International Journal of Environment and Climate Change

Volume 14, Issue 7, Page 824-835, 2024; Article no.IJECC.120672
ISSN: 2581-8627
(Past name: British Journal of Environment & Climate Change, Past ISSN: 2231–4784)

Degradation Dynamics of Flonicamid Insecticide Residues in Rice Crop and Soil in Southern Kerala and Its Dietary Risk Assessment

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Authors' contributions

This work was carried out in collaboration among all authors. Author ST carried out the processing operations and instrumental analysis, wrote and drafted the manuscript. Author TG designed the study, managed the literature searches, supervised the study and reviewed the draft. Author VKS carried out the instrumental analysis and reviewed the draft of the manuscript. Author RB assisted in conceptualizing the study and draft writing. Author AKN assisted in data analysis, reviewed and edited the draft. Authors AB and GP assisted in review and editing of the draft. All authors read and approved the final manuscript.

Article Information

DOI: https://doi.org/10.9734/ijecc/2024/v14i74322

Open Peer Review History:
This journal follows the Advanced Open Peer Review policy. Identity of the Reviewers, Editor(s) and additional Reviewers, peer review comments, different versions of the manuscript, comments of the editors, etc are available here: https://www.sdiarticle5.com/review-history/120672

Original Research Article

Received: 17/05/2024
Accepted: 20/07/2024
Published: 27/07/2024

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Cite as: *T, Sakthiselvi, Thomas George, Visal Kumar S, Rani B, Anith K N, Aparna B, and Gowri Priya. 2024. "Degradation Dynamics of Flonicamid Insecticide Residues in Rice Crop and Soil in Southern Kerala and Its Dietary Risk Assessment". International Journal of Environment and Climate Change 14 (7):824-35. https://doi.org/10.9734/ijecc/2024/v14i74322.*

ABSTRACT

Flonicamid is extensively used to manage rice crop from sucking insect pests owing to its high efficacy and relatively non-hazardous nature. Frequent sprayings over the course of the crop season elevate concerns regarding the possibility of residues on crops and soils. The study aimed to investigate the dissipation of foliar-applied flonicamid in rice ecosystem after single, double and triple application frequencies using a modified QuEChERS method combined with UHPLC-MS/MS. Recoveries of 74.34-116.36% were obtained for flonicamid in rice and soil matrices with relative standard deviation less than 7 and Horwitz ratio within 0.3. In the field experiment, flonicamid had half-lives of 2.75 to 3.15 days in leaves and 9.01 days in grains. No significant differences in residues were found after each application frequency owing to the similar environmental conditions prevailed during the growing season. A waiting period of 25 days is recommended for flonicamid when considering crop use for fodder purposes. In soil, no residues were detected regardless of the frequency of application. Upon harvest, residues were detected only in grains treated three times with flonicamid. Dietary risk assessment indicated that risk quotient values were below 1, suggesting no associated risks.

Keywords: flonicamid; rice; soil; application frequencies; risk assessment.

1. INTRODUCTION

Rice (*Oryza sativa* L.), a foremost cereal grass crop of the Gramineae family domesticated thousands of years back continues to serve as a dominant nutritious food for the global population providing a major proportion of dietary energy as well as vitamins, minerals and phytochemicals [1]. India remains the largest producer and consumer of rice after China with Indian rice holding the highest export value among the world's countries [2]. The versatility of rice crop as a part of people's diet, livestock feed and numerous industrial products contribute significantly to the food, nutrition and income security of the Indian sub-continent [3]. However, population growth and consumer preference for rice are increasing while production and productivity are being threatened by a variety of factors of which pest damage is a major concern [4,5]. Brown plant hopper (BPH), white-backed plant hopper (WBPH) and green leaf hopper (GLH) are major sucking insect pests of rice challenging agriculturists over decades [6]. Insecticide spray is quite popular in rice crop for managing the sucking insects, owing to their quick action, efficiency, economy and accessibility, although there is a growing emphasis on sustainable methods [7]. This necessitates the development and use of chemicals with novel chemistries to overcome pest resistance, secondary pest outbreak problems and the complications they pose to the environment like non-thermal plasma (NTP) technology showing potent action for resistant bacteria eradication in medical applications [8], action of hydrophilicity [9], synergy with spray to enhance surface-volume ratio [10], cell permeabilization [11,12].

