. British Crop Protection Council, Surrey

Tsiropoulos NG, Aplada-Sarlis P, Miliadis GE (1999) Evaluation of teflubenzuron residue levels in grapes exposed to field treatments and in the must and wine produced from them. J Agric Food Chem 47:4583–4586