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Environmental Impact of Chlorantraniliprole in Bell Peppers: Residue Dynamics and Sustainable Practices

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Abstract

Bell peppers (Capsicum annuum) are integral to global agriculture and nutrition due to their rich nutrient profile and culinary uses. To protect these crops from pest infestations, Chlorantraniliprole, a widely employed insecticide, has gained prominence. This research investigates the environmental fate of Chlorantraniliprole in bell pepper ecosystems, emphasizing its effects on soil, water quality, and overall ecological health. The study employs a multifaceted approach, conducting field experiments in the Sangli district to observe the real-world behavior of Chlorantraniliprole in agricultural settings. Advanced sample preparation techniques and UPLC-MS/MS analysis provide precise measurements of pesticide residues. Results indicate that Chlorantraniliprole residues in bell peppers typically remain below the maximum residue limits established by regulatory bodies, with occasional exceptions at specific intervals post application. Based on these findings, the study recommends optimal dosage and harvest intervals tailored to the local climatic conditions, ensuring effective pest management while minimizing environmental impact. Additionally, method validation confirms the reliability and accuracy of the analytical processes employed. Ultimately, these insights contribute to developing robust monitoring practices that promote the safe use of Chlorantraniliprole in bell pepper cultivation, balancing agricultural productivity with environmental sustainability.

Keywords: Bell peppers, chlorantraniliprole, environmental fate, pesticide residues, uplc-ms/ms analysis, sustainable agriculture

INTRODUCTION

Bell peppers (Capsicum annuum) hold significant economic and agricultural value, contributing substantially to global crop production and human nutrition (Rehman et al., 2022) [1]. The effective cultivation and protection of bell peppers often involve the use of pesticides, with Chlorantraniliprole being a widely used synthetic insecticide from the anthranilic diamide class. Known for its efficacy against a broad spectrum of insect pests, Chlorantraniliprole plays a crucial role in safeguarding bell pepper crops.

However, concerns have arisen regarding the environmental fate of Chlorantraniliprole and the potential repercussions of its degradation (Zhang et al., 2012) [2]. This introduction delves into the pathways and mechanisms underlying the environmental degradation of Chlorantraniliprole within bell pepper ecosystems. By exploring its impact on soil, water, and overall environmental health (Yong et al., 2015) [3], this introduction lays the groundwork for a comprehensive understanding of Chlorantraniliprole's degradation pathways, which is essential for developing sustainable agricultural practices and mitigating ecological risks.

