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Residue dissipation kinetics, risk assessment and decontamination of spiromesifen in tomato fruits and cabbage heads

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12 ABSTRACT

Spiromesifen is one of the most popular insecticides used for the chemical control of several 13 insect in many vegetable crops, but its residues may remain in the crops. Residues were 14 extracted using ethyl acetate from tomato and cabbage. Samples were cleaned using graphitized 15 carbon black, primary secondary amine, and magnesium sulfate. At 0.01, 0.02, 0.05, 0.10, and 16 0.50 mg kg⁻¹