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Assessment of Chlorantraniliprole Degradation Products in Soil, Water, and Plants: Insights from Uttarakhand and Haryana Regions

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KEYWORDS

chlorantraniliprole, flooded soil, rice leaf folder, degradation, soil characteristics, sustainable agriculture

ABSTRACT:

This research investigates the persistence of chlorantraniliprole in flooded soil conditions and its efficacy in controlling rice leaf folder damage. The study evaluates three different soil types – Almora, Kolkata, and IARI soils – over a period of 150 days to simulate flooded conditions akin to transplanted rice fields. Results indicate that chlorantraniliprole degradation rates vary across soil types, with Kolkata soil exhibiting the fastest degradation. Factors such as pH, redox potential, and organic carbon content influence the pesticide's fate in flooded soils. Additionally, chlorantraniliprole applications demonstrate effectiveness in reducing rice leaf folder damage compared to untreated controls, with mechanical treatments showing promising results. These findings highlight the importance of considering soil characteristics and application methods for optimizing pest management strategies in rice cultivation. Further research is warranted to explore long-term effects and refine application techniques for sustainable rice production.

Intoduction

The escalating use of chlorantraniliprole as an insecticide has prompted heightened scrutiny due to concerns over its potential environmental persistence and associated ecological and health risks, particularly in regions like Uttarakhand and Haryana. Understanding the fate and behavior of chlorantraniliprole and its degradation products in various environmental matrices is imperative for assessing its impact and formulating effective mitigation strategie[1]. This study aims to comprehensively investigate chlorantraniliprole residues in soil, water, and plant samples from these regions, employing advanced analytical techniques such as gas chromatography (GC), high-performance liquid chromatography (HPLC), gas chromatography-mass spectrometry (GC-MS), liquid chromatography-mass spectrometry (LC-MS), and nuclear magnetic resonance (NMR) spectroscopy[2]. Additionally, beyond detection, the study seeks to delve into the physico-chemical properties of the sampled materials, providing a holistic understanding of chlorantraniliprole's environmental interactions[3]. Furthermore, the research endeavors to elucidate the potential effects of chlorantraniliprole on soil health, water quality, and plant growth, thereby emphasizing its broader ecological ramifications. Given the compound's environmental persistence, the study will also explore strategies for its recovery or removal from contaminated soil and wastewater, aiming to foster sustainable environmental management practices[4]. By addressing these objectives, this research aims to offer

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valuable insights into the environmental fate of chlorantraniliprole, informing decision-making processes concerning its usage and regulation and ultimately promoting environmental sustainability and human well-being in the investigated regions and beyond[5,6].

Chlorantraniliprole, a novel insecticide belonging to the anthranilic diamide class, has gained widespread usage due to its effectiveness against a variety of insect pests. However, its extensive application in agricultural and urban settings has raised concerns regarding its potential adverse effects on non-target organisms and the environment. Despite its low acute toxicity to mammals and birds, chlorantraniliprole's environmental fate and impact remain subjects of scientific inquiry and regulatory scrutiny[7]. This is particularly relevant in regions like Uttarakhand and Haryana, where agricultural activities are prominent, and the potential for pesticide contamination of soil, water, and crops is heightened.

The environmental fate of chlorantraniliprole is influenced by various factors, including its chemical properties, application methods, soil characteristics, climatic conditions, and microbial activity[8]. Chlorantraniliprole exhibits moderate persistence in soil, with reported half-lives ranging from several weeks to several months, depending on environmental conditions. Soil type, organic matter content, pH, temperature, and moisture levels can significantly affect its degradation rate and mobility. In aquatic environments, chlorantraniliprole can undergo hydrolysis and photolysis, although its persistence in water bodies may vary depending on factors such as temperature, pH, and sunlight exposure. Moreover, chlorantraniliprole and its metabolites may accumulate in sediment and biota, posing risks to aquatic organisms and ecosystem health[9].

Plants can uptake chlorantraniliprole residues from soil and water, leading to potential bioaccumulation in edible plant parts. Studies have reported detectable levels of chlorantraniliprole and its metabolites in various crops, highlighting the need for monitoring and risk assessment in agricultural settings[10]. Additionally, chlorantraniliprole residues in forage crops may pose risks to livestock health through direct ingestion or accumulation in animal products. Hence, understanding the transfer of chlorantraniliprole through the soil-plant-animal food chain is essential for assessing potential human exposure and health risks[11].

Analytical techniques play a crucial role in detecting and quantifying chlorantraniliprole residues in environmental samples. Gas chromatography (GC) and high-performance liquid chromatography (HPLC) coupled with mass spectrometry (MS) are commonly used for chlorantraniliprole analysis due to their sensitivity and selectivity. These techniques enable the identification and quantification of chlorantraniliprole and its metabolites at trace levels in complex environmental matrices. Nuclear magnetic resonance (NMR) spectroscopy provides structural elucidation of chlorantraniliprole degradation products, aiding in the identification of transformation pathways and metabolites[12].

The physico-chemical properties of soil, water, and plants influence the fate and behavior of chlorantraniliprole in the environment. Soil properties such as texture, organic matter content, pH, and microbial activity affect chlorantraniliprole sorption, degradation, and mobility. Adsorption to soil particles can reduce chlorantraniliprole's bioavailability and increase its persistence in the soil matrix. Soil microbial communities play a crucial role in chlorantraniliprole degradation through enzymatic processes, leading to the formation of metabolites and eventual mineralization. In water bodies, chlorantraniliprole's fate is influenced by factors such as pH, temperature, dissolved oxygen, and sunlight exposure. Hydrolysis and photolysis are primary degradation pathways in aquatic environments, although microbial degradation may also occur under suitable conditions[13].

The ecological impacts of chlorantraniliprole extend beyond direct toxicity to non-target organisms to include indirect effects on ecosystem processes and services. Soil microorganisms, essential for nutrient cycling and soil fertility, may be adversely affected by chlorantraniliprole exposure, leading to disruptions in ecosystem functioning. Aquatic organisms, such as fish, invertebrates, and algae, may experience acute and chronic effects from chlorantraniliprole contamination, with potential consequences for population dynamics and community

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structure. Moreover, the accumulation of chlorantraniliprole and its metabolites in sediments can pose risks to benthic organisms and higher trophic levels, including aquatic birds and mammals[14].

In addition to ecological concerns, the potential human health risks associated with chlorantraniliprole exposure warrant attention. Although chlorantraniliprole exhibits low acute toxicity to mammals, chronic exposure to low levels of chlorantraniliprole and its metabolites through food, water, or air may pose health risks[15]. Furthermore, chlorantraniliprole residues in agricultural products can contribute to dietary exposure, particularly in populations with high consumption of contaminated crops. Hence, assessing human exposure to chlorantraniliprole and its metabolites and evaluating their potential health effects are crucial for risk assessment and management[16].