Flonicamid is one of the comparatively non-hazardous chemicals aligning with the principles of integrated pest management, registered in India for controlling BPH, WBPH and GLH in rice [13,14]. It is highly selective against sucking insect pests of Hemiptera and Thysanoptera with outstanding translaminar and systemic activity through the vascular system [15]. Flonicamid is a pyridine carboxamide insecticide of the trifluoromethyl nicotinamide class discovered by Japan-based Ishihara Sangyo Kaisha Limited and commercialized by Food, Machinery and Chemical (FMC) Corporation. It targets the A-type potassium channels and chordotonal organs of nerve cells of insects, leading to the cessation of feeding and death [16,17]. It has a high water solubility (S_W) of 5.2 g l^{-1}, low vapour pressure, Henry's law constant and octanol water-partition coefficient (log K_{ow}) of 9.43 x 10^{-4} mPa, 4.20 x 10^{-8} Pa m^3 mol^{-1} and -0.24, respectively, with moderate mobility and faster degradation in soil [18]. It is relatively innocuous to beneficial insects, honey bees and other non-target organisms [15,19]. Repeated sprayings of this compound depending on the pest severity are adopted by farmers at all growth stages of rice which raises concerns about residual deposition in the environment [20]. Analysing the residual behaviour of the insecticide become crucial to ensure the safety of human and animal health as well as the well-being of the environment. However, the dissipation kinetics of flonicamid in rice crop remains unclear as very few studies are reported in India [21,22]. Therefore, a study was

proposed to address the persistence and dissipation behaviour of flonicamid insecticidal residues after repeated applications in open-field rice crop utilising a simple, rapid and effective method employing UHPLC-MS/MS. The insights gained from this study aim to facilitate the judicious use of these chemicals in agricultural practices, balancing effective pest management with environmental and health considerations.

2. MATERIALS AND METHODS

2.1 Analytical Standards, Chemicals and Solutions

Certified reference material of flonicamid ($C_9H_6F_3N_3O$, 99.5% purity) was supplied by United Phosphorous Limited, Mumbai. HPLC grade acetonitrile (CH_3CN), methanol (CH_3OH) and sodium chloride (NaCl), GR grade sodium sulfate (Na_2SO_4) as well as AR grade magnesium sulfate heptahydrate ($MgSO_4.7H_2O$) were bought from Merck Specialities Pvt. Ltd, Mumbai. The salts were activated through a 4-hour heating process in a muffle furnace at 400°C and were subsequently used after cooling to room temperature. Primary Secondary Amine (PSA) was provided by Agilent Technologies, USA. An Elga water purification system was used to obtain Type I water. Commercial formulations of flonicamid marketed as Ulala 50% Water dispersible granules (WG) was purchased from a nearby local market.

Individual standard stock solutions (400 µg ml^{-1}) of flonicamid were prepared in methanol. Intermediate standard (100 µg ml^{-1}) and working standard mix solutions 10, 1, 0.50, 0.25, 0.10, 0.05, 0.025 and 0.1 µg g^{-1} were prepared by serial dilution of stock standard and intermediate standard respectively. Similarly, matrix-matched standard solutions were obtained by addition of untreated matrix (rice leaf, straw, grain and soil) extracts to each serially diluted standard solution. The prepared extracts were stored at -20°C in freezer till analysis.

2.2 Field Study

The supervised field investigation aiming to evaluate the residue dynamics of insecticide formulation viz., flonicamid 50% WG was conducted during *Kharif*-2022 at the Integrated Farming Systems Research Station (IFSRS) in Karamana, Kerala, India. The experiment was laid out in randomized block design with treatments structured in accordance with the recommendations on the pesticide labels. In specific, flonicamid was applied to a medium duration rice variety Uma as foliar treatments at the recommended dosages of 75 g a.i. ha^{-1} at three application frequencies (single @ 25, double @ 25 and 50 and triple @ 25, 50 and 75 days after transplanting (DAT)). The experiment utilised an area of approximately 15 cents with each treatment covering 20 m^2 space (5 m x 5 m) in four replications along with absolute control with no insecticide application. A 1-meter buffer zone was upheld between each plot to prevent cross-contamination. All other crop management practices beginning from nursery to harvest followed the Kerala package of practices recommendations. Representative plant and soil samples were randomly collected from each plot at intervals of 0 (2 hour after spray), 1, 3, 5, 7, 10, 15, 20 and 25 days after each sprays and at the time of harvest for studying the dissipation pattern. The physico-chemical properties of the experimental field are given in Table 1.

