Türk. entomol. derg., 2025, 49 (1): 27-38
DOI: http://dx.doi.org/10.16970/entoted.1617716

ISSN 1010-6960
E-ISSN 2536-491X

Original article (Orijinal araştırma)

Effect of pepper variety on the degradation behaviors of pirimicarb[1]

Biber çeşitlerinin pirimicarb'ın bozunma davranışları üzerindeki etkisi

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Abstract

In pesticide residue trials, selecting crop varieties that accurately represent agricultural practices and morphological diversity is essential to obtaining reliable and applicable results. Generally, widely grown varieties are given priority, but differences in pesticide residues may occur due to the morphological and physiological characteristics of plant varieties. This study investigated the degradation behaviors of pirimicarb in five pepper varieties in Tokat, Türkiye, in 2023. Pirimicarb, an insecticide registered against the peach aphid *Myzus persicae* (Sulzer, 1776) (Hemiptera: Aphididae), is widely used in peppers, tomatoes, sugar beets, and citrus fruits. While effective in pest control, pirimicarb inhibits acetylcholinesterase, posing neurotoxic risks to target and non-target organisms. Prolonged exposure may cause endocrine disruption and oxidative stress, making residue monitoring essential for food safety. Initially, a rapid and sensitive QuEChERS-LC-MS/MS method was verified to analyze pirimicarb in peppers. Analysis results show that pirimicarb in all varieties decreased below EU-MRL (0.5 mg kg^{-1}) 24 hours after application. Significant variations in degradation rates and half-lives were observed among the varieties, attributed to their morphological and physiological differences. This research fills a critical gap by revealing the impact of varietal differences on the fate of pesticides, providing valuable data to optimize application strategies and ensure consumer safety.

Keywords: Acute risk, chronic risk, dissipation kinetics, method verification, pesticide residue

Öz

Pestisit kalıntısı denemelerinde, tipik tarımsal uygulamaları ve morfolojik çeşitliliği doğru bir şekilde temsil eden ürün çeşitlerinin seçilmesi, güvenilir ve uygulanabilir sonuçlar elde etmek için önemlidir. Genellikle yaygın olarak yetiştirilen çeşitlere öncelik verilmekle birlikte, bitki çeşitlerinin morfolojik ve fizyolojik özellikleri nedeniyle pestisit kalıntılarında farklılıklar meydana gelebilir. Türkiye'nin Tokat ilinde 2023 yılında yürütülen bu çalışmada beş biber çeşidinde pirimikarb'ın bozunma davranışları araştırılmıştır. Şeftali yaprak bitine, *Myzus persicae* (Sulzer, 1776) (Hemiptera: Aphididae) karşı tescilli bir insektisit olan pirimicarb, biber, domates, şeker pancarı ve turunçgillerde yaygın olarak kullanılmaktadır. Pirimicarb zararlı kontrolünde etkili olmasına rağmen asetilkolinesterazı inhibe ederek hedef ve hedef olmayan organizmalar için nörotoksik riskler oluşturur. Uzun süreli maruziyet endokrin bozulmasına ve oksidatif strese yol açabilir, bu da gıda güvenliği için kalıntı izlemeyi zorunlu hale getirir. Başlangıçta, biber örneklerinde pirimicarb'ı analiz etmek için hızlı ve hassas bir QuEChERS-LC-MS/MS yöntemi doğrulanmıştır. Analiz sonuçları, tüm çeşitlerde pirimicarb'ın uygulamadan 24 saat sonra AB-MRL (0,5 mg kg^{-1}) altına indiğini göstermektedir. Farklı biber çeşitleri arasında bozunma oranları ve yarı ömürlerde önemli farklılıklar gözlemlenmiştir. Bu farklılıkların, çeşitlerin morfolojik ve fizyolojik özelliklerinden kaynaklandığı düşünülmektedir. Bu araştırma, çeşit farklılıklarının pestisitlerin akıbeti üzerindeki etkisini ortaya koyarak, pestisit uygulama stratejilerini optimize etmek ve tüketici güvenliğini sağlamak için değerli veriler sağlayarak kritik bir boşluğu doldurmaktadır.

Anahtar sözcükler: Akut risk, kronik risk, parçalanma kinetiği, metot doğrulama, pestisit kalıntısı

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[1] This study was a part of the Master thesis of the first author, and supported by Tokat Gaziosmanpaşa University, Scientific Research Unit, Tokat, Türkiye, Grant Project No: 2023/54.

