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Investigation of the dissipation kinetics of lufenuron in pepper grown under field conditions

Tarla koşullarında yetiştirilen biberlerde lufenuron'un parçalanma kinetiğinin araştırılması

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Abstract

Pepper, *Capsicum annuum* L. (Solanales: Solanaceae) production is widely cultivated worldwide, with Türkiye ranks third in global pepper production. However, pests in pepper cultivation often necessitate pesticide use, leading to concerns about pesticide residue levels and their potential impact on food safety. This study investigated the dissipation behavior of lufenuron in pepper under field conditions in Tokat, Türkiye in 2022. Liquid chromatography-tandem mass spectrometry coupled with the quick, easy, cheap, effective, rugged, and safe technique was used to analyze residues of lufenuron in pepper. The average recoveries varied from 77% to 97%, with relative standard deviations of 13% for lufenuron. Lufenuron residues administered as recommended dose and double dose degraded in pepper following a first-order kinetic model, with an estimated half-life ($t_{1/2}$) of 4.33 and 6.42 days in Tokat, 6.80 and 7.45 days in Niksar, respectively. Furthermore, a health risk assessment was conducted, which showed that the chronic risk quotient for lufenuron was much lower than 1. The present results indicated that the health risks posed for consumers by the lufenuron residues were negligible at the recommended dosages.

Keywords: Chronic risk, degradation kinetics, method verification, QuEChERS, pesticide residue

Öz

Biber, *Capsicum annuum* L. (Solanales: Solanaceae), dünyada üretimi son derece yaygın olan bir kültür bitkisi olup, biber üretiminde Türkiye global ölçekte üçüncü sırada yer almaktadır. Biber yetiştiriciliğinde üretimi sınırlayan zararlılar genellikle pestisit kullanımını gerekli kılmakta, bu durum pestisit kalıntıları ve gıda güvenliği ile ilgili endişelere yol açmaktadır. Bu çalışmada, 2022 yılında Türkiye'nin Tokat ilinde tarla koşullarında biberde lufenuron'un parçalanma davranışı araştırılmıştır. Analizler hızlı, kolay, ucuz, etkili, sağlam ve güvenilir bir yöntem olan QuEChERS tekniği ile sıvı kromatografisi-tandem kütle spektrometresi kullanılarak gerçekleştirilmiştir. Lufenuron için ortalama geri kazanım oranları %77 ile %97 arasında değişirken, bağıl standart sapma değeri %13 olarak kaydedilmiştir. Lufenuron kalıntıları, tek doz ve çift doz uygulamaları sonrasında, biberde birinci dereceden kinetik modele uygun olarak bozunmuş ve yarılanma ömrü Tokat'ta sırasıyla 4,33 ve 6,42 gün, Niksar'da ise 6,80 ve 7,45 gün olarak hesaplanmıştır. Ayrıca yapılan sağlık risk değerlendirmesi yapılmış ve lufenuron için akut ve kronik risk katsayı değerleri 1'den çok daha düşük olarak belirlenmiştir. Ayrıca yapılan sağlık risk değerlendirmesi sonucunda lufenuron için kronik risk katsayısının 1'den çok daha düşük olduğu görülmüştür. Elde edilen sonuçlara göre, önerilen dozlarda lufenuron kullanılmasının tüketiciler için herhangi bir sağlık riski oluşturmadığı ortaya konulmuştur.

Anahtar sözcükler: Kronik risk, parçalanma kinetiği, metot doğrulama, QuEChERS, pestisit kalıntısı

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Introduction

The pepper, *Capsicum annuum* L. (Solanales: Solanaceae), native to Central and South America (Mexico, Chile, Peru), is a significant crop with numerous varieties cultivated in many countries (Yıldırım & Çiftçi, 2022). Pepper is a vegetable species with vitamin content rich in human nutrition (Çınar, 2022). Green sweet bell peppers are rich in vitamins A, B1, B2, and C, and elements such as P and K, and alkaloids called capsaicin. Pepper is among the plants most resistant to drought stress due to its large leaf surface, high stoma conductivity and superficial root system (Tezcan & Kaman, 2018). Türkiye is a suitable country for growing peppers and is the world's third-largest producer of peppers (Altuntas et al., 2021; FAOSTAT, 2023). In Türkiye, peppers are consumed freshly and processed into various forms such as canned products, paste, pickles, sauces, roasted peppers, crushed peppers, and powdered peppers (Şeker, 2018). According to Turkish Statistical Institute data, Türkiye's pepper production amounts to 3018 ktons, with 172 tons exported (TUIK, 2022, 2024a).