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MATERIALS AND METHODS

- *Materials & Reagents:* In this study, acetonitrile, methanol, and formic acid were sourced from J.T. Baker. Ultra-pure water for dissolution and dilution was sourced from a Milli-Q reverse osmosis system, ensuring high purity levels necessary for accurate analytical procedures (Millipore). Chlorantraniliprole suspension concentrate (SC) with an 18.5% concentration was purchased from the local market and used without further purification. Additionally, primary and secondary amine (PSA, 40–60 µm), C18 (40–60 µm), and Graphitized Carbon Black (GCB, 40–60 µm) were acquired from Agilent Technologies. The reference standard of Chlorantraniliprole used for the analysis was sourced from Dr. Ehrenstorfer.
- *Field experiment:* The field experiment was carried out in the Sangli district of India, providing a localized context for the study. Chlorantraniliprole 18.5% formulation was applied at different doses: A – Untreated control, B – Chlorantraniliprole 18.5% at 250 g/ha, and C – Chlorantraniliprole 18.5% at 312.5 g/ha. The experimental plots were organized using a randomized block design, incorporating three replicates for each treatment, along with an untreated control plot for comparative analysis.
- Bell pepper samples (Capsicum annuum) were systematically collected from all treated and untreated experimental plots. Specifically, samples were taken 2 hours after the last application and subsequently at intervals of 1, 3, 5, 7, 10, and 15 days until the final harvest. To maintain the cold chain and prevent further degradation (Dong et al., 2022) [4], of the applied compound, all samples were carefully packed in dry ice. After the final harvest, seed, harvest, and bell pepper samples were collected from both treated and untreated plots.
- *Sample preparation:* To prepare homogenized bell pepper (Capsicum annuum) samples, approximately 10 g of each sample was weighed and transferred into a 50 mL fluorinated ethylene propylene (FEP) centrifuge tube. To the sample, 10 mL of double-distilled water and 10 mL of acetonitrile were added, followed by vortexing the mixture for about 1 minute. Next, 4 g of activated $MgSO_4$ and 1 g of sodium chloride were incorporated, and the mixture was vortexed again for 2 minutes. The tube was then placed on a rotary mixer, where it was allowed to mix for approximately 30 minutes at a speed of 50 rpm. (Godfrey et al., 2022, Luo et al., 2022, Wu et al. 2023) [5–7]. After this, the sample was centrifuged using a high-speed, refrigerated centrifuge for about 5 minutes at 5000 rpm. The resulting supernatant extract was carefully collected for further clean-up procedures.
- During the clean-up, 1.5 mL of the extract was transferred into a 2 mL centrifuge tube (Lin et al. 2023, Wang et al. 2023) [8, 9]. The dispersive solid-phase extraction (d-SPE) method was used, involving the addition of 50 mg of PSA and 150 mg of activated $MgSO_4$. The extract was vortexed for 1 minute and then centrifuged at 5000 rpm for 5 minutes. After centrifugation, 1 mL of the supernatant was filtered through a 0.22 µm nylon membrane filter and transferred to a vial for UPLC-MS/MS analysis.
- *Chromatographic Conditions:* Chromatographic separation was conducted using a Waters Acquity H-class UPLC-MS/MS system. An ACQUITY UPLC BEH C18 Column (1.7 µm x 2.1 mm x 100 mm) was utilized, maintained at a temperature of 30°C. The mobile phase was composed of solvent A (0.1% formic acid in water) and solvent B (acetonitrile).
- Initial conditions were set at 5% B, maintained for 0.5 minutes. A linear gradient was then introduced, increasing to 95% B at 1.5 minutes and held for 2.0 minutes. The gradient was then reverted back to initial conditions at 4.5 minutes, with a total run time of 5.0 minutes. The flow rate was set to 0.4 mL/min, with an injection volume of 5 µL. (Sardar et al., 2022) [10].
- *Detection Conditions:* Detection was carried out using a Waters Acquity H-class UPLC-MS/MS system, which was equipped with electrospray ionization (ESI) probe operating in positive ion mode. The optimized parameters for Chlorantraniliprole included a capillary voltage of 3500 V and an ion source temperature. Detection was performed in multiple reaction monitoring (MRM) mode, using argon as the collision gas at a pressure of 3.2 mbar. The retention time for Chlorantraniliprole was determined to be 2.4 minutes and reported in Table 1.
- *Method Validation:* The method's linearity was determined by analyzing Chlorantraniliprole reference standard levels ranging from 0.005 to 1.0 mg/L in acetonitrile. Calibration curves were

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plotted for the concentration of the calibration solution versus the peak area, (SANCO/3030/99 rev.5) and Linearity was assessed based on the correlation coefficient ($r^2 = 0.999$) obtained from the calibration curve. The accuracy of the method was verified by a recovery experiment at three fortification levels: LOQ, LOQ × 5, and LOQ × 10. Fortified samples were allowed to stand for 1 hour before extraction to allow the standard solution to penetrate the matrix. The recovery pattern is shown in Table 2.

RESULTS AND DISCUSSION

- *Method Performance:* In recent studies, various methods have been explored to understand pesticide residues and their impacts on horticultural crops. Fuchs et al. (2022) [11] investigated the environmental effects of pesticide residues and their behavior in different ecosystems. Similarly, Blythe et al. (2022) [12] provided insights into the biochemical mechanisms of pesticide degradation. The effects of insecticide toxicity and pesticide residues on horticultural crops have also been comprehensively reviewed Donkor et al. (2016) [13] Further research by Khoshnam et al. (2022) [14] focused on the environmental pollution caused by pesticide residues and their long-term effects Lee et al. (2019) [15] explored the analytical methods for detecting pesticide residues in agricultural products. Tian et al. (2023) [16] highlighted recent advancements in food composition analysis related to pesticide residues. Do et al. (2013) [17] provided detailed methodologies for microchemical analysis of pesticide residues. Additionally, Li et al. (2023) [18] reviewed the impact of environmental factors on pesticide residue levels.

The above studies collectively contribute to a deeper understanding of pesticide residue dynamics and their impact on both the environment and agricultural fields (Figure 1). The present work is based on these studies and its details of the Chlorantraniliprole method is outlined in Table 1.