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Received (Alınış): 11.01.2025 Accepted (Kabul ediliş): 04.04.2025 Published Online (Çevrimiçi Yayın Tarihi): 05.04.2025

Introduction

Peppers are one of the most widely consumed vegetables globally and in Türkiye, either fresh or processed. Pepper cultivation is practiced in almost every region of Türkiye, both in open fields and greenhouses (Altuntaş et al., 2021). Beyond domestic markets, pepper production contributes significantly to the national economy, with Türkiye exporting 312.213 tons of pepper valued at approximately $89 million in 2021. The primary export destinations included Germany (57%), the Netherlands (13%), and the United Kingdom (6%) (TUIK, 2024a). However, various biotic stress factors, including insect pests and plant diseases, pose serious threats to pepper production. Pests such as two-spotted spider mite [*Tetranychus urticae* Koch, 1836 (Acarina: Tetranychidae)], aphids [*Aphis gossypii* Glover, 1877; *Myzus persicae* (Sulzer, 1776) (Hemiptera: Aphididae)], and whiteflies [*Bemisia tabaci* (Gennadius, 1889); *Trialeurodes vaporariorum* (Westwood, 1856). (Hemiptera: Aleyrodidae)], as well as diseases like bacterial canker (Cmm), *Clavibacter michiganensis* subsp. *michiganensis* (Smith) (Actinobacteriota: Microbacteriaceae), and gray mold, *Botrytis cinerea* Pers. (Ascomycota: Sclerotiniaceae), leading to significant economic losses if not effectively managed (Anonymous, 2022; Can & Ulusoy, 2022).

Chemical control remains one of the most employed strategies for pest management due to its effectiveness, rapid results, and cost-efficiency, especially in large-scale production systems. Compared to biological and cultural control methods, chemical pesticides provide immediate and broad-spectrum protection against a wide range of pests, making them indispensable in intensive agricultural practices where high yields and economic sustainability are prioritized. However, the excessive or improper use of pesticides can result in the accumulation of harmful residues in food products, potentially exceeding the maximum residue limits (MRLs) established by regulatory bodies. Consuming such contaminated foods can result in acute or chronic poisoning in humans, with symptoms ranging from mild irritation to severe health issues, including death (Solomon, 2000). These effects may manifest as mild headaches, nausea, flu-like symptoms, skin rashes, and blurred vision (WHO, 2010). In more severe cases, pesticides pose serious threats to human health, leading to neurological disorders, paralysis, blindness, and even death (Damalas & Eleftherohorinos, 2011). Additionally, studies have linked pesticide exposure to cancer, reproductive damage, and endocrine disruption (Whyatt et al., 2007; Thongprakaisang et al., 2013; Donkor et al., 2016). Epidemiological studies highlight the increased risk of leukemia and lymphoma among agricultural workers exposed to pesticides (Alavanja et al., 2004; Jurewicz & Hanke, 2008). Furthermore, prenatal exposure to certain pesticides has been associated with developmental delays and behavioral issues in children (Eskenazi et al., 2007; Rauh et al., 2006). Consequently, monitoring pesticide degradation in agricultural products is essential for ensuring food safety and compliance with legal residue limits.

Pirimicarb is a systemic carbamate insecticide widely used for controlling aphids, particularly the peach aphid (*M. persicae),* in various crops, including peppers, tomatoes, sugar beets, and citrus fruits (Anonymous, 2024). Its mode of action involves the inhibition of acetylcholinesterase (AChE), leading to an accumulation of acetylcholine at synaptic junctions, which results in neurotoxicity and paralysis in target pests (Riva et al., 2018). Pirimicarb can enter the human body through inhalation, dermal contact, or oral intake (Archibald et al., 1994; Zhou et al., 1996). Evidence also suggests its carcinogenic and mutagenic potential (Piel et al., 2019). Recent studies indicate that pirimicarb exposure may disrupt the endocrine system and contribute to developmental and reproductive issues (Gupta et al., 2020). Moreover, chronic exposure to pirimicarb has been associated with liver and kidney damage in animal studies. Its potential to induce oxidative stress and DNA damage further highlights the importance of monitoring its residue levels in food products (Zhang et al., 2022). Despite these concerns, pirimicarb continues to be approved for use in the European Union, as outlined in the latest European Food Safety Authority (EFSA) pesticide assessment reports (EFSA, 2024). Given its systemic nature, pirimicarb can penetrate plant tissues and persist in different plant parts, necessitating detailed investigations into its degradation behavior and residue dissipation patterns. The dissipation of pirimicarb in crops is influenced by numerous factors, including environmental conditions, application method, and crop morphology (Jacobsen et al., 2015; Alister et al., 2017).