Table 1. Physico-chemical attributes of field soil

Soil type	Riverine alluvium soil
Texture	Sandy clay loam
Sand (%)	56.28
Silt (%)	14.30
Clay (%)	29.42
Bulk density (Mg m^{-3})	1.42
Particle density (Mg m^{-3})	2.50
Porosity (%)	43.20
Field moisture (%)	18.20
pH	5.05
Electrical conductivity (EC) dS m^{-1}	0.20
Organic matter (%)	1.59
Available N (kg ha^{-1})	273.42
Available P (kg ha^{-1})	28.97
Available K (kg ha^{-1})	153.00

2.3 Pesticide Extraction and Clean-up Methodology

QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) methodology was adopted for extracting residues from plant and soil samples with some modifications [23] which are detailed under:

2.3.1 Soil

Soil samples (1 kg) were collected from the top 0-15 cm furrow slice layer from more than 5

random sites per plot and mixed well. About 10 g was taken in a 50 ml polypropylene centrifuge tube, 20 ml of CH_3CN was added and shaken well for better interaction of solvent and soil matrices to improve extraction efficiency of insecticides. To this, 4 g of anhydrous $MgSO_4$ and 1 g of NaCl were added, vortexed for 30 sec to facilitate mixing and centrifuged at 3300 rpm for 4 min at 8°C. About 10 ml of the upper organic liquid layer was carefully withdrawn without disturbing the precipitated samples into a 15 ml centrifuge tube prefilled with 0.25 g PSA, 1.5 g anhydrous $MgSO_4$, vortexed for 30 sec and centrifuged at 4400 rpm for 10 min at 8°C. Then, 4 ml of the aliquot was taken in a turbo tube and evaporated to dryness under a gentle stream of nitrogen in turbovap at 40 °C. The dry residues were reconstituted in CH_3OH to about 1 ml, filtered through 0.22 µm microporous filter membrane and stored in vials.

2.3.2 Rice

Healthy leaf, grain and straw samples (500 g) were randomly collected from more than five sites from each treated plot for residue analysis. The samples were crushed in a blender from which 15 g of leaf and 25 g of grain were taken for analysis in a 250 ml centrifuge bottle. The leaf was extracted with 30 ml CH_3CN to which 6 g NaCl was added, shaken for 5 mins in a mechanical shaker and centrifuged at 4500 rpm for 5 min at 8°C. The supernatant solution was transferred to 50 ml centrifuge tubes containing 6 g Na_2SO_4, shaken and vortexed for a min. The contents were poured into a 15 ml centrifuge tube already filled with 0.2 g PSA and 1.2 g $MgSO_4$ and centrifuged at 8000 rpm for 8 min at 8°C. The grain samples were mixed with 25 ml of distilled water, 50 ml of CH_3CN plus 12 g NaCl, shaken for 30 min in a mechanical shaker and centrifuged at 8000 rpm for 8 min at 8°C. About 16 ml of supernatant was drawn in to a 50 ml polypropylene centrifuge tube containing 2 g $MgSO_4$ and 2 g Na_2SO_4, vortexed for 30 sec and centrifuged at 8000 rpm for 8 min at 8°C. The supernatant liquid was introduced into a 15 ml tube containing 0.1 g PSA and 0.75 g $MgSO_4$ and centrifuged at 8000 rpm for 8 min at 8°C. For straw, 5 g of samples were taken in 250 ml centrifuge bottle to which 40 ml of distilled water, 50 ml of CH_3CN and 10 g of NaCl were added, shaken for 5 min and centrifuged at 8000 rpm for 8 min at 8°C. Supernatant (25 ml) was drawn in to a 50 ml polypropylene centrifuge tube prefilled with 5 g of Na_2SO_4, vortexed for 30 sec and centrifuged at 8000 rpm for 8 min at 8°C. Supernatant (10 ml) was drawn in to a 15 ml centrifuge tube having 2 g $MgSO_4$ and 0.125 g PSA, followed by vortexing for 30 sec and centrifugation at 4500 rpm for 5 min at 8°C. About 3 ml of the centrifuged cleaned extracts of leaf, grain and straw matrices were evaporated to dryness under a gentle stream of nitrogen in turbovap at 40°C and reconstituted to 1 ml with CH_3OH for analysis.