Pests in pepper cultivation cause significant losses when conditions are favorable. Farmers typically prefer to use pesticides to control these pests. Although these toxic chemicals are effective in protecting the product, they have environmental impacts and potential risks to human health due to the residue. In this context, research on the dissipation kinetics, half-lives, and pre-harvest interval (PHI) of pesticides used during the crop growth period is of great importance (Li et al., 2020; Vijay et al., 2024).

Excessive pesticide use may lead to residue levels surpassing European Union (EU) or international Maximum Residue Levels (MRLs). The pesticide dissipation rate is a key indicator for assessing residue dynamics after application. Additionally, residue dissipation kinetics provide a scientific basis for estimating the timeframe required for pesticide levels to decline below established MRLs. Therefore, commercial pesticide formulations specify a PHI, defining the required time between the final pesticide application and harvest to ensure residue levels comply with safety standards. However, PHI is not a fixed value and may vary based on ecological parameters (MacLachlan & Hamilton, 2010). Therefore, to set appropriate PHI standards for maintaining food safety and promoting sustainable agricultural practices, pesticide residues should be evaluated under the actual climatic conditions where the pesticide is used (Bletsou et al., 2013; Cheng et al., 2022).

In Türkiye, there are 26 insecticides licensed for pepper pests, one of which is lufenuron (21 formulations). Lufenuron controls *Dialeurodes citri* (Ashmead, 1885) (Hemiptera: Aleyrodidae), rust mites, and manages Lepidoptera and Coleoptera larvae on cotton, grains, and vegetables (Tomlin, 2004). This compound is also utilized for the control of the cotton leafworm, *Spodoptera littoralis* (Boisduval, 1833) (Lepidoptera: Noctuidae), in *Capsicum* species. Lufenuron, as a member of the benzoylurea insecticide group, is an effective insect growth regulator used to destroy pests by inhibiting insect molting via acting on chitin synthesis (Rachid et al., 2008). The mechanism of action in insects has been reported by Insecticide Resistance Action Committee as "Inhibitors of chitin biosynthesis affecting CHS1" (IRAC, 2024).

The Joint FAO/WHO Expert Committee on Food Additives (JECFA) has concluded that setting an acute reference dose (ARfD) for lufenuron is not required, indicating a low risk of acute toxicity from short-term dietary exposure. JECFA has established an acceptable daily intake (ADI) for lufenuron at 0-0.02 mg kg^{-1} body weight, based on the no observed adverse effect level (NOAEL) from chronic studies and applying appropriate uncertainty factors. Chronic exposure studies on lufenuron have revealed potential adverse effects at higher doses. Higher doses resulted in tonic-clonic seizures and histopathological changes in the lungs, liver, gastrointestinal tract, and urinary tract (WHO, 2006). Lufenuron causes profound histological and histochemical damage in mammals (Farrag & Shalby, 2007).

Food safety policies are progressively influencing research into developing and applying advanced methodologies for quantitatively determining pesticide residues (Xu et al., 2022). High-sensitivity methods provide significant advantages in detecting residues at trace levels, which is essential for meeting global pesticide residue standards. In this study, lufenuron detection was conducted using the QuEChERS-LC-MS/MS methodology.