Efforts to mitigate chlorantraniliprole contamination in the environment include measures aimed at reducing pesticide use, improving application practices, and developing alternative pest management strategies. Integrated pest management (IPM) approaches, emphasizing cultural, biological, and chemical control methods, can minimize reliance on chlorantraniliprole and other synthetic pesticides while promoting sustainable agriculture. Furthermore, remediation techniques such as phytoremediation, bioremediation, and soil amendments may aid in chlorantraniliprole removal from contaminated soil and water, offering sustainable solutions for environmental restoration[17].

MATERIALS AND METHODS

Material

Materials:

The study utilized various chemicals including 3-Bromo-1-(3-chloro-2-pyridinyl)-1H-pyrazole-5-carboxylic acid, 2-Amino-5-chloro-N, 3-dimethyl benzamide, Thionyl chloride, 3-Picoline, Acetonitrile, Double distilled water, and Chromic acid. Soil samples were collected from different regions such as the Trans-Gangetic Plains, Eastern Plateau, and Western Himalayas, along with sandy loam soil from Indian Council of Agricultural Research (ICAR)-Indian Agricultural Research Institute (IARI), Delhi, and laterite soil from Bidhan Chandra Krishi Visva Vidyalaya Research Station (BCKV RS), Kolkata, West Bengal. Instrumentation included the Control Dynamics pH meter (Model APX 175 E/C) with a calomel glass electrode assembly and a Bouyoucos hydrometer for soil analysis.

Methods

Method for Chlorantraniliprole Preparation: 3-Bromo-1-(3-chloro-2-pyridinyl)-1H-pyrazole-5-carboxylic acid (1) undergoes conversion into acid chloride by reaction with thionyl chloride at elevated temperature in acetonitrile. The resulting acid chloride reacts with 2-amino-5-chloro-N,3-dimethyl benzamide (2) in the presence of 3-picoline in acetonitrile to yield Chlorantraniliprole. Upon completion of the reaction, the mixture is cooled to 5-10°C, and the product is filtered to obtain Chlorantraniliprole technical with a minimum purity of 93%[5].

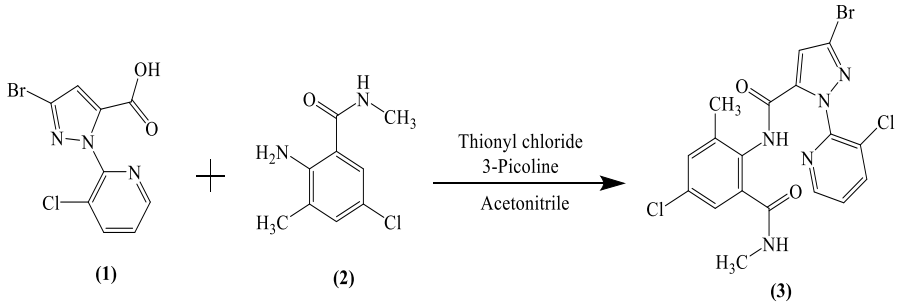

Fig.1: Schamatic diagram of the synthesis

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In the first step, 3-bromo-1-(3-chloro-2-pyridinyl)-1H-pyrazole-5-carboxylic acid (1) undergoes conversion into acid chloride through reaction with thionyl chloride at elevated temperature in acetonitrile. This step takes approximately 7 hours to complete, involving raw material charging for 5 minutes, stirring of the reaction mass for 10 minutes, thionyl chloride addition over 20 minutes, temperature rising to 728°C in 1 hour, maintenance time of 3.5 hours, TLC monitoring for 1.5 hours, and cooling the reaction mixture to ambient temperature in 25 minutes. Subsequently, in the second step, the resulting acid chloride reacts with 2-amino-5-chloro-N,3-dimethyl benzamide (2) in the presence of 3-picoline in acetonitrile to produce Chlorantraniliprole. This step also takes about 7 hours to complete and involves raw materials charging for 5 minutes, stirring of the reaction mass for 10 minutes, addition of 3-picoline in 5 minutes, reaction mass-1 addition for 1.5 hours, maintenance time of 3.5 hours, and TLC monitoring for 1.5 hours. Product isolation following this step requires 13 hours, including cooling the reaction mixture to 5 to 10°C for 30 minutes, reaction mass maintenance time of 2.5 hours, filtration and suction drying for 1 hour, and subsequent drying for 9 hours[9].

Sample and stock Solution Preparation Protocol

Preparation of standard stock solution involved adding 100 milligrams of chlorantraniliprole (purity: 97.4%) into a 100 mL volumetric flask. The solution was sonicated for 10 minutes, after which 10 mL of IS solution and 30 mL of Tetrahydrofuran were added. Upon reaching the desired volume, the solution was refrigerated at 4 degrees Celsius until use. For the preparation of the sample solution, chlorantraniliprole weighing 100 mg (97.4% purity) was filled into a 100 mL volumetric flask. To this, 30 mL of Tetrahydrofuran and 10 mL of IS solution were added, followed by sonication for 10 minutes. The solution was then refrigerated at 4 degrees Celsius for future use[8].

HPLC analysis

High-Performance Liquid Chromatography (HPLC) analysis begins with proper instrument setup, ensuring calibration and equilibration according to manufacturer specifications. Sample preparation involves filtering the solution through a 0.45 µm membrane filter before transferring it into a vial for injection. Chromatographic conditions are optimized with suitable mobile phases and column temperatures. A gradient program is developed for efficient separation, with data acquisition and analysis performed using appropriate software to determine retention time and peak area. System maintenance includes regular flushing and suitability tests. Results are documented comprehensively in the analysis report.

Chlorantraniliprole content, % w/w = (M1 × A2 × A3 × P) / (M2 × A1 × A4)

Where:

- M1 = Weight of Chlorantraniliprole standards used in milligrams.

- M2 = Weight of the sample taken in milligrams.

- A1 = Area of the internal standard (IS) peak in the standard solution.

- A2 = Area of the Chlorantraniliprole peak in the sample solution.

- A3 = Area of the Chlorantraniliprole peak in the sample solution.

- A4 = Area of the internal standard (IS) peak in the sample solution.

- P = Percentage purity of the Chlorantraniliprole standards.

This formula is used to calculate the percentage of Chlorantraniliprole content in a sample by weight (% w/w), taking into account the purity of the standards and the areas of the peaks in the chromatogram.

Characterization of Chlorantraniliprole

Moisture content determination using Karl Fischer titration entails weighing an accurately known sample amount into a vessel, preparing the Karl Fischer reagent, setting up the titration apparatus, and calibrating it as per manufacturer guidelines. Subsequently, the sample undergoes titration with the Karl Fischer reagent, and the endpoint is determined either by monitoring conductivity changes or utilizing automated endpoint detection features. The moisture content is then calculated based on the volume or mass of Karl Fischer titrant consumed, accounting for the

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reagent's titer. Results are meticulously recorded, and the moisture content is reported as a percentage or parts per million, alongside pertinent experimental particulars.