2.4 Instrumental Analysis

Chromatographic analytical method for identification and quantification of flonicamid was achieved by Dionex Ultimate 3000 UHPLC system (Thermo Scientific, Germany) equipped with a TSQ Quantiva mass spectrometer (Thermo Scientific, US). The binary mobile phase consisted of 5 mM ammonium formate and 0.1% formic acid (v/v) in aqueous solution (A) and 5mM ammonium formate and 0.1% formic acid (v/v) in methanol (B). The chromatographic separation was carried out using Thermo Scientific, Accucore aQ (100 mm x 2.1 mm, 2.6 µ particle size) column. The elution was carried out in gradient mode 0-0.5 min: 2% elute B, 0.5-2 min: elute B increase to 60%, 2-8 min: elute B further increase to 95%, 8-9.0 min: hold 95% elute B, 9-9.1 min: elute B decrease to 2%, 9.1-10 min: held at 2% elute B. The column and sample temperature were set at 30 °C and 10 °C, respectively, with a flow rate of 0.3 ml min^{-1}.

The residues of flonicamid was qualified and quantified by positive ionization mode using heated electrospray ionisation (H-ESI) mass spectrometry. The analysis employed multiple reaction monitoring mode with mass spectrometric conditions including an ion transfer tube temperature of 350°C and vapourizer temperature of 450°C. Sheath gas, auxiliary gas and sweep gas were maintained at 60, 5 and 1 respectively, in arbitrary units with a dwell time of 158.06 milli seconds. Table 2 lists the MS parameters of flonicamid. The chromatogram and mass spectrum of the compound is depicted in Fig. 1. The retention time of the compound was at 3.27 min (Fig. 1A). The mass spectrum shows the product ions with maximum intensities viz., 203, 174 and 148 m/z originated from parent ion with a mass of 230 m/z by H-ESI (Fig. 1B).

2.5 Method Optimisation

To assess the practicality of the suggested extraction method in the accurate identification of flonicamid residues in rice and soil matrices, the

method's performance, encompassing aspects such as linearity, sensitivity, accuracy and precision were scrutinised based on SANTE criteria [24].

The linearity of the method was verified by constructing a matrix-matched calibration curve ranging from 0.01 to 1.00 µg ml^{-1} using mixed standards of flonicamid in soil and rice matrices. The limit of detection (LOD) and limit of quantification (LOQ) were determined with the signal-to-noise ratio of three and ten, respectively, with reference to the noise achieved from blank matrices. The accuracy/trueness and precision of the method were assessed through a recovery experiment, in five replicates, wherein the control matrices of soil, rice leaf, grain and straw were spiked at concentrations of LOQ, 5xLOQ and 10xLOQ and then processed using the method mentioned in Section 2.3. Precision was determined by calculating the relative standard deviation (RSD) through intra-day repeatability checks. The horwitz ratio (HorRat), as proposed by AOAC guidelines, is an index to assess intra-laboratory precision was computed as per the method given by [25] to determine the reproducibility of the method.

2.6 Statistical Analysis

2.6.1 Dissipation kinetic study

The dissipation kinetics of flonicamid in fresh rice leaves and grains were studied by plotting graphs in first-order linear kinetics model between log of concentrations and time [26]. Dissipation rate constants (k), dissipation half-lives (DT_{50}) and safe waiting period (SWP) were calculated using the equations of $\ln [C_t] = -kt + \ln [C_0]$, $DT_{50} = \log (2)/k$ and $SWP = [\log (C_0) - \log (MRL)]/k$, where C_0 represents the initial residue deposition (µg g^{-1}), C_t stands for the residual level (µg g^{-1}) at various days (t) post-application and MRL is the maximum residue limit of flonicamid in rice crop.