Each pesticide has unique properties. The fate of pesticides after application depends on their chemical and physical characteristics. The residue levels of a pesticide are influenced by its chemistry and environmental factors such as temperature, rainfall, and soil pH. Investigating the fate of pesticide residue in crops is crucial to preventing their adverse effects (Osman et al., 2010). Therefore, rigorous surveillance of pesticide residues in agricultural environments and accurately assessing the optimal harvest period are critical for maintaining food safety and minimizing potential health risks (Cheng et al., 2022). Despite few studies have been conducted on the dissipation kinetics of lufenuron (Khay et al., 2008; Malhat et al., 2012; Bletsou et al., 2013; Cheng et al., 2022; Li et al., 2022; Feng et al., 2022; Álvarez-Vilca et al., 2023; Tang et al., 2023; Vijay et al., 2024), no published data exist regarding its fate in sweet bell peppers. This study examines the dissipation behavior of lufenuron in peppers cultivated under field conditions in Türkiye. Furthermore, Turkish consumers' health risks associated with lufenuron residues were assessed.

Materials and Methods

Chemicals and reagents

The pesticide reference material of lufenuron (with 98.51% purity) was procured from Dr. Ehrenstorfer GmbH in Augsburg, Germany. The commercial formulation of lufenuron, an emulsion concentrate containing 50 g/l, was obtained from Hektaş in Kocaeli, Türkiye. Chemicals such as acetonitrile, methanol, anhydrous magnesium sulfate, anhydrous sodium acetate, ammonium formate with purity over 99.0%, and acetic acid were supplied by Merck in Darmstadt, Germany. Additionally, PSA (Primary Secondary Amine) with a particle size of 40 µm was provided by Supelco Analytical in Bellefonte, PA, USA.

Field trials

Field studies were conducted at the Agricultural Applications and Research Center of Gaziosmanpaşa University and Niksar, Türkiye in 2022. The Anemon F1 pepper variety was used, and the total experimental area spanned 500 m^2, with plants spaced 40 cm apart within rows and 1.4 m apart between rows. Pepper plants were grown without pesticide applications, following recommended agronomic practices. Drip irrigation was used to cultivate experimental plants. Pesticides were applied according to established guidelines for 'On data requirements for setting maximum residue levels, comparability of residue trials and extrapolation of residue data on products from plant and animal origin' (SANTE, 2019). The pesticide was applied using a knapsack sprayer at concentrations of 30 mL da^{-1} (recommended dose, RD) and 60 mL da^{-1} (double dose, DD). A randomized block design with three replications was used, with each plot containing 20 pepper plants. Pepper samples were harvested and analyzed 24 hours before the application of the pesticide confirming the absence of residues. Spraying occurred at the early fruit ripening stage, one week before the expected harvest. During the study, Tokat recorded an average relative humidity of 69.9% (ranging from 65.0% to 74.7%) and an average temperature of 24.5°C (ranging from 22.8°C to 26.9°C), while Niksar had an average relative humidity of 58.2% (ranging from 50.1% to 63.5%) and an average temperature of 25.6°C (ranging from 23.6°C to 27.4°C). There was no precipitation during the study period.

Sample collection and storage

Pepper samples were collected according to the Commission's 2002/63/EC regulation, which outlines the protocols for the formal sampling of pesticide residues in plant and animal products. Samples, each weighing approximately 1 kg (EC, 2002), were gathered at specific intervals: 0 day (2 hours post-spraying, zero-time sample), 1st, 3rd, 7th, 10th, and 14th day after pesticide application (OECD, 2021). To mitigate contamination risks during harvesting, disposable latex gloves and polyethylene bags were utilized. Upon collection, the samples were rapidly transported to the laboratory and analyzed immediately. The QuEChERS AOAC Method 2007.01 was applied to the extraction and clean-up procedures (Lehotay, 2007).

Sample preparation, extraction, and clean-up

The extraction and clean-up steps were performed according to the QuEChERS AOAC Method 2007.01, as described by Association of Official Agricultural Chemists (AOAC, 2007). During the QuEChERS extraction, 6 g of anhydrous magnesium sulfate and 1.5 g of anhydrous sodium acetate were used. For the clean-up step, 1.2 g of magnesium sulfate and 0.4 mg of PSA were utilized. A 4-blade blender (Groupe SEB, France) was used to homogenize the pepper samples. Lufenuron residue analyses of peppers were conducted in triplicate using LC-MS/MS.