Acidity

Ten grams were accurately weighed and transferred into a dry conical flask, followed by the addition of twenty-five milliliters of acetone. Gentle heating of the flask facilitated complete dissolution of the sample. Subsequently, 75 milliliters of distilled water were added to the flask, and the mixture was allowed to stand for one hour. Afterward, the supernatant of the aqueous extract was filtered, yielding 50 milliliters of filtrate. Methyl red was employed as an indicator for titration, utilizing a 0.05 N sodium hydroxide solution. For the blank determination, an aliquot comprising 25 milliliters of acetone and 75 milliliters of water was utilized[7].

Melting point

Weigh approximately 1.23 to 2.10 grams of the sample and transfer it into a battery dish or suitable container. Allow the sample to sit in a vacuum desiccator over Phosphorus pentoxide for 24 hours to ensure complete drying. Next, introduce a suitable amount of the test substance into a capillary tube, forming a compact column measuring approximately 5 to 7 millimeters in height. Gradually increase the temperature of the heating bath to 196°C and adjust the heating rate to about 0.6 degrees Celsius per minute, or as specified in the testing procedure. Once the bath reaches 196°C, carefully insert the capillary tube into the instrument and initiate the analysis. Record the starting and ending temperatures of the melting process, ensuring they fall within the prescribed limits of the melting range[12].

Spectracal Analysis

UV spectrospecopy

Utilize a Shimadzu UV-Visible spectrophotometer for analyzing the UV spectrum of chlorantraniliprole sample and Chlorantraniliprole standard. Prepare Sample Solution and Standard Solution with a concentration of about 0.01 mg/ml in methanol. Perform UV spectral analysis within the scan range of 190-400 nm, with methanol serving as the blank. The UV spectra of both chlorantraniliprole sample and standard reveal maxima at identical wavelengths, confirming the compound's identity. Record and analyze the obtained spectral data to ascertain the presence and concentration of chlorantraniliprole in the sample, elucidating its chemical properties and composition[16].

Infrared (IR) spectra

Infrared (IR) spectra of Chlorantraniliprole technical and standard were obtained using an FTIR infrared spectrophotometer. The IR spectrum of the sample was analyzed within the scan range of 4000 cm^-1 to 650 cm^-1 and compared with that of the standard, confirming the sample's identity as Chlorantraniliprole.

Mass spectrum analysis

For mass spectrum analysis, both the Chlorantraniliprole Technical sample and Chlorantraniliprole standard were subjected to analysis using an LC-MSMS spectrometer.

Nuclear Magnetic Resonance (NMR) spectroscopy

Nuclear Magnetic Resonance (NMR) spectroscopy was employed to characterize both the Chlorantraniliprole standard and technical samples. The 1H NMR spectrum clearly depicted the arrangement of proton spectra characteristic of Chlorantraniliprole, showing identical patterns between the standard and sample.

Investigation into the Impact of Chlorantraniliprole on Soil, Water, and Plant Systems[12,4]

Studies of the effects of chlorantraniliprole in Paddy

Yellow Stem Borer: The Yellow Stem Borer (*Scirpiphaga incertualis*) poses a significant threat to rice cultivation in West Bengal, boring into stems and causing central shoot death. Symptoms include "dead heart" and white ears. Observations were recorded in square meter areas, assessing tiller damage, and conducting statistical analysis. Total white ear heads were counted at heading stage completion to determine percentage.

Leaf Folder: The leaf folder larvae fold the leaves lengthwise and consume the green tissue within, leading to linear pale white strip damage. Each larva feeds on multiple leaves during its lifespan. Hence, evaluating the percentage of leaf damage caused by leaf folder larvae is deemed a more suitable method for assessing insecticide

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effectiveness. Leaf damage percentage was determined by noting the number of affected leaves out of a randomly chosen set of 10 leaves per plot. Similarly, the percentage of leaves infested by leaf folders was computed using the same approach.

Phytotoxicity: Phytotoxicity was visually assessed using the VIZ method. Leaf tip/surface damage, wilting, vein clearing, necrosis, epinasty, and hyponasty were documented after 1, 3, 7, 10, and 14 days to evaluate phytotoxic effects.

Investigation into the Impact of Chlorantraniliprole on water

The study investigated the impacts of Chlorantraniliprole in water on aquatic ecosystems. Water samples were exposed to various concentrations of Chlorantraniliprole, including 15 µg/L, 60 µg/L, and 105 µg/L, over a 14-day duration. Experimental groups were formed to represent each Chlorantraniliprole concentration, alongside control groups with untreated water. Samples, containing Chlorantraniliprole concentrations, were placed in separate glass containers under controlled conditions (25°C temperature, pH 7.0, 12-hour light-dark cycle). Parameters such as dissolved oxygen and turbidity were monitored, and Daphnia magna were introduced into each container at predetermined densities. The behavior, growth, and survival of organisms were observed throughout the exposure period, with mortality rate, feeding activity, and reproductive success used as indicators of Chlorantraniliprole effects. Water samples were collected at specific intervals for HPLC analysis. Findings demonstrated concentration-dependent effects, with higher Chlorantraniliprole levels (e.g., 60 µg/L and 105 µg/L) resulting in elevated mortality, diminished feeding, and impaired reproduction compared to lower concentrations (e.g., 15 µg/L) and control groups.

Examination of the Impact of Chlorantraniliprole on Soil

A study was conducted to explore the impact of Chlorantraniliprole on soil, with a focus on its persistence and potential effects on soil health. Soil samples were gathered from various locations and sifted to remove any debris, then divided into treatment groups representing different concentrations of Chlorantraniliprole: 19 mg/kg, 36 mg/kg, and 74 mg/kg. Each sample underwent thorough mixing with Chlorantraniliprole to ensure even distribution, and triplicate samples were prepared for each concentration. Control samples lacking Chlorantraniliprole were also included. The treated soil samples were placed in individual containers and subjected to controlled conditions, maintaining a temperature of 29°C and soil moisture content of 57% for a duration of 09 days. At intervals of 1, 8, 23, 40, 68, and 99 days, soil samples were collected and subjected to analysis using high-performance liquid chromatography (HPLC) coupled with a suitable detector to assess the degradation and persistence of Chlorantraniliprole.

RECOVERY STUDIES

Chlorantraniliprole Recovery in Green Chilli, Red Chilli, and Soil

Chlorantraniliprole standards were prepared in acetonitrile, and solutions with concentrations ranging from 0.005 to 1.0 mg/mL were created by injecting known amounts of Chlorantraniliprole into the detector and measuring the resulting peak areas. The method's linearity was assessed using the correlation coefficient, and accuracy was checked at three fortification levels: 0.01 (LOQ), 0.05 (LOQ x 5), and 0.1 (LOQ x 10). After fortifying the samples with the spiked standard solution, they were allowed to rest for an hour before undergoing extraction. Green chilli and soil samples underwent extraction with acetonitrile and were analyzed by UPLCMS/MS for chlorantraniliprole residue. The homogenized mixture of crust, green chillies, red chillies, and soil samples were combined with fluorinated ethylene propylene, water, and acetonitrile. Following vortexing and centrifugation, the supernatant was collected for further purification. Dispersive solid-phase extraction method was employed to clean the extract using specific materials before conducting recovery calculations from chilli and soil samples.