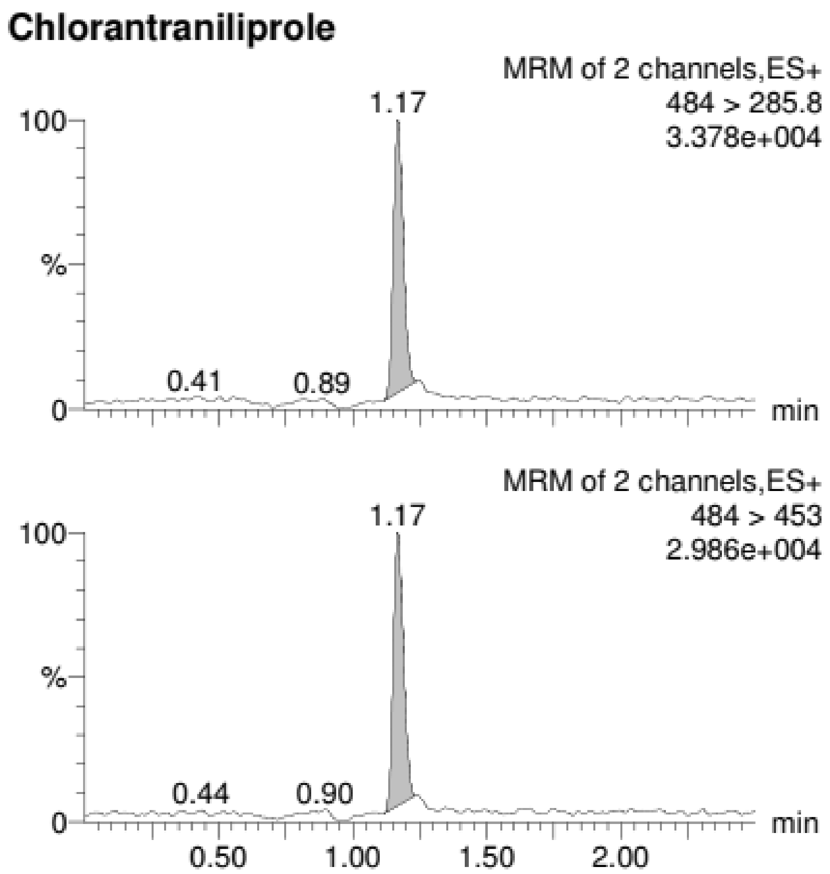

Figure 1. MRM Chromatograms of Chlorantraniliprole in standard solution 1.0 ug/L.

Table 1. Retention time and LC–ESI–MS/MS parameters for Chlorantraniliprole.

Retention Time and LC–ESI–MS/MS Parameters for Chlorantraniliprole					
Retention Time (min)	***Parent Ion (m/z)***	***Daughter Ion (m/z)***	***Dwell Time (s)***	***Collision Energy (eV)***	***Cone Voltage (V)***
2.44 Min	484	285.80	0.025	30	28
	484	453.00	0.025	25	28

The linearity of Chlorantraniliprole was individually determined within the concentration range of 0.005–1.0 mg/L for the solvent and 0.007–1.0 mg/kg for the matrix match, ensuring a correlation coefficient (r) ≥ 0.99.

Table 2. Percent recovery, relative standard deviation of chlorantraniliprole measurement in bell paper leaves.

Recovery (%) and the Relative Standard Deviation (RSD, %) of Chlorantraniliprole Measurement in Bell Paper Leaves		
Fortified Concentration (mg/kg)	**Recovery**	**RSD**
0.01	88.60	3.44
0.05	90.32	4.93
0.10	91.10	3.91

- *Chlorantraniliprole residue in bell paper:* Chlorantraniliprole residues exhibited a gradual decrease over time, conforming to first-order kinetics with a notably high correlation coefficient (Figure 2). The calculated half-lives of Chlorantraniliprole were determined to fall within the range of 2.10–2.18 days. Upon reaching the harvest stage, Chlorantraniliprole residues (Chang *et al.* 2023, Huang et al. 2023, Wang et al. 2022) [19–21] were consistently detected below the limit of quantification, as indicated in Table 3.

This study focused on the kinetics of Chlorantraniliprole residues in bell peppers. The final residues were consistently found to be below the maximum residue limit (MRL) of 0.02 mg/kg, except for the 7-day pre-harvest interval (PHI) at double the recommended dosage. Based on these findings, a dosage of 150 mL a.i./ha is proposed as safe for human consumption, with a recommended 14-day interval between pesticide application and harvest. This recommendation considers the prevailing natural climatic conditions, with an average temperature of 28.1°C and humidity of 82%. These findings contribute to the establishment of robust monitoring practices for Chlorantraniliprole residues, enhancing pest management strategies in bell pepper cultivation and ensuring consumer safety.