Analytical instruments and conditions

The analyses were conducted using a Shimadzu® LC-MS 8050 system, renowned for its advanced UPLC and MS/MS capabilities. Chromatographic separation was executed on a Synergi Fusion-RP 100A HPLC column (2.0 mm x 50 mm, 2.5 µm particle size) from Phenomenex™ (California, USA). The mobile phase comprised 10 mmol L^{-1} ammonium formate in distilled water (A) and methanol (B). The mobile phase gradient initiated at 70% B, ramped up to 95% B over 10 minutes, returned to 40% B at 10.01 minutes, and was maintained at 40% B from 10.01 to 12.0 minutes. Each sample injection volume was precisely 10 µL. The mobile phase flow rate was consistently maintained at 0.4 mL min^{-1}, with the column temperature regulated at 40°C. LabSolution® software (version 5.118) was used to precisely manage all instrument parameters.

Method verification

The analytical method was subject to rigorous in-house verification following European SANTE parameters, which cover a variety of critical metrics such as linearity, mean recovery, limit of determination (LOD), limit of quantitation (LOQ), accuracy, precision (repeability and reproducibility in the laboratory) and measurement uncertainty (SANTE, 2021). Linearity was evaluated using matrix-matched calibration standards, with concentrations ranging from 5 to 200 µg kg^{-1}. The recovery of lufenuron from the matrix was assessed by analyzing blank samples that were fortified at three concentration levels (10, 50, and 100 µg kg^{-1}).

Statistical analysis

The dissipation kinetics of pesticides in pepper over a period were characterized by a single first-order kinetic model. Determining half-life ($t_{1/2}$) has been executed according to the following equations 1 and 2 (EPA, 2015).

$$C_t = C_0 \times e^{(-kt)} \tag{1}$$

$$t_{1/2} = \ln 2 / k \tag{2}$$

where, C_0 is the initial concentration of pesticide residues obtained from field experiments, while Ct is the pesticide residue concentration at a given time, k is the dissipation coefficient, $t_{1/2}$ is the time interval required for the pesticide residue concentration to decline to half of its initial value (C_0) after application.

In assessing the acute and chronic risks, the estimated dietary exposure was compared to ARfD, expressed in mg kg^{-1} bw day^{-1} and ADI, expressed in mg kg^{-1} bw day^{-1}. ADI values were set at 0.015 mg kg^{-1} bw day^{-1} and ARfD (None allocated) (IUPAC, 2024). The acute hazard quantity (HQ_a), which represents an acute or short-term consumer health risk, is calculated by dividing the estimated short-term intake (ESTI, expressed in mg kg^{-1} day^{-1}) by the ARfD. On the other hand, chronic hazard quantities (HQ_c), which pose chronic or long-term consumer health risks, were determined by dividing the estimated daily intake (EDI is expressed in mg kg^{-1} $days^{-1}$) by ADI (EFSA, 2015). For the Turkish population, the average adult body weight was assumed to be 73.7 kg (TUIK, 2024b; Yelaldı et al., 2024), with a reported daily pepper consumption (FC) of 0.077 kg per person (TUIK, 2022). Additionally, median pesticide residue (MR) and high pesticide residue (HR) observed for 7, 10 and 14 days (mg kg^{-1}) was taken into account. The following formulas were used for these calculations.

$$ESTI=HR \times FC/\text{body weight} \quad (3)$$

$$HQ_a=ESTI/ARfD \quad (4)$$

$$EDI=MR \times FC/\text{body weight} \quad (5)$$

$$HQ_c=EDI/ADI \quad (6)$$

HQ_a and HQ_c values exceeding 1 were categorized as indicative of unacceptable risk. Higher values were associated with elevated levels of risk.