Accurate pesticide residue analysis is essential for understanding dissipation behavior and ensuring food safety. This study analyzed pirimicarb residue levels using Liquid Chromatography coupled with Tandem Mass Spectrometry (LC-MS/MS), a highly sensitive and selective analytical technique. LC-MS/MS enables detecting and quantifying pesticide residues at trace levels, ensuring precise and reliable results. Its high specificity and ability to separate complex sample matrices make it an indispensable tool in pesticide residue studies. Furthermore, LC-MS/MS offers high-throughput capabilities, which are particularly advantageous for evaluating pesticide degradation under varying environmental conditions (Chen et al., 2020).

The degradation behaviors of pesticides in plants depend heavily on factors such as the cultivated species (Lu et al., 2014), plant variety (İş, 2019), growth rate and metabolism (Jacobsen et al., 2015), application frequency (Şarkaya-Ahat, 2015), application timing, formulation type (Alister et al., 2017), volatilization (Jacobsen et al., 2015), and abiotic factors like rainfall, temperature, sunlight, and humidity (Liu et al., 2014; Sharma et al., 2014; Malhat, 2017; Balkan & Kara, 2023). Numerous studies worldwide have examined the dissipation kinetics of pesticides in peppers (Antonious, 2004; Feng-Shou et al., 2008; Hem et al., 2011; Lu et al., 2014; Feng et al., 2021). However, research on this topic in Türkiye is limited (Cönger et al., 2012; Şarkaya-Ahat, 2015; Balkan et al., 2024). Most existing studies have been conducted on a single plant variety. Studies investigating the degradation behaviors of pesticides based on plant variety were scarce globally and in Türkiye.

Selecting crop varieties accurately representing agricultural practices is critical in pesticide residue trials. Test Guideline No. 509 Crop Field Trial emphasizes the importance of prioritizing commonly cultivated crop varieties to ensure the relevance and applicability of the results (OECD, 2021). However, pepper fruits vary significantly in shape, color, and size depending on their type (e.g., bell, long, or capia peppers), so solely focusing on commonly cultivated varieties may not fully capture the variability in residue degradation patterns. Therefore, while prioritizing commonly cultivated varieties is essential for generating relevant data, it is equally important to consider the potential variability introduced by less common varieties. Residue dissipation patterns may differ significantly due to each variety's morphological and physiological characteristics, such as flesh thickness, surface texture, and fruit size. To the best of our knowledge, no studies have been conducted on the degradation behaviors of pirimicarb in different pepper varieties. This study aims to investigate the degradation behaviors of pirimicarb in five different pepper varieties under field conditions. The findings will provide valuable insights into the role of varietal differences in pesticide dissipation and contribute to developing more effective pesticide residue management strategies.

Materials and Methods

Chemicals and reagents

The pesticide reference material of pirimicarb and its metabolites of pirimicarb-desmethyl and pirimicarb-desmethyl-formamido (with 99.17%, 99.30%, and 98.52% purity, respectively) was procured from Dr. Ehrenstorfer GmbH in Augsburg, Germany. The commercial wettable powder formulation of pirimicarb containing 50%, was obtained from Doğal Kimya, 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

The field studies were conducted in 2023 at the Agricultural Application and Research Center of Tokat Gaziosmanpaşa University, in Tokat, Türkiye. The study utilized five different pepper varieties. The selection of pepper varieties was based on their commercial importance and widespread cultivation in Türkiye. The varieties Köylüm f1 (three-lobed), Tufan f1 (charleston), İstek f1 (bell pepper), Forte f1 (long green), and Nefer f1 (capia) were chosen as they represent different morphological and physiological characteristics such as fruit shape, size, flesh thickness, and surface texture. The experimental plots were designed with a length of 5 m and a width of 2.8 m, with plants spaced 25 cm apart within rows and 140 cm apart between rows. A randomized block design with three replications was used, with each plot containing 20 pepper plants. Pepper plants were grown without pesticide applications, following recommended agronomic practices. Drip irrigation was used to cultivate experimental plants. Pesticides were applied according to SANTE/2019/12752 guideline (SANTE, 2019). The pesticide was applied using a battery-powered knapsack sprayer equipped with a conical spray nozzle at a pressure of 0.4 MPa. The pesticide was applied at the recommended dose of 50 g 100 L^{-1}. 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 applying the pesticide, confirming the absence of residues. Pepper samples were collected and analyzed 24 hours before pesticide application to confirm the absence of residues. This step was conducted to establish a baseline residue level, ensuring that any detected residues post-application could be attributed exclusively to the applied treatment, thereby eliminating potential confounding factors such as prior contamination or environmental deposition. Spraying occurred at the early fruit ripening stage, one week before the expected harvest. During the study, Tokat recorded an average relative humidity of 55.6% (ranging from 48.3% to 61.3%) and an average temperature of 22.5°C (ranging from 20.4°C to 24.5°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 (EC, 2002). Pepper samples (12-24 pieces, approximately 2 kg) for dissipation kinetics were collected at zero time (2 hours post-spraying), 1st, 3rd, 5th, 7th,10th, and 14th after pesticide application (OECD, 2021). Latex gloves and polyethylene bags were used to minimize the risk of contamination during the harvesting process. After being collected, the samples were swiftly delivered to the laboratory for immediate analysis.