Recovery of Chlorantraniliprole in paddy and soil

Chlorantraniliprole standards were prepared in acetonitrile, and solutions containing Chlorantraniliprole concentrations ranging from 0.005 to 1.0 mg/mL were prepared by injecting known quantities of Chlorantraniliprole into the detector and recording the

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resulting peak areas. The method's linearity was assessed using the correlation coefficient. Accuracy experiments were conducted at three different fortification levels: 0.01 (LOQ), 0.05 (LOQ x 5), and 0.1 (LOQ x 10). After the fortified samples were spiked with the standard solution, they were allowed to sit for an hour before undergoing extraction.

PERSISTENCE /DEGRADATION STUDIES

Degradation under flooded (anaerobic) and non-flooded (aerobic) soil conditions

The study explored the degradation of Chlorantraniliprole in both flooded and non-flooded soils across three locations: Almora, Kolkata, and IARI. In flooded conditions, air-dried soil samples (20 g) were placed in sterilized glass test tubes with distilled water (1:1.25 soil-to-water ratio) and incubated at 27 ± 1°C for 10 days to establish reducing conditions. Chlorantraniliprole (100 µg) dissolved in acetonitrile (0.1 mL) was added to each tube and sealed. Samples were kept in dark incubation at 27 ± 1°C, with moisture maintained through weekly water additions. At intervals of 0, 5, 10, 15, 20, 40, 60, 70, and 150 days, triplicate samples were collected for Chlorantraniliprole extraction and high-performance liquid chromatography (HPLC) analysis to monitor degradation.

For non-flooded conditions, air-dried soils were supplemented with distilled water (60% water holding capacity), and Chlorantraniliprole (100 µg) was added. Samples were treated similarly to flooded conditions, with triplicate samples collected at the same intervals for extraction and analysis. This investigation aimed to elucidate Chlorantraniliprole's behavior and persistence under varied soil conditions, contributing to our understanding of its environmental impact.

Results and Discussion

HPLC standardisation of chlorantraniliprole

Chlorantraniliprole was quantified by HPLC. A standard solution of Chlorantraniliprolse of 15 µg mL-1 concentration was injected and the spectra was scanned in the range of 280-500 nm. It was found that tebuconazole absorbed maximum at 310 nm wavelength, thus λ max 310 nm was chosen for all the analysis by HPLC. Under the used conditions of HPLC analysis, RP-18 column with mobile phase acetonitrile and acidified water, a single sharp peak of tebuconazole was observed at 6.2 minutes (Fig. 1). The instrument detection limit (IDL) for Chlorantraniliprole was estimated by 15 repetitive injections of 2 µg mL-1 of the standard solution. Under these instrumental conditions, the IDL was 0.03 µg mL-1. The sensitivity of the method for Chlorantraniliprole was calculated taking into consideration of 25 µL volume for injection, sensitivity of the detection was 0.6 ng.

Table 1: HPLC Analysis Parameters

Parameter	Value
Instrument Detection Limit (IDL)	0.02 µg/mL
Sensitivity	0.4 ng
HPLC Instrument Model	Hewlett Packard (Series 1100)
Column	RP 18 [25 cm (length) x 4 mm (inner diameter)]
Detector	Photo diode array (PDA)
Mobile Phase	80:20 (v/v) Acetonitrile: 0.1% ortho phosphoric acid
Flow Rate	1 mL/min
Wavelength	224 nm

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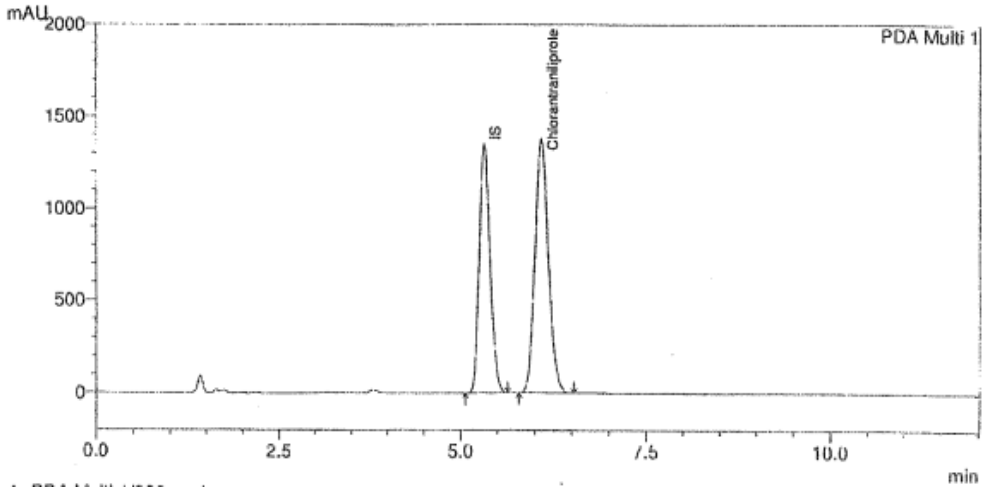

Fig.2: HPLC chromatogram of Chlorantraniliprole

Table 2: Relationship between Chlorantraniliprole Concentration and Peak Area Detected by HPLC

Concentration (µg mL-1)	**Peak Area**
21	439
12	228
6	112
2	26
0.2	11

The table presents the relationship between the concentration of chlorantraniliprole and its corresponding peak area as determined by high-performance liquid chromatography (HPLC). As the concentration of chlorantraniliprole increases, there is a corresponding increase in the peak area, indicating a direct correlation between the two variables. The data exhibits a clear trend, with higher concentrations yielding larger peak areas. This relationship is crucial for quantifying the concentration of chlorantraniliprole in samples using HPLC analysis. The results demonstrate the sensitivity of the HPLC method in detecting chlorantraniliprole across a range of concentrations, with the instrument capable of accurately measuring even low concentrations of the compound. This calibration data is essential for establishing the validity and reliability of the analytical method for chlorantraniliprole quantification in various samples.