Result and Discussion

Method verification

Matrix-matched calibration solutions with the concentrations of 5, 10, 25, 50, 100, and 200 µg L^{-1} were rigorously prepared and analyzed as triplicate by Liquid chromatography-tandem mass spectrometry. The calibration curve exhibited a linearity by a coefficient of correlation (R^2) exceeding 0.997. LODs and LOQs of 2.26 and 7.55 µg kg^{-1}, respectively have been determined to be lower than the MRLs set by the EU for pepper (0.8 mg kg^{-1}) (EU-MRL, 2024). The mean recovery ranged from 77.14% to 97.23%, with a maximum relative standard deviation (RSD) of 13.45% (Table 1). The expanded measurement uncertainty (U') is 36.96% and does not exceed the default value (50%) (SANTE, 2021). Recovery results across all spiking levels confirmed compliance with the method's performance criteria for pesticide residue analysis, thereby reaffirming its reliability and efficacy.

Table 1. Method optimization and verification data of lufenuron

Precursor ion m/z	Product ions, m/z (CE, eV)	RT (min)	Linear regression equation	Correlation coefficient (r^2)	LOD (µg kg^{-1})	LOQ (µg kg^{-1})	Spike level (µg kg^{-1})	Repeatability Recovery, % (RSD, %)	Reproducibility Recovery, % (RSD, %)	U'%
509.0	175.1 (37)	8.669	Y= 99942.5X + 624807	0.99655	2.26	7.55	10	77.14 (9.13)	78.62 (9.12)	36.96
	201.8 (24)						50	97.23 (8.51)	89.51 (13.45)	
	325.8 (18)						100	86.31 (8.84)	82.88 (9.92)	

CE, Collision energy; RT, Retention time; LOD, limit of detection; LOQ, limit of quantification; U', expanded measurement uncertainty.

Dissipation kinetics

Pesticide residues pose a significant threat to food safety, making it crucial to understand the residue behavior of pesticides after application in agricultural fields. Research on the dissipation of lufenuron in peppers is limited. Most existing studies focus on the behavior of this compound in other plant species.

Table 2 provides detailed information regarding the kinetic equations, R^2 and $t_{1/2}$ of lufenuron, facilitating a quantitative comparison of its dissipation dynamics across different plant species. Additionally, Figure 1 visually depicts the dissipation curve of lufenuron specifically in pepper under field conditions, offering a graphical representation of its temporal behavior post-application. Through these analytical tools, we aim to provide a comprehensive understanding of the dissipation kinetics of lufenuron in pepper plants.