Sample preparation, extraction, and clean-up

The QuEChERS AOAC Method 2007.01 was applied to the extraction and clean-up procedures (Lehotay, 2007). A 4-blade blender homogenized the pepper samples (2 kg). A 15 g portion of the homogenized pepper sample was accurately weighed into a 50 mL Falcon tube. Subsequently, 15 mL of acetonitrile containing 1% acetic acid was added to facilitate extraction. During the QuEChERS extraction, 0.4 g of anhydrous magnesium sulfate and 0.1 g of anhydrous sodium acetate per gram of sample enhanced phase separation and improved analyte recovery. The mixture was vigorously shaken for 60 seconds to ensure thorough interaction between the sample and the solvent. The tube was centrifuged at 5000 rpm for 5 minutes to separate the organic phase. An 8 mL aliquot of the supernatant was transferred into a new 15 mL Falcon tube for further purification. 150 mg of magnesium sulfate and 50 mg of PSA per milliliter sample were added to eliminate co-extractive matrix components and potential interferences. The tube was then shaken for approximately 60 seconds to ensure effective adsorption of unwanted compounds. Subsequently, the sample was centrifuged again at 5000 rpm for 5 minutes. A 1 mL portion of the purified extract was filtered and transferred into glass vials for analysis. The final pesticide residue was determined using LC-MS/MS, ensuring high sensitivity and selectivity in quantifying pirimicarb and its metabolites.

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 Raptor Biphenyl (2.1 mm x 100 mm, 2.7 µm particle size) from Restek Pure Chromatography (USA). The mobile phase comprised 10 mmol/L ammonium formate in distilled water (A) and methanol (B). The mobile phase gradient initiated at 50% B, ramped up to 95% B over 3.2 minutes, returned to 50% B at 3.21 minutes, and was maintained at 50% B from 3.21 to 4.75 minutes. Each sample injection volume was precisely 5 µL. The mobile phase flow rate was consistently maintained at 0.5 mL min^{-1}, with the column temperature regulated at 50°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, limits of detection (LOD) and quantification (LOQ), accuracy, precision and measurement uncertainty (SANTE, 2021). Linearity was evaluated using matrix-matched calibration, with concentrations ranging from 5 to 200 µg kg^{-1}. The recovery of pirimicarb and its metabolites from the matrix was assessed by analyzing blank samples that were fortified at three concentration levels (10, 50, and 100 µg kg^{-1}). Chromatograms of pirimicarb and its metabolites obtained through LC-MS/MS analysis are provided in Figure 1, demonstrating the separation and detection efficiency of the analytical method.