2.6.2 Dietary intake risk assessment

The dietary risk quotient (RQ_d) was utilized to assess the potential danger posed by flonicamid residues present in rice grains. RQ_d was determined by dividing the estimated daily intake (EDI, mg kg^{-1} bw) by the acceptable daily intake (ADI, mg kg^{-1} bw) levels. ADI values of flonicamid is 0.07 mg kg^{-1} bw day^{-1} [27]. EDI was calculated by dividing the maximum residues occurred in grains on respective days and rice intake rate by average body weight of adult male. In India, per capita consumption of rice by the general population weighing 60 kg is 300 g per day [28,29,30]. RQ_d values below 1 indicate acceptable risk levels, while those above 1 suggest unacceptable levels of risk [31].

3. RESULTS AND DISCUSSION

3.1 Method Performance Validation

The parameters evaluated for method validation of flonicamid viz., accuracy, precision, linearity and sensitivity are presented in Table 3. The average recovery rates for flonicamid were within the allowable range of about 75.11-94.51, 93.42-101.33, 105.39-116.36, and 74.34-88.34% with corresponding RSDs ranging from 2.65-3.75, 1.51-2.51, 1.06-6.04 and 1.61-3.34% respectively in rice leaf, straw, grain and soil matrices. Besides this, the HorRat values were below 0.3 for flonicamid in all matrices at all spiking levels. As repeatability was carried out in a shorter time period, not all variability parameters were considered, possibly resulting in significantly low HorRat values. A valid and satisfactory linearity calibration curve with correlation coefficient (R^2) greater than 0.99 was obtained in rice and soil matrices when average peak areas of flonicamid were plotted across corresponding concentration ranges (0.01, 0.025, 0.05, 0.10, 0.25, 0.5 and 1 µg g^{-1}). The LOD and LOQ of the proposed method were 0.003 and 0.01 µg g^{-1}, respectively. The LOQ attained by the developed method was found to be 5-100 fold lower than the maximum residue limit (flonicamid: 0.05 µg g^{-1}; dinotefuran: 8 µg g^{-1}) established by the Food Safety and Standards Authority of India (FSSAI) in rice [32]. The validated method was used for the routine analysis of residual flonicamid in rice and soil samples.

3.2 Field Dissipation Study

3.2.1 Rice leaf

The mean residues, DT_{50} and SWP in leaves after each application frequency for flonicamid is given in Table 4. Dissipation curves of flonicamid in rice leaf at different application frequencies are shown in Fig. 2A. The initial concentrations of flonicamid in leaves after 2 h of spraying were 15.84, 14.80 and 17.38 µg g^{-1} at single, double and triple applications, respectively. Residues declined gradually with time to about 95% on the 10^{th} day. Residues reached below limit of

quantification (BLQ) on the 25th day. The dissipation kinetics fitted with first-order equation showed a DT_{50} of around 3 days after each spray (Table 4 and Fig. 2A). Several literatures reported nearest DT_{50} values for flonicamid in various crops of about 2.5 days in cucumber [33], 3 days in okra [34], 2.8 days in strawberry [35] and 2.5 days in rice leaves [22]. The estimated SWP of flonicamid in leaves were 22.88, 25.21 and 25.11 days at single, double and triple sprays, respectively. Hence, the harvested straw following 25 days after 3rd application of flonicamid is considered safe for utilisation as livestock fodder. A SWP of 16 days in okra [34] and 33 days in cotton seed and oil [36] were reported for flonicamid.

Table 2. Multiple reaction monitoring (MRM) parameters for LC-MS/MS determination of target insecticides

Target compound	Polarity	Precursor ion (m/z)	Daughter ion (m/z)	Collision energy (V)	Retention time (min)
Flonicamid	Positive	230.038	203.000 (Q) 174.042 (C) 148.042 (C)	26.91 20.69 18.00	3.27

Q: Quantitative ion; C: Confirmatory ion.