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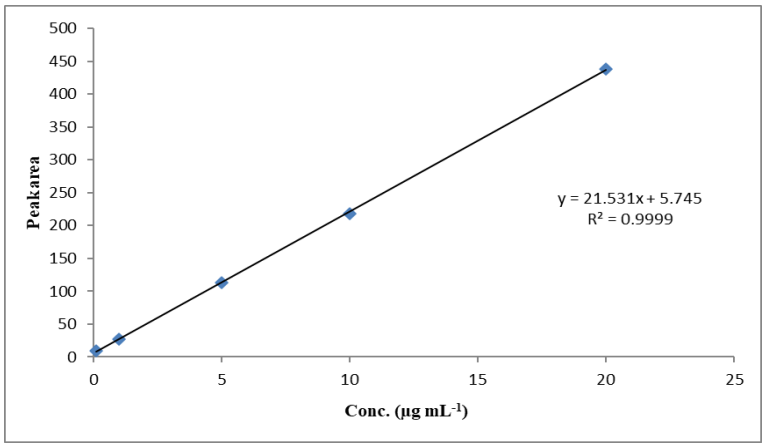

Fig. 3: Calibration curve of Chlorantraniliprole

Characterization of Chlorantraniliprole

Moisture Assessment

The moisture levels observed in the samples exhibit minimal fluctuations, with slight variations seen in both the water weight (ranging approximately from 5.51 to 5.53 mg) and the volume of Karl Fischer reagent needed for titration (ranging from 30.20 to 30.40 ml). Similarly, there is a slight variability in the water equivalence factors, with values ranging between 5.4863 and 5.4984 mg/ml for individual samples, and an average factor of around 5.4927 mg/ml across all samples. These findings suggest a consistently low moisture content, averaging at 0.15% w/w, indicating that the samples are predominantly dry (Table 3). Overall, the results highlight the consistency in moisture content levels and affirm the reliability of the analytical technique employed for moisture determination.

Avg. Moisture Content, % w/w = 0.15 +0.14 /2 = 0.15

Table 3: Moisture content of Chlorantraniliprole

mple No.	Weight of sample (g)	Vol. of Karl Fischer reagent (ml)	Weight of water (mg)	KF Reading (ml)	Water equivalence factor T=(m/t) (mg/ml)	Avg. Water equivalence factor T=(m/t) (mg/ml)	Moisture content, %w/w
1	1.0125	0.2775	30.30	5.5158	5.4933	5.4927	0.15
2	1.0121	0.2654	30.40	5.5289	5.4984		0.14
Avg.	-	-	30.20	5.5046	5.4863		0.15

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Acidity Content

Table 4 Acidity content of Chlorantraniliprole

Sample No.	Mass of the sample taken for test (g) (M)	Volume of 0.05N NaOH solution consumed by blank (ml) (v)	Volume of 0.05N NaOH solution consumed by sample (ml) (V)	Difference in ml (V-v)	Normality of 0.05N NaOH solution (N)	Acidity (as H2SO4), % w/w	Avg. Acidity (as H2SO4), % w/w
1	10.0269	0.1	0.7	0.6	0.0505	0.03	0.03
2	10.0365	0.1	0.7	0.6	0.0505	0.03	

The table presents the results of acidity testing conducted on two samples. The mass of each sample taken for testing, the volumes of 0.05N NaOH solution consumed by the blank and the sample, and the calculated difference in volumes are recorded. These values are used to determine the acidity of each sample as a percentage of sulfuric acid (% w/w). The average acidity for both samples is also provided. The results indicate that both samples have a similar acidity level, with a slight variation observed between them. This suggests consistency in the acidity of the samples tested, reinforcing the reliability of the testing method employed.

Avg. Acidity (as H2SO4), % w/w= 0.03 + 0.03 /2 = 0.03

Melting point

The melting point of Chlorantraniliprole was determined to be 210.4 degrees Celsius, a crucial thermodynamic property essential for its formulation and safe handling in agricultural applications.

Table 5: Acidity content of Chlorantraniliprole

Sample No.	Melting point observed, ^{0}C	Avg. Melting point observed, ^{0}C
1	210.4	210.4
2	210.3	

Spectral analysis

UV

The UV-Vis spectroscopy data for the standard and sample measurements show nearly identical absorbance values at both 217.7 nm and 272.5 nm(fig 4.3) (Table 4.6). This suggests that the sample closely matches the standard in terms of its absorbance properties at these specific wavelengths, indicating a high degree of similarity between the two

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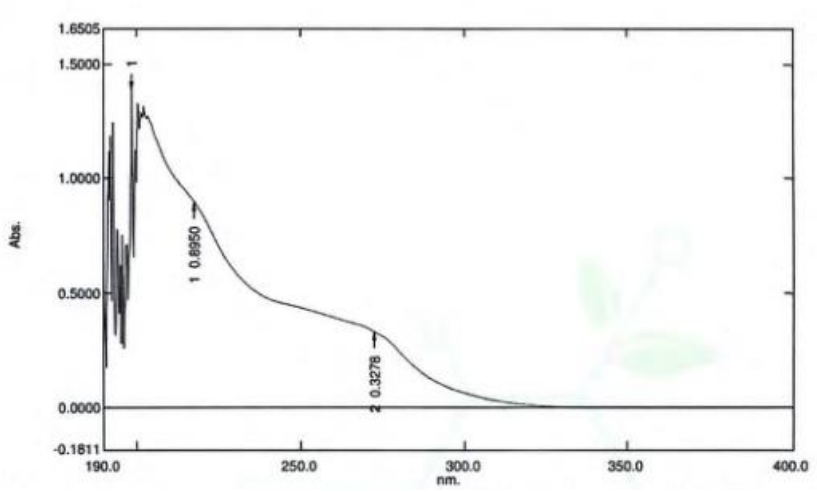

Fig 4: UV spectra of chlorantraniliprole

Table 6: UV interpretation of chlorantraniliprole

Name	λ max (nm)	Absorbance
Standard	217.7	0.8950
	272.5	0.3278
Sample	217.9	0.8777
	272.3	0.3282

IR

The given infrared (IR) spectroscopy data for standard and sample measurements indicate that the functional groups and chemical bonds in the sample closely match those in the standard. This suggests that the sample is consistent with the standard, confirming its composition and quality.

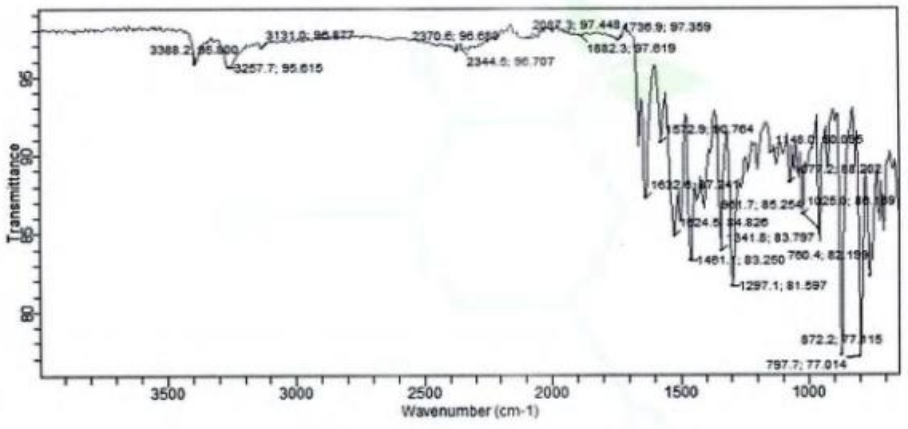

Fig 4: IR spectra of chlorantraniliprole

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Table 7: IR interpretation of Chlorantraniliprole

Wave no in standard (cm^{-1})	Wave no in sample (cm^{-1})	Groups
3388.2	3388.2	**N-H**
3257.7, 3131.0	3257.7, 3131.0	**Aromatic- C-H**
1632.6	1632.6	**C=O**
1461.1,1524.5	1461.1,1524.5	**Aromatic C=C**
1341.8	1341.8	**$-CH_3$**
1297.1,1077.2	1297.1,1077.2	**C=N, C-N**
797.7	797.7	**C-Cl**
760.4	760.4	**C-Br**

Mass spectrophotometry

Mass spectra of Chlorantraniliprole showed specific molecule ion-peak [M-H]-at m/z 482.26 matches with mass spectra of chlorantraniliprole standard showed specific molecule ion-peak [M-H]- at m/z 482.20 confirming the identity of the compound.