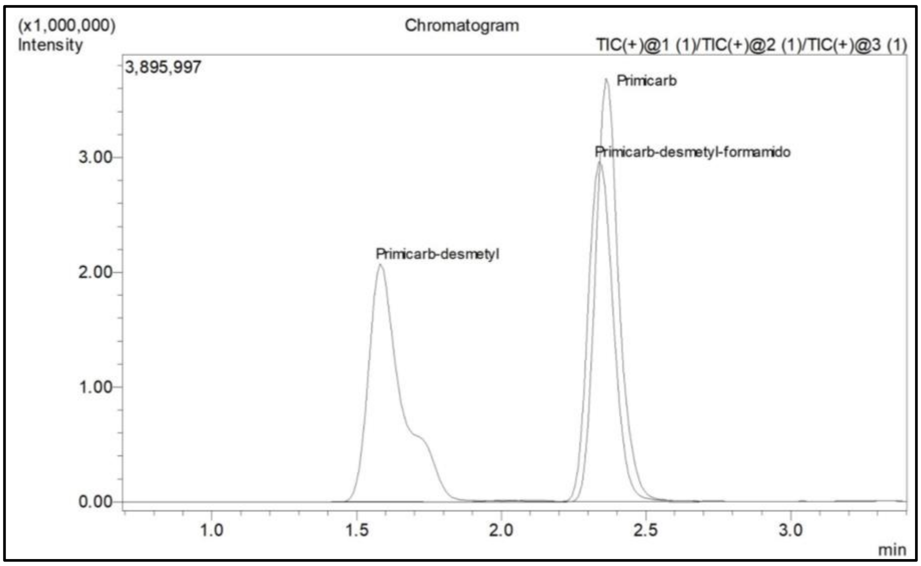

Figure. 1. Chromatogram of pirimicarb and its metabolites.

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 Eq 1 and Eq 2 (EPA, 2015).

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

$$t_{1/2}=\ln 2/k \quad (2)$$

where C_0 is the initial (zero-time) concentration of pesticide residues obtained from field experiments, while C_t is the residue concentration at a given time, k is the dissipation coefficient, $t_{1/2}$ is the time interval required for the residue concentration to decline to half of its initial value (C_0) after application. An one-way analysis of variance (ANOVA) was conducted on the data using the SPSS 20.0 package software. The Tukey multiple comparison test was employed to ascertain whether the means differed at the 5% level.

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}. The ADI was established at 0.035 mg kg^{-1} body weight per day, while the ARfD was determined to be 0.1 mg kg^{-1} body weight per day

(IUPAC, 2025). The acute hazard quotient (HQa), representing the risk to consumer health from short-term or acute exposure, is calculated by dividing the estimated short-term intake (ESTI, mg kg^{-1} day^{-1}) by the acute reference dose (ARfD). In contrast, chronic hazard quotients (HQc), which assess the risk associated with long-term or chronic exposure, are derived by dividing the estimated daily intake (EDI, mg kg^{-1} day^{-1}) by the acceptable daily intake (ADI) (EFSA, 2015). For the Turkish population, an average adult body weight of 73.7 kg was assumed (TUIK, 2024b; Yelaldı et al., 2024), along with an average daily pepper consumption (FC) of 0.077 kg per person (TUIK, 2022). Furthermore, median pesticide residue (MR, mg kg^{-1}) and high pesticide residue (HR, mg kg^{-1}) values observed at 7, 10, and 14 days were included in the analysis. The calculations were performed using the following equations.

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

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

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

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

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

Results and Discussion

Method verification

Matrix-matched calibration solutions at concentrations of 5, 10, 25, 50, 100, and 200 µg/L were meticulously prepared and analyzed in triplicate using LC-MS/MS. The calibration curve demonstrated excellent linearity, with a correlation coefficient (R^2) greater than 0.998. The LODs and LOQs were found to be below the MRLs established by the EU for peppers (0.5 mg kg^{-1}) (EU-MRL, 2025). The mean recovery ranged from 89.30% to 109.83%, with a maximum relative standard deviation (RSD) of 10.82% (Table 1).

Table 1. Method optimization and verification data of pirimicarb, pirimicarb-desmethyl, and pirimicarb-desmethyl-formamido

Analyte	Precursor ion, m/z	Product ion, m/z (CE, eV)	RT (min)	Linear regression equation Y = aX + b	Correlation coefficient (r^2)	LOD (µg kg^{-1})	LOQ (µg kg^{-1})	Spike level (µg kg^{-1})	Repeatability Recovery, % (RSD, %)	Reproducibility Recovery, % (RSD, %)	U'%
Pirimicarb	239.2	72.1 (-22)	2.407	Y=184.492X - 5604.52	0.99977	1.90	6.34	10	98.52 (8.09)	99.95 (7.51)	18.14
		182.2 (-15)						50	103.53 (7.42)	104.10 (8.27)	
								100	109.83 (7.77)	105.61 (5.08)	
Pirimicarb-desmethyl	225.1	72.1 (-23)	1.689	Y=139.231X-234.789	0.99899	1.84	6.13	10	90.66 (9.35)	93.67 (8.83)	14.01
	224.9	168.1(-15)						50	105.33 (7.75)	103.40 (6.13)	
								100	104.94 (6.87)	104.11 (4.39)	
Pirimicarb-desmethyl-formamido	253.1	72.1 (-22)	2.395	Y=114.347X+88366.2	0.99848	2.01	6.69	10	94.22 (10.82)	89.30 (8.19)	23.79
		225.1 (-10)						50	99.49 (5.82)	108.76 (6.64)	
								100	105.25 (6.75)	103.35 (4.78)	

CE, Collision energy; RT, Retention time; LOD, limit of detection; LOQ, limit of quantification; U', expanded measurement uncertainty. Y represents the instrument response, X is the analyte concentration, 'a' denotes the slope of the calibration curve, and 'b' is the intercept.