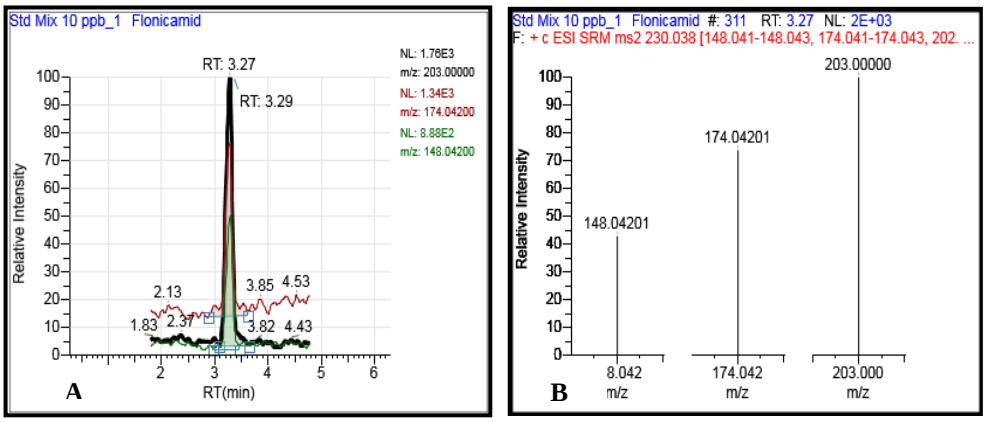

Fig. 1. (A) LC-MS/MS chromatogram and (B) Mass spectrum of flonicamid

Table 3. Method validation parameters of flonicamid in rice and soil matrices

Matrix	Accuracy and Precision (n = 5)				Linearity		Sensitivity
	Spiked level (µg g^{-1})	Recovery (%) ± SD	RSD (%)	Horwitz ratio	Equation	R^2	LOQ (µg g^{-1})
Grain	0.01	116.36 ± 7.03	6.04	0.19	Y = 1.795x – 8.951	0.9997	0.01
	0.05	105.39 ± 1.12	1.06	0.04			
	0.10	110.10 ± 4.91	4.46	0.20			
Leaf	0.01	101.33 ± 1.53	1.51	0.05	Y = 2.172x + 9.542	0.9995	0.01
	0.05	93.42 ± 2.34	2.51	0.10			
	0.10	98.16 ± 1.90	1.93	0.09			
Straw	0.01	75.11 ± 2.82	3.75	0.23	Y = 5.195x – 1.987	0.9968	0.01
	0.05	93.00 ± 3.46	3.72	0.15			
	0.10	94.51 ± 2.50	2.65	0.11			
Soil	0.01	78.79 ± 2.64	3.34	0.10	Y = 2.202x + 2.655	0.9954	0.01
	0.05	74.34 ± 1.94	2.61	0.10			
	0.10	88.34 ± 1.42	1.61	0.07			

SD: Standard deviation; RSD: Relative standard deviation; R2: Correlation coefficient; LOQ: Limit of quantification.

Chawla et al. [36] observed higher initial deposit of flonicamid up to 23.80 µg g^{-1} in cotton leaves attributed to the lightweight nature and larger surface area of the leaves, offering greater pesticide retention areas. This suggests that various aspects of plants such as the size and shape of leaf, type of cuticle, kind of fruit and their physiological traits can significantly impact the deposition and degradation of pesticides [37]. Environmental parameters like temperature, rainfall, relative humidity and sunlight can produce significant differences on the dissipation of flonicamid [38,39,40]. However, the consistent environmental conditions that prevailed throughout the crop season had resulted in similar dissipation behaviour after each application frequencies.

3.2.2 Rice field soil

Flonicamid was undetected in soils at each application frequency (Table 4). Volatilisation loss is negligible owing to low vapour pressure and henry's law constant of both chemicals [41]. Insecticide was sprayed towards the closely spaced rice plants, so much of the residues were found concentrated in the plant system. This can be ascribed to the conditions created by highly soluble and systemic nature of the chemical. The mobility of a substance in soil is assessed using K_{ow} which indicates the partitioning of chemical between soil matrix and solution. Chemicals with lower K_{ow} like flonicamid have poor sorption onto soil matrices with higher mobility. This would have caused faster movement and degradation of these chemicals in lowland rice field soil. [42] disclosed that flonicamid undergoes rapid degradation when the solution's hydroxyl radical increases ie., decrease in pH. Thus, strongly acidic pH of the studied soil facilitated a more rapid dissipation of chemicals. This depicts that in addition to pesticide properties, the physicochemical characteristics of soil notably soil type, moisture content, pH, soil organic matter (SOM) and humus play a significant role in determining the longevity of flonicamid in soils [43,44].