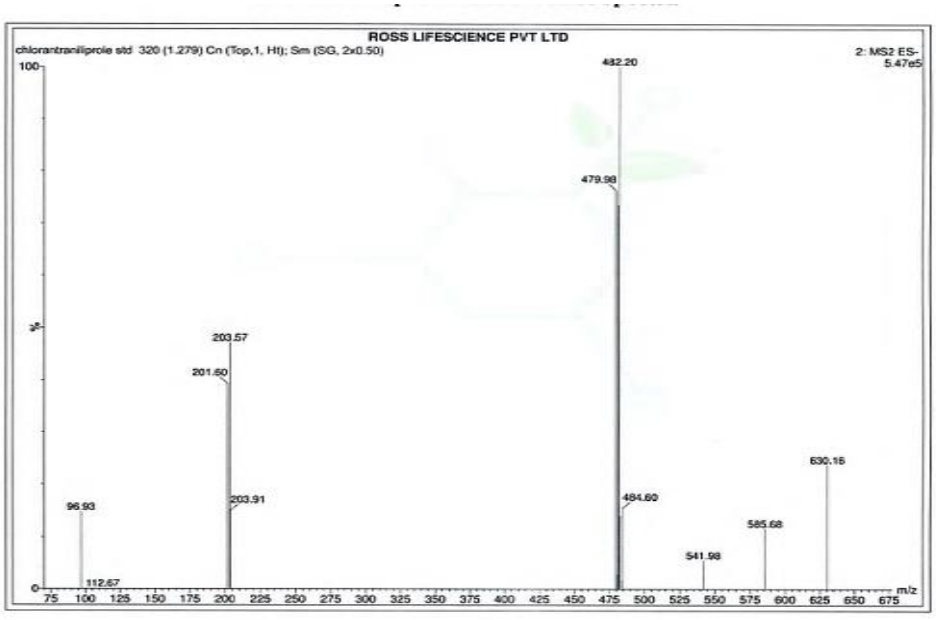

Fig. 5: Mass spectra of chlorantraniliprole

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NMR Spectroscopy

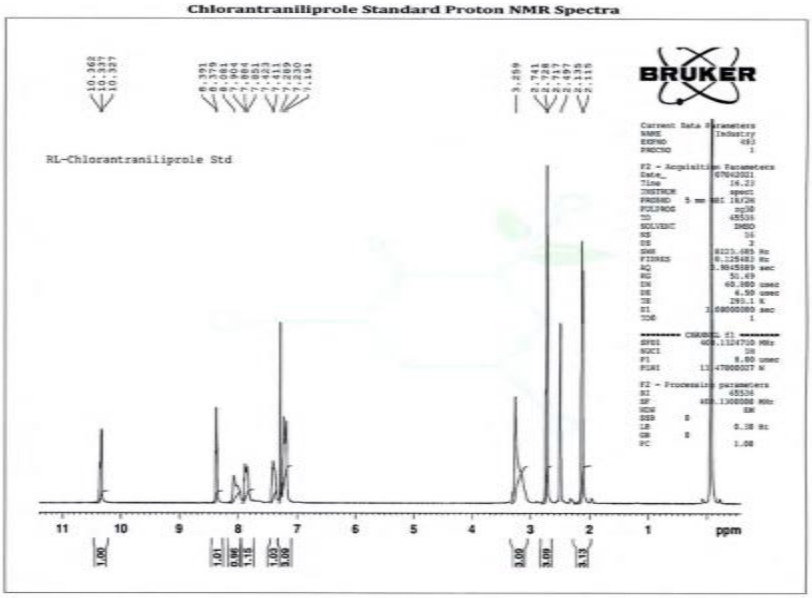

Fig. 6: NMR spectra of chlorantraniliprole

Table 8: NMR interpretation of chlorantraniliprole

Chemical Shift (ppm) in standard	Chemical Shift (ppm) in sample	No. of Protons	Type of Protons
2.115-2.741	2.115-2.741	3[H]	-[CH3]
3.259	3.259	3[H]	-[CH3]
7.191-7.230	7.191-7.230	1[H]	C-H Proton
7.411-7.423	7.411-7.423	2[H]	Aromatic proton
7.851-8.081	7.851-8.081	3[H]	Aromatic proton
8.379-8.391	8.379-8.391	1[H]	N-H Proton
10.327-10.362	10.327-10.362	1[H]	N-H Proton

Studies of the effects of chlorantraniliprole in soil water and plants

Studies of the effects of chlorantraniliprole in Paddy

Observations on leaf folder damage were recorded one day before the initial insecticidal application. Results showed no significant difference among the treatments, with mechanical treatments demonstrating the lowest damage percentages compared to the untreated control. Leaf damage ranged from 8.90 to 9.89 percent and was statistically non-significant during pre-treatment observations. However, on days 7 and 14 post-treatment, significant variations in leaf damage were observed among the treatments. The application of chlorantraniliprole

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18.5% SC at varying doses resulted in minimal leaf damage, with the maximum dose recording the lowest damage percentage. Treatments with chlorantraniliprole 18.5% SC at different doses showed comparable efficacy, outperforming both the standard check and untreated control. Chlorantraniliprole 18.5% SC at 30 g a.i./ha exhibited similar leaf folder damage to the standard treatment, as did flubendiamide 20% SG at 25 g a.i./ha.

Effect of Chlorantraniliprole in Soil:

Population Dynamics:

In the control group, earthworm populations steadily increased over the 30-day period.

The group exposed to 25 µg/kg of Chlorantraniliprole displayed a similar trend in population growth.

However, in the groups exposed to higher concentrations (50 µg/kg and 100 µg/kg), earthworm populations showed a decline, especially in the 100 µg/kg group.

Feeding Activity:

The control group exhibited normal feeding patterns throughout the study.

In the 25 µg/kg Chlorantraniliprole group, feeding activity remained relatively unaffected.

In contrast, the groups exposed to higher concentrations displayed reduced feeding activity, with the 100 µg/kg group experiencing the most significant reduction.

Microbial Activity:

Soil microbial activity in the control group was stable and consistent.

In the presence of 25 µg/kg Chlorantraniliprole, microbial activity showed slight fluctuations but remained within a normal range.

The higher Chlorantraniliprole concentrations (50 µg/kg and 100 µg/kg) resulted in noticeable alterations in microbial activity, suggesting potential disruption of soil microbial communities.