The expanded measurement uncertainty (U') remained below the default threshold of 50% (SANTE, 2021). Recovery results at all spiking levels confirmed that the method performance criteria for pesticide residue analysis, underscoring its accuracy and robustness.

Degradation behaviors of pirimicarb in different pepper varieties

In Commission Regulation (EU) 2016/71, pirimicarb residues are expressed as the sum of pirimicarb and pirimicarb-desmethyl (European Union, 2016). In this study, the total of pirimicarb, pirimicarb-desmethyl, and pirimicarb-desmethyl-formamido was represented as pirimicarb. The required waiting period before harvest, known as the pre-harvest interval (PHI), was set at 7 days for pirimicarb applied to peppers. This means that after the pesticide application, a minimum of 7 days must pass before the peppers can be harvested to ensure residue levels have declined sufficiently. The European Union has also established MRL for pirimicarb in peppers, which is 0.5 mg kg^{-1}. This limit represents the highest legally permissible concentration of pesticide residue allowed in the final product to ensure food safety (EU-MRL, 2025). The residues, half-lives, and dissipation rates of pirimicarb in different pepper varieties are presented in Table 2. The dissipation kinetics of pirimicarb residues in different pepper varieties over time are shown in Figure 2.

Table 2. Residues, rate of degradation, and half-life of pirimicarb in different pepper varieties

Time after application, day	Three-lobed Residue, µg kg^{-1} (Loss, %)	Bell pepper Residue, µg kg^{-1} (Loss, %)	Long green Residue, µg kg^{-1} (Loss, %)	Charleston Residue, µg kg^{-1} (Loss, %)	Capia Residue, µg kg^{-1} (Loss, %)
Zero time*	829.55	870.57	947.37	247.68	581.69
1	376.75 (54.58)	456.38 (44.99)	353.07 (57.44)	113.55 (86.31)	183.31 (77.90)
3	201.15 (75.75)	283.23 (65.86)	127.05 (84.69)	51.23 (93.82)	93.20 (88.77)
5	128.79 (84.47)	95.95 (88.43)	75.90 (90.85)	26.96 (96.75)	72.29 (91.29)
7**	78.25 (90.57)	87.88 (89.41)	49.88 (93.99)	23.09 (97.22)	62.66 (92.45)
10	39.13 (95.28)	54.43 (93.44)	28.42 (96.57)	12.11 (98.54)	40.30 (95.14)
14	3.43 (99.59)	6.38 (99.23)	8.73 (98.95)	3.48 (99.58)	12.61 (98.48)
Kinetics equation	$C_t = 713.55e^{-0.348x}$	$C_t = 722.64e^{-0.316x}$	$C_t = 492.76e^{-0.302x}$	$C_t = 157e^{-0.276x}$	$C_t = 293.83e^{-0.226x}$
k (day^{-1})	0.348	0.316	0.302	0.276	0.226
R^2	0.936	0.957	0.854	0.895	0.844
$t_{1/2}$ (day)	1.99a	2.19a	2.30a	2.51ab	3.07b

*: Samples were taken after two hours of spraying, **PHI, R^2: Determination coefficient;
a-c: means with the same letter are not significantly different from each other (p>0.05 ANOVA followed by Tukey test).

The dissipation kinetics of pirimicarb residues in different pepper varieties over time are depicted in Figure 2. As observed, the initial residue levels varied across the pepper varieties, with bell pepper exhibiting the highest and charleston pepper the lowest concentration. The residues declined rapidly within the first 24 hours, and by the seventh day, all varieties had residue levels below the MRL of 500 µg kg^{-1}. The differences in degradation rates are thought to be influenced primarily by the morphological (e.g., fruit color, size, shape, flesh thickness, and surface structure), physiological, and biochemical characteristics of the pepper varieties. These inherent traits likely account for the variation in residue levels observed among the different pepper types.