3.2.3 Rice grain

Table 5 represents the residues and DT_{50} of flonicamid in rice grain. The matured rice grains obtained after the third spray were processed and analysed for residues to understand the dissipation pattern. Mean residues after the third application of flonicamid were 3.042 µg g^{-1} on the 0^{th} sampling day. The residue dissipation explained using a first-order kinetics reaction showed DT_{50} of 9.01 days with R^2 of ≥0.93 (Fig. 2B). The residue levels detected in rice grains were notably lower compared to those found in leaves, indicating a limited translocation of chemicals into rice grains. By harvest time, flonicamid residues persisted at about 0.12 µg g^{-1}.

3.3 Risk Assessment

The results obtained from the dissipation study were used for dietary risk assessment of rice crop. The maximum residue values observed from the field study on the respective days were taken for computing RQ_d values. The computed RQ_d values remained consistently below 1, even

Table 4. Residue dissipation and reaction rate parameters of flonicamid in rice leaf and soil at different frequencies of application

DAS	Residues (µg g^{-1}) ± SD in leaf (n = 4)			Residues (µg g^{-1}) ± SD in soil (n = 4)		
	Single spray	Double spray	Triple spray	Single spray	Double spray	Triple spray
0	15.84 ± 0.06	14.80 ± 0.31	17.38 ± 1.37	BLQ	BLQ	BLQ
1	10.60 ± 0.19	13.08 ± 0.13	9.83 ± 1.02	BLQ	BLQ	BLQ
3	6.93 ± 0.14	6.20 ± 0.14	3.80 ± 0.49	BLQ	BLQ	BLQ
5	2.73 ± 0.10	3.68 ± 0.29	1.77 ± 0.24	BLQ	BLQ	BLQ
7	1.24 ± 0.12	2.09 ± 0.25	1.46 ± 0.18	BLQ	BLQ	BLQ
10	0.55 ± 0.22	1.55 ± 0.18	0.76 ± 0.04	BLQ	BLQ	BLQ
15	0.28 ± 0.09	0.69 ± 0.09	0.32 ± 0.06	BLQ	BLQ	BLQ
20	0.11 ± 0.06	0.14 ± 0.02	0.12 ± 0.01	BLQ	BLQ	BLQ
25	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ
Harvest	BLQ	BLQ	BLQ	BLQ	BLQ	BLQ
DT_{50}	2.75	3.14	2.97	-	-	-
SWP	22.88	25.21	25.11	-	-	-

DAS: Days after spray; SD: Standard deviation; BLQ: Below limit of quantification (0.01 µg g-1); DT50: Half-life; SWP: Safe waiting period.

Table 5. Residue degradation and half-life of flonicamid in rice grain after triple application

DAS	Residues (µg g^{-1}) ± SD (n = 4)	Dissipation (%)
0	3.02 ± 0.55	-
1	2.05 ± 0.27	32.12
3	1.71 ± 0.29	43.38
5	1.83 ± 0.11	39.40
7	1.64 ± 0.29	45.70
10	1.38 ± 0.18	54.30
15	1.06 ± 0.11	64.90
20	0.79 ± 0.12	73.84
25	0.54 ± 0.05	82.12
Harvest	0.12 ± 0.02	96.03
DT_{50}	9.01	

DAS: Days after spraying; SD: Standard deviation; BLQ: Below limit of quantification (0.01 µg g-1); DT50: Half-life.