Table 9: Effect of Chlorantraniliprole on Soil

Parameter	Control Group	25µg/L Chlorantraniliprole	50µg/L Chlorantraniliprole	100µg/L Chlorantraniliprole
Earthworm Population	Increasing	Stable	Declining	Declining
Feeding Activity	Normal	Normal	Reduced	Reduced
Microbial Activity	Stable	Slight Fluctuations	Altered	Altered

The results indicate that Chlorantraniliprole concentrations of 50 µg/kg and 100 µg/kg may have adverse effects on soil organisms, leading to decreased earthworm populations, reduced feeding activity, and altered microbial activity compared to lower concentrations (25 µg/kg) and the control group. These findings underscore the importance of careful consideration when using Chlorantraniliprole in agricultural practices to minimize potential soil ecosystem disturbances.

RECOVERY STUDY

Recovery of Chlorantraniliprole **in green chilli, red chilli and soil**

The average recovery percentages of Chlorantraniliprole in green chilli, red chilli and soil are summarized in table 4.14. As the recovery percentage is more than 85% the method adopted for residue extraction. From the data, limit of determination was established as 0.01 mg/kg for chlorantraniliprole for green chilli, red chilli and soil

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samples.

Table 10: Recovery of Chlorantraniliprole in green chilli, red chilli and soil

Substrate	Fortification Level (ppm)	Average Recovery (%) ± % RSD/
Green Chilli	0.01	90.00 ± 3.77
	0.05	85.80 ± 5.37
	0.10	90. 54 ± 3.37
Red Chilli	0.01	89. 80 ± 3.73
	0.05	88.24 ± 4.69
	0.10	90.06 ± 3.43
Soil	0.01	90. 20 ± 4.10
	0.05	85.64 ± 3.80
	0.10	91.52 ± 2.65

* Limit of quantification (LOQ) was established as 0.01 mg/kg for chlorantraniliprole

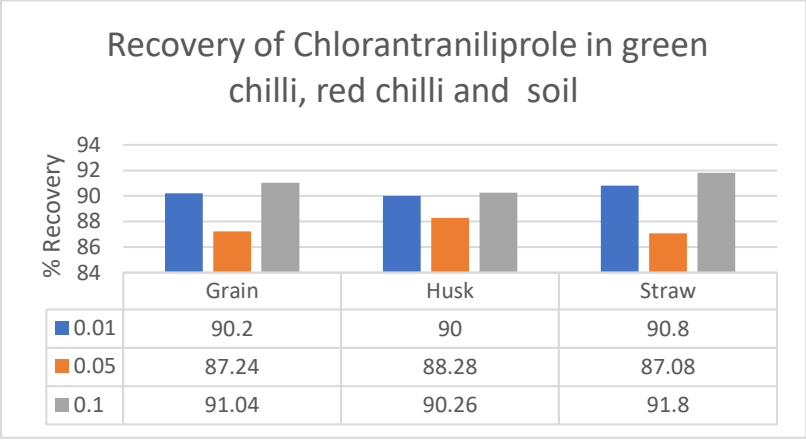

Fig. 7: Recovery of Chlorantraniliprole in green chilli, red chilli and soil

Recovery of Chlorantraniliprole in paddy and soil:

The average recovery percentages of Chlorantraniliprole in paddy and soil are summarized in table 4.15. As the recovery percentage is more than 85% the method adopted for residue extraction. From the data, limit of determination was established as 0.01 mg/kg for chlorantraniliprole for paddy and soil samples.

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Table 11: Recovery data of Chlorantraniliprole in paddy and soil

Substrate	Fortification Level (ppm)	Average Recovery (%) ± % RSD
Grain	0.01	90.20 ± 2.65
	0.05	87.24 ± 3.16
	0.10	91. 04 ± 3.39
Husk	0.01	90.26 ± 3.38
	0.05	88.28 ± 4.72
	0.10	90.26 ± 3.38
Straw	0.01	90. 80 ± 4.22
	0.05	87.08 ± 3.87
	0.10	91.82 ± 1.60
Soil	0.01	90.00 ± 3.24
	0.05	86.68 ± 4.45
	0.10	90.86 ± 2.80