The initial concentrations of pirimicarb residues for three-lobed, bell pepper, long green, charleston, and capia pepper varieties were determined as 829.55, 870.57, 947.37, 247.68, and 581.69 µg kg^{-1}, respectively. The initial residue concentrations of pirimicarb varied among the five pepper varieties, which can be attributed to their distinct morphological and physiological characteristics. Factors such as surface texture, cuticle composition, wax content, fruit size, and differences in surface-area-to-volume ratio may play a role in pesticide deposition. The half-lives of these varieties were calculated as 1.99, 2.19, 2.30, 2.51, and 3.07 days. Except for charleston pepper, the initial concentrations of pirimicarb residues in the other pepper varieties exceeded the MRL. Within 24 hours, the residues in all varieties decrease below the MRL, indicating that peppers could be safely consumed one day after application, considering the MRL for pirimicarb (500 µg kg^{-1}) (EU-MRL, 2025). However, the residue level of bell pepper on the first day (456.38 µg kg^{-1}) was close to the MRL, emphasizing the importance of monitoring residue dissipation in this variety. The degradation rates of pirimicarb residues varied across pepper varieties, with capia pepper exhibiting the longest half-life.

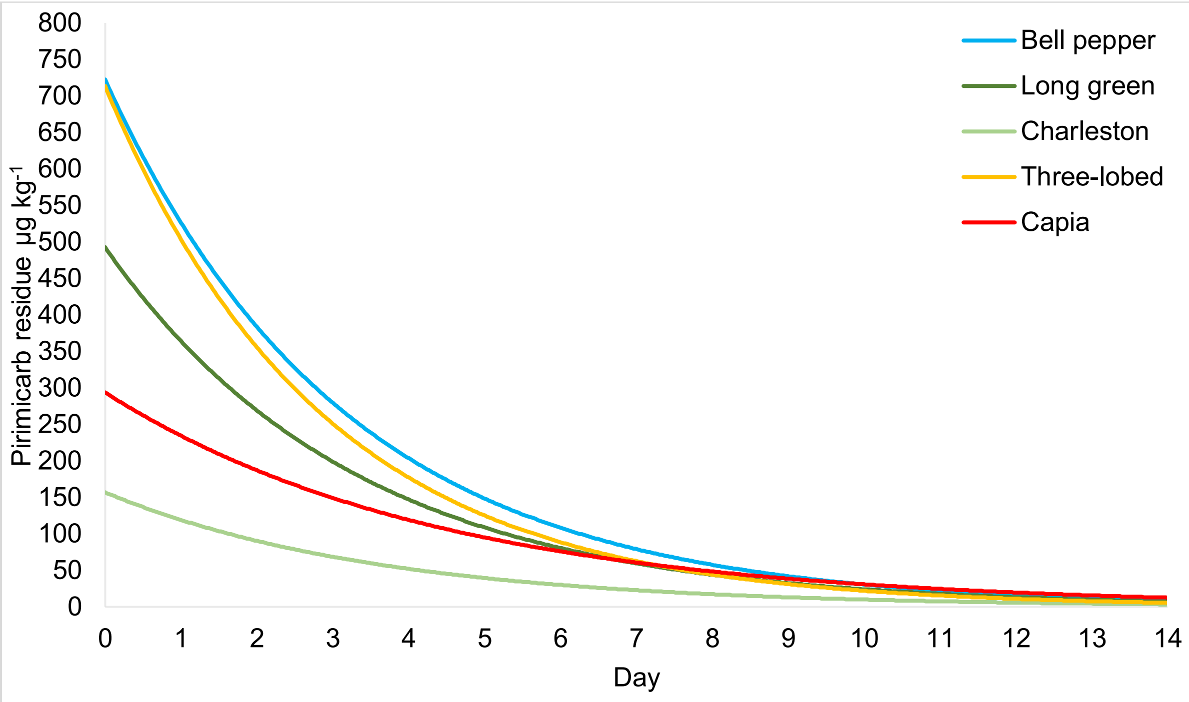

Figure. 2. Dissipation kinetic curves of pirimicarb in different pepper varieties.