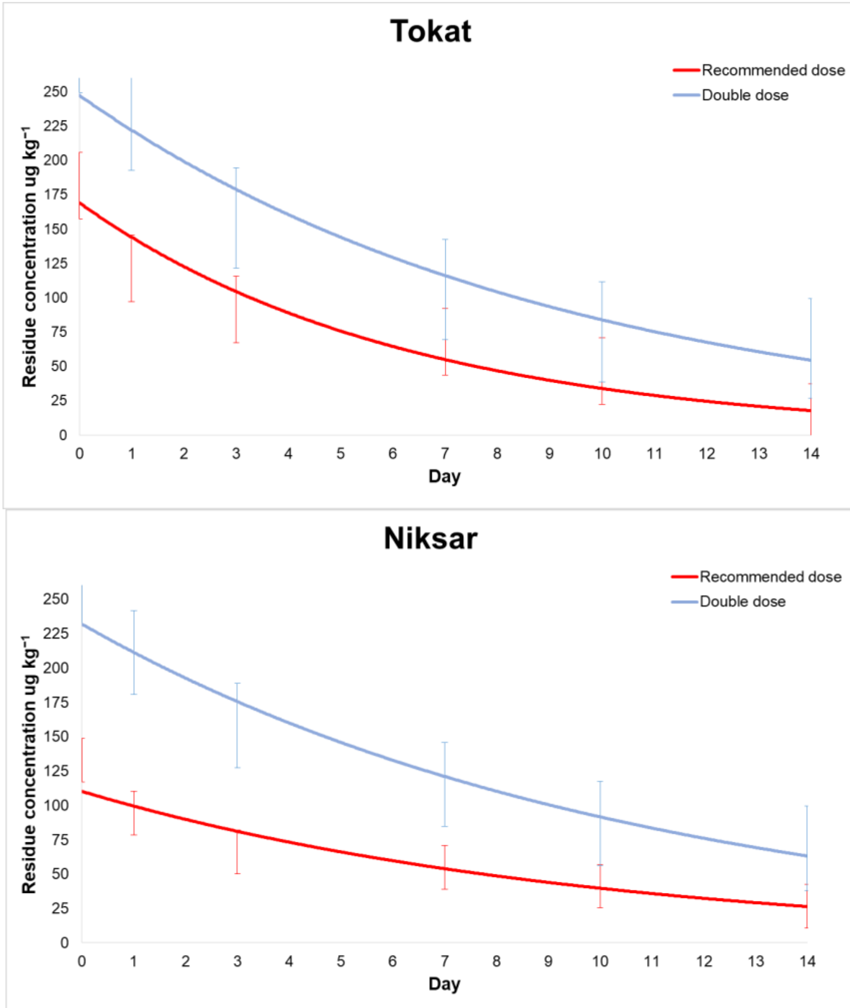

Figure. 1. Dissipation kinetic curves of lufenuron. Error bars represent the SD of triplicates.

Table 2. The parameters for the single first-order kinetic model of lufenuron, along with the residue concentrations at the PHI

Pesticide	Experiment site	Treatment	Kinetics equation	k (day^{-1})	Determination coefficient (R^2)	$t_{1/2}$ (day)	Residue at PHI (7th day)
Lufenuron	Tokat	Recommended dose	$C_t = 169.31e^{-0,160x}$	0.160	0.9375	4.33a	67.97±7.58
	Tokat	Double dose	$C_t = 247.47e^{-0,108x}$	0.108	0.9568	6.42b	105.96±3.31
	Niksar	Recommended dose	$C_t = 110.22e^{-0,102x}$	0.102	0.9039	6.80c	54.98±1.35
	Niksar	Double dose	$C_t = 231.99e^{-0,093x}$	0.093	0.9599	7.45d	115.29±2.82

a-d—means in the column marked by the same letters they do not differ significantly p=0.05; level of significance (Tukey test).

For recommended dose (RD) and double dose (DD) applications, the initial concentrations of lufenuron were 181.58 and 286.07 μg kg^{-1} in Tokat, with corresponding half-lives of 4.33 and 6.42 days. In Niksar, the initial concentrations for RD and DD were 133.10 and 262.35 μg kg^{-1}, with half-lives of 6.80 and 7.45 days, respectively. These findings indicate that lufenuron dissipated more quickly in Tokat compared to Niksar. Analysis of climatic conditions revealed that Niksar had an average relative humidity of 58.2% and an average temperature of 25.6°C, whereas Tokat experienced a higher average relative humidity of 69.9% and a slightly lower average temperature of 24.5°C. The observed differences in dissipation rates between the two locations are likely influenced by these climatic factors, underscoring the impact of environmental conditions on the degradation kinetics of lufenuron.

To the best of our knowledge, there are no papers on the dissipation kinetics of lufenuron in peppers. However, the dissipation kinetics of lufenuron in some agricultural products other than peppers has been studied. Dong et al. (2015) found half-lives ranging from 1.74 to 5.04 days in cabbage. Wang et al. (2023) reported in their studies in Anhui and Guangdong that the half-life of lufenuron in cabbage was 3.24 and 6.80 days, respectively. Cheng et al. (2022) investigated the effect of different formulations of lufenuron on half-life in maize plants and found that lufenuron in commercial formulation (3.00 days) had a longer half-life compared to nano-microemulsion formulation (2.51 days). In a study on the dissipation kinetics of lufenuron in *Pisum sativum* L., Alvarez-Vilca et al. (2023) found that the dissipation varied with the application dose and frequency. Half-lives were found to range between 1.67 and 4.84 days in pea pods and 1.88 and 13.35 days in pods. The highest half-life values were observed at a dose of 24 g a.i. ha^{-1} with an 8-day frequency. Applications with a 4-day frequency resulted in higher residue levels but shorter half-lives. At higher doses (30 g a.i. ha^{-1}), the residue levels increased, yet the dissipation kinetics remained similar. Vijay et al. (2024) found the half-life of lufenuron in cauliflower to be 3.27 days. When the half-lives in the studies are examined, it is seen that there are various values. The reasons for this difference are seen to be locations with different climate characteristics, different doses, and plant varieties. The findings of this study align with those reported in previous research.