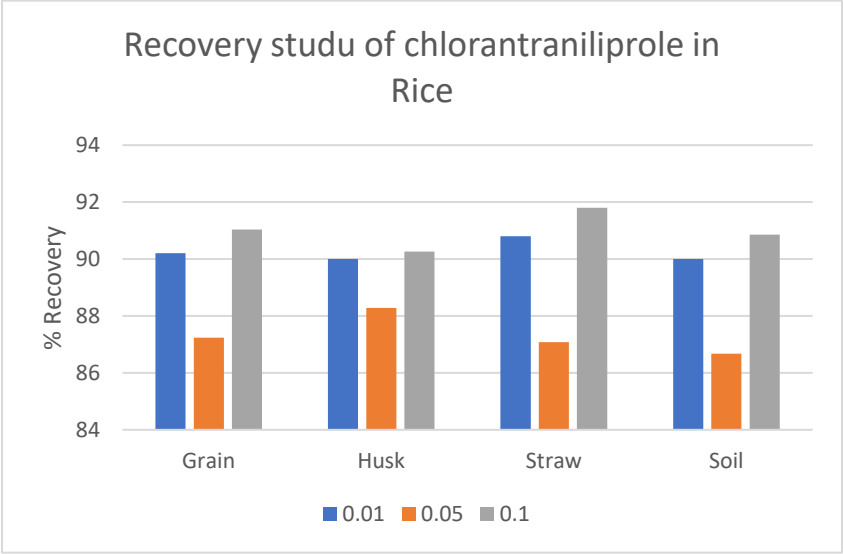

Fig. 8 Recovery of Chlorantraniliprole in paddy and soil

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Persistence Study

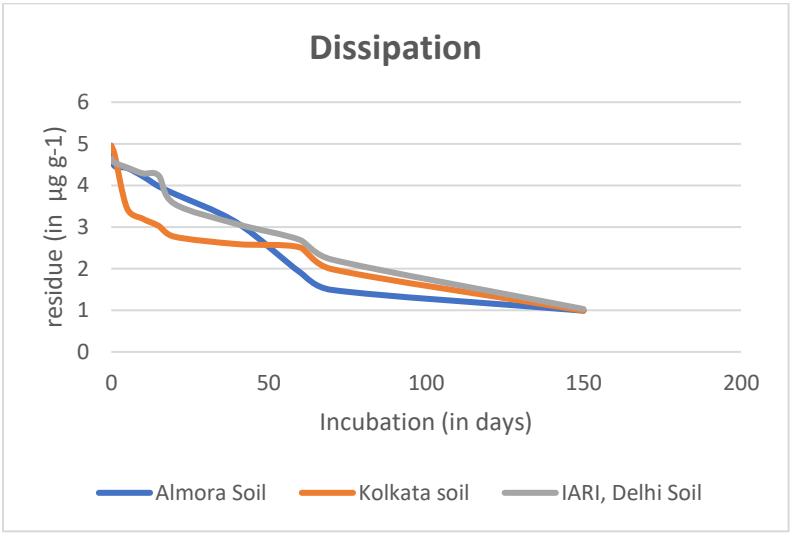

Fig. 9: Dissipation of chlorantraniliprole in flooded soils for 150 days

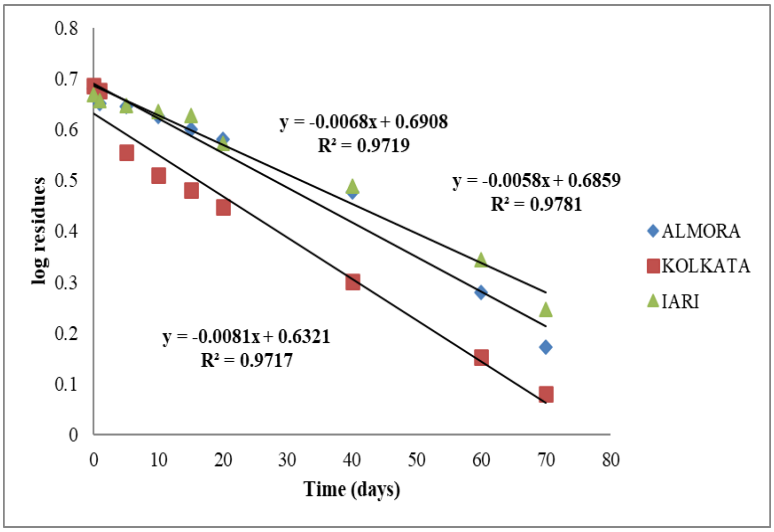

Fig. 10: Linearised plots for the dissipation of chlorantraniliprole in flooded soils till 70 days

The persistence of chlorantraniliprole in flooded soil exhibited a trend with the highest persistence observed in IARI soil, followed by Almora and Kolkata soils. Initially, mean residues on day 0 were 4.86 µg g-1, 4.79 µg g-1, and 4.67 µg g-1 for Kolkata, Almora, and IARI soils, respectively. Throughout the study period, degradation was notably faster in Kolkata soil compared to Almora and IARI soils, with 26.13%, 7.73%, and 4.93% dissipation observed on the 5th day, respectively. This can be attributed to lower sorption and higher desorption observed

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in Kolkata soil, likely due to its acidic nature. By the 20th day, residues in Almora and IARI soils decreased to similar levels of 3.80 µg g-1 and 3.58 µg g-1, respectively, representing degradation of 20.66% and 23.34%, while Kolkata soil showed a residue of 2.80 µg g-1 with 42.39% dissipation. From the 40th to the 70th day, degradation rates slowed, with Kolkata soil exhibiting the highest degradation. This can be attributed to reduced redox potential and lower organic carbon content in Kolkata soil, facilitating faster pesticide decomposition by anaerobic microbial communities. In comparison, Almora soil showed higher degradation rates due to its higher organic carbon content, leading to more effective degradation by anaerobic microbes. By the end of the study, nearly equal residual amounts were recovered, with IARI soil showing 1.03 µg g-1 and Almora and Kolkata soils showing 0.99 µg g-1.

Persistence in Paddy Plants

Analysis of Paddy leaf samples collected on day 0 showed residues of 0.014 mg/kg and 0.021 mg/kg in T1 and T2 tested doasages. Complete dissipation of chlorantraniliprole residues to below determination levels occurred by 3rd day in both the osages (T1) and (T2). All untreated control paddy leaf samples showed no detectable residues of chlorantraniliprole.

Table 12: chlorantraniliprole residue levels in Paddy Leaves

Occasions (Days)	Average residues (mg/kg)		
	T0	T1	T2
0	ND	0.014	0.021
3	ND	BDL	BDL
5	ND	BDL	BDL

BDL: Below Determination Level; ND: Not detected

Table 13: Calibration details of Chlorantraniliprole

Concentration (ng/mL)	Quantifier Ion Response (Peak Area Counts)	Qualifier Ion Response (Peak Area Counts)
0.15	18390	17195
0.25	31216	28172
1.26	121698	112298
2.52	247928	226737
5.04	486081	441756
Average Response Factor	**9.4354E-06**	**1.0295E-05**
RSD %	**12.5**	**12.7**
Correlation Coefficient	**0.9999**	**0.9999**

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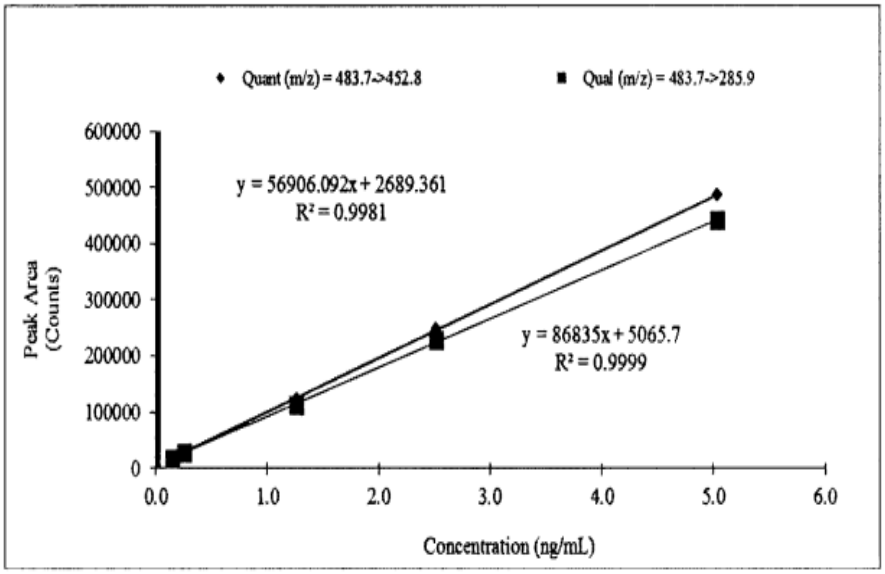

Fig. 11: Calibration curve of Chlorantraniliprole

Conclusion

The study revealed significant variations in the persistence of chlorantraniliprole across different soil types, with Kolkata soil exhibiting the fastest degradation rates. The findings suggest that factors such as pH, redox potential, and organic carbon content play crucial roles in determining the fate of chlorantraniliprole in flooded soil conditions. Furthermore, the efficacy of chlorantraniliprole in controlling rice leaf folder damage was demonstrated, with treated plots showing notable reductions in pest infestation compared to untreated controls. Mechanical treatments and chlorantraniliprole applications resulted in significant decreases in leaf folder damage, indicating their effectiveness in pest management strategies. Overall, these findings underscore the importance of considering soil characteristics and pesticide application methods for optimizing pest control measures in rice cultivation. Further research is needed to explore the long-term effects of chlorantraniliprole and refine application techniques to ensure sustainable rice production in the future.

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