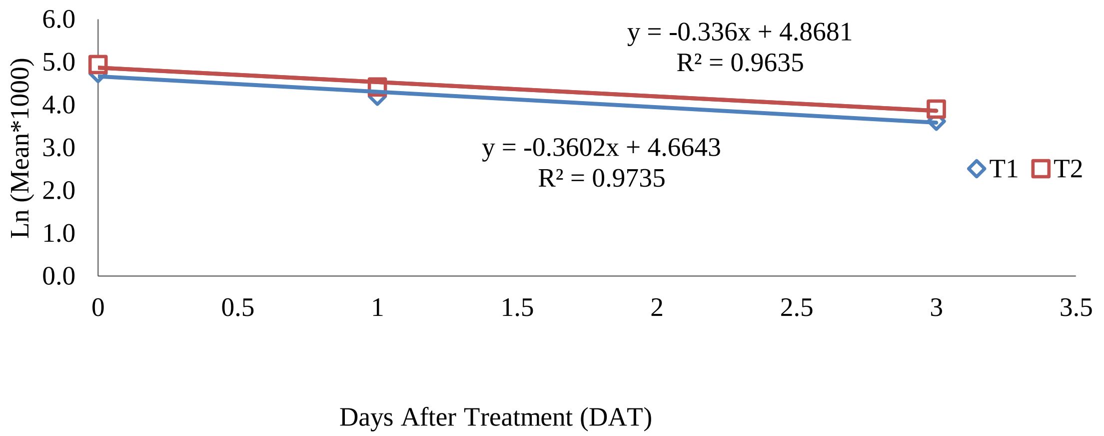

Figure 2. Kinetics of Chlorantraniliprole in Bell paper.

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Table 3. Treatment of Chlorantraniliprole residues in Bell Paper.

Days After Treatment	Treatment	Residue in mg/kg		
0	A	Not detected.	Not detected.	Not detected.
	B	0.1236	0.1045	0.1128
	C	0.1556	0.1287	0.1365
1	A	Not detected.	Not detected.	Not detected.
	B	0.0754	0.0652	0.0597
	C	0.0927	0.0822	0.0741
3	A	Not detected.	Not detected.	Not detected.
	B	0.0426	0.0354	0.0338
	C	0.0556	0.0485	0.0438
5	A	Not detected.	Not detected.	Not detected.
	B	Below determination level.	Below determination level.	Below determination level.
	C	Below determination level.	Below determination level.	Below determination level.
7	A	Not detected.	Not detected.	Not detected.
	B	Below determination level.	Below determination level.	Below determination level.
	C	Below determination level.	Below determination level.	Below determination level.
10	A	Not detected.	Not detected.	Not detected.
	B	Below determination level.	Below determination level.	Below determination level.
	C	Below determination level.	Below determination level.	Below determination level.
15	A	Not detected.	Not detected.	Not detected.
	B	Below determination level.	Below determination level.	Below determination level.
	C	Below determination level.	Below determination level.	Below determination level.
Harvest	A	Not detected.	Not detected.	Not detected.
	B	Below determination level.	Below determination level.	Below determination level.
	C	Below determination level.	Below determination level.	Below determination level.

Note: ND: Not Detected, BDL (Below Determination Level) < 0.01 mg/kg for Chlorantraniliprole.

CONCLUSIONS

This study successfully evaluated the kinetics of Chlorantraniliprole residues in bell pepper (Capsicum annuum), providing essential insights into the dissipation behavior of this pesticide under field conditions. The UPLC-MS/MS method developed for the detection and quantification of Chlorantraniliprole demonstrated high precision, accuracy, and linearity ($r^2 \geq 0.99$), with acceptable recovery rates across multiple fortification levels. Chlorantraniliprole residues were observed to decline over time, following first-order kinetics, with half-lives ranging between 2.10 and 2.18 days. By harvest time, the residue levels in all bell pepper samples were consistently below the MRL of 0.02 mg/kg, except for those sampled 7 days postapplication at the higher dose. These findings underscore the effectiveness of Chlorantraniliprole when applied within the recommended dosages, highlighting a dosage of 150 mL a.i./ha as safe for human consumption when a 14-day PHI is observed. This study's results contribute to improved pest management strategies, ensuring the safety of produce while supporting sustainable agricultural practices. Furthermore, the method developed and validated here offers a valuable tool for ongoing monitoring of pesticide residues in agricultural products, thereby enhancing food safety and regulatory compliance.

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Authorship Contribution Statement

The author Mr. Bablu Chavan did the field trial and laboratory work, Dr. Avinash Ramteke write the manuscript and refine the data as per the journal guidelines and Dr. Neeraj Prasad has been refine and suggested the improvement in the manuscript.

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