Pesticide dissipation kinetics have demonstrated that elevated temperatures and high humidity can significantly impact pesticide residue levels and metabolites. Furthermore, residue levels vary due to various factors, including crop species, variety, developmental phase, pesticide chemical formulation, application method, timing, dosage, light exposure, microbial activity, and other environmental conditions (Lee et al., 2018; Balkan & Kara, 2023; Balkan et al., 2024). A study conducted in greenhouses at two different locations highlighted that the half-life of azoxystrobin in Swiss chard is related to changes in temperature and humidity (Kabir et al. 2018). Similarly, Sun et al. (2019) revealed in their study that environmental factors such as light, temperature, humidity and plant species (especially growth dilution factors) affect the half-life of methoxyfenozide. Their findings indicated higher temperature, humidity, or precipitation levels were associated with a reduced pesticide half-life.

Health risk assessment

Pesticide hazard evaluations have attracted considerable consumer attention in recent years, particularly in Türkiye (Çatak & Tiryaki, 2020; Balkan & Kara, 2022; Balkan & Yılmaz, 2022; Serbes & Tiryaki, 2023; Yelaldı et al., 2024). In this study, health risk assessment of lufenuron residues in pepper was conducted and the results are shown in Table 3. As a result of the risk assessment, the chronic health risk values were below 1 and there was no health risk.

Table 3. The results of long-term and short-term risk assessments of lufenuron

Experiment Site	Treatment	MR (mg kg^{-1})	HR (mg kg^{-1})	EDI (mg $kg^{-1}day^{-1}$)	ESTI (mg $kg^{-1}day^{-1}$)	HQ_c
Tokat, Niksar	RD	0.042	0.055	0.00004	0.00006	0.003
	DD	0.086	0.115	0.00009	0.00014	0.006

RD, Recommended dose; DD, Double dose ; MR, Median pesticide residue; HR, High pesticide residue; EDI, estimated daily intake; ESTI, estimated short-term intake; HQ_c, chronic hazard quantities.

Under recommended dose application, the EDI and ESTI values ranged from 0.00004 to 0.00009 mg kg^{-1} bw day^{-1}, whereas for double dose (DD) application, these values were 0.00006 and 0.00014 mg kg^{-1} bw day^{-1}, respectively. The Chronic Hazard Quotient (HQ_c) remained below 1 for both applications, indicating acceptable risk levels. Notably, the HQ_c for DD application was twice as high as that for RD application. The health risk assessment determined that the risk value due to lufenuron residues was less than one and did not pose a health risk. Studies investigating the health risks of lufenuron residues in different plants have similar results to our study (Cheng et al., 2022; Mujahid et al., 2022; Wang et al., 2023). Based on existing studies, lufenuron, when administered at appropriate dosages, does not exhibit any health risks.

Conclusion

In this study, an LC-MS/MS-QuEChERS method was verified for the detection of lufenuron residues in peppers. The dissipation kinetics of lufenuron were investigated in peppers grown in two different regions, Tokat and Niksar. Additionally, the health risk assessment of lufenuron residues was performed. This study emphasizes the critical impact of environmental factors on the dissipation of lufenuron in peppers. Faster degradation was observed in Tokat due to its higher relative humidity (69.9%) and lower temperature (24.5°C) compared to Niksar (58.2% humidity, 25.6°C). These results underscore the critical role of climate in the pesticide degradation process, highlighting the importance of environmental conditions in evaluating agricultural pesticide applications. Health risk assessments for both recommended and double-dose applications of lufenuron revealed that the HQ_c values were well below safety thresholds, suggesting a minimal risk to human health. The fact that double dosing causes a twofold increase in HQc indicates that overdoses potentially increase the health risk. Therefore, it is important to use lufenuron at recommended doses.

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