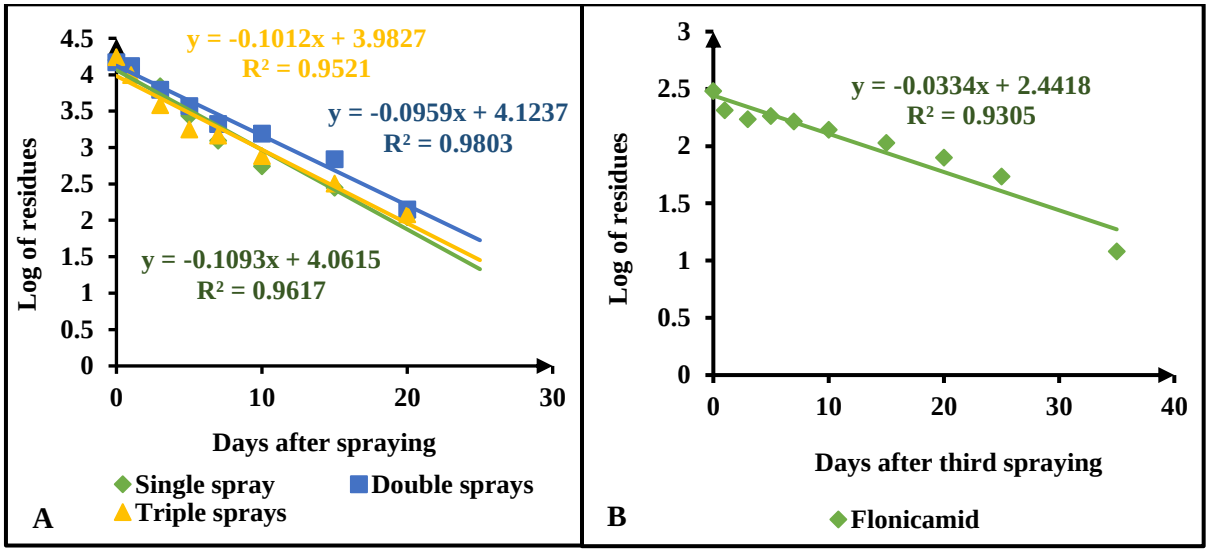

Fig. 2. Residue dissipation curves of flonicamid in A) Leaf and B) Grain

Table 6. Dietary risk assessment of flonicamid residues in grain

DAS	Maximum residues in grain (µg g^{-1})	EDI	RQ
0	3.93	0.021	0.30
1	2.49	0.013	0.19
3	2.17	0.012	0.17
5	1.93	0.010	0.14
7	1.80	0.010	0.14
10	1.47	0.008	0.11
15	1.19	0.006	0.09
20	0.83	0.004	0.06
25	0.65	0.004	0.06
Harvest	0.18	0.0009	0.01

DAS: Days after spraying; EDI: Estimated daily intake; RQ: Risk quotie[nt]

on the initial day of application. By the time of harvest, the RQ_d values for flonicamid were notably low, approximately at 0.0009 (Table 6). This indicates that the application of flonicamid to rice crops at three different frequencies is deemed safe for consumption. Similar findings were observed for flonicamid in cotton [36].

4. CONCLUSION

A precise method for detecting residues of flonicamid in rice crop and soil using LC-MS/MS was validated ensuring linearity, sensitivity, recovery and precision. The validation process yielded satisfactory results, with recovery rates falling within the range of 70-120% and RSD below 20%. Field observations revealed that flonicamid degraded rapidly within the rice field ecosystem. Human dietary risk assessment based on the consumption of rice grains with residues of flonicamid indicated no associated risks. In summary, the study confirms that applying flonicamid to rice crops at recommended dosages at three different frequencies is safe. This conclusion is supported by the rigorous validation of the detection method and the favourable outcomes of the dietary risk assessments.

DISCLAIMER (ARTIFICIAL INTELLIGENCE)

Author(s) hereby declare that NO generative AI technologies such as Large Language Models (ChatGPT, COPILOT, etc) and text-to-image generators have been used during writing or editing of manuscripts.

ACKNOWLEDGEMENTS

The authors would like to extend their appreciation for the resources provided by the Pesticide Residue Research and Analytical Laboratory, Kerala Agricultural University, as well as the Department of Soil Science and Agricultural Chemistry, College of Agriculture, Vellayani, which facilitated the execution of the study.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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Peer-review history:
The peer review history for this paper can be accessed here:
https://www.sdiarticle5.com/review-history/120672