To the best of our knowledge, no studies have specifically examined the degradation behaviors and residue levels of pirimicarb in different pepper varieties. By focusing on multiple pepper types, this research fills a significant gap and provides new insights into how varietal differences influence pesticide behavior. Although no directly comparable studies exist, İş (2019) demonstrated the impact of peach variety on pesticide degradation, highlighting the role of morphological traits in degradation rates. Similarly, Alister et al. (2017) reported that grape berry size influenced pesticide residue distribution, emphasizing the importance of morphological factors in residue degradation. These findings underscore the significance of physical and structural characteristics, such as surface texture, fruit size, and flesh thickness, in determining degradation behaviors. For instance, the surface texture of peppers may affect the adherence and penetration of pirimicarb, thereby influencing its degradation rates. Furthermore, differences in fruit size and flesh thickness likely impact the internal distribution and retention of the pesticide.

This study emphasizes the need to understand better how specific morphological and physiological traits of pepper varieties interact with pesticide behavior. Future research should systematically investigate these factors under controlled conditions to clarify the relationship between varietal characteristics and degradation dynamics. Such studies would facilitate the development of more tailored pesticide application strategies, improving both efficacy and safety in vegetable production. Given the scarcity of studies in this area, further research is needed to validate these findings under varying environmental and agronomic conditions and to assess their implications for consumer safety and sustainable agricultural practices. Additionally, the results could inform region-specific guidelines for safe pesticide use, particularly in areas where pepper cultivation is economically significant.

Health risk assessment

In recent years, the evaluation of pesticide hazards has garnered significant attention from consumers, particularly in Türkiye. This growing concern is reflected in a range of studies, which highlight the potential risks associated with pesticide residues in agricultural products (Çatak & Tiryaki, 2020; Balkan & Yılmaz, 2022; Serbes & Tiryaki, 2023; Balkan et al., 2024; Polat & Tiryaki, 2024; Yelaldı et al., 2024; Isci et al., 2025; Keklik et al., 2025a, b). Increased awareness has prompted more rigorous pesticide safety assessments, emphasizing the need for effective risk management strategies to ensure public health and food safety. In this study, the health risk assessment of pirimicarb residues in different pepper varieties was conducted, and the results are presented in Table 3.

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

Pepper variety	MR (mg kg^{-1})	HR (mg kg^{-1})	EDI (mg kg^{-1}day^{-1})	ESTI (mg kg^{-1}day^{-1})	HQ_c	HQ_a
Three-lobed	0.040	0.078	4.19E-05	8.14E-05	0.120	0.081
Bell pepper	0.050	0.088	5.16E-05	1.04E-04	0.147	0.104
Long green	0.029	0.050	2.90E-05	4.99E-05	0.083	0.050
Charleston	0.013	0.023	1.29E-05	2.31E-05	0.037	0.023
Capia	0.039	0.063	3.85E-05	6.27E-05	0.110	0.063

MR, Median pesticide residue; HR, High pesticide residue; EDI, estimated daily intake; ESTI, estimated short-term intake; HQ_a; acute hazard quotient, HQ_c; chronic hazard quotient.

All varieties' HQc values were below 1, indicating no significant health risk. Similarly, the HQa values were within acceptable limits, confirming the safety of pirimicarb residues in the tested pepper varieties under the current usage conditions. However, it was observed that bell pepper and three-lobed pepper had slightly higher HQc and HQa values compared to the other varieties, suggesting the importance of monitoring residue levels, particularly in these varieties.

Conclusion

This study provides a comprehensive analysis of the degradation behaviors and residue levels of pirimicarb in different pepper varieties, offering valuable insights into the influence of varietal differences on pesticide behavior. The findings demonstrated that pirimicarb residues degrade rapidly across nearly all pepper varieties, falling below the EU-MRL of 500 µg kg^{-1} within 24 hours of application. The significant variation in half-lives among the pepper types highlights the role of intrinsic morphological and physiological traits, such as surface texture, fruit size, and flesh thickness, in influencing degradation rates. By addressing a critical gap in the literature, this research emphasizes the importance of understanding how varietal differences impact pesticide dissipation. The results substantially affect consumer safety and sustainable agricultural practices, particularly optimizing pesticide application strategies.

The health risk assessment confirmed that chronic (HQc) and acute (HQa) health risk values for all pepper varieties were within acceptable limits, indicating no significant health risks under current usage conditions.

Future studies should focus on validating these findings under diverse environmental and agronomic conditions. Additionally, controlled experiments are necessary to systematically examine the effects of varietal differences on pesticide behavior, which could guide the development of region-specific guidelines for safe pesticide use in pepper production.

Acknowledgments

We are grateful to Tokat Gaziosmanpaşa University Scientific Research Projects Coordination Unit for financial support with Grant Project No: 2023/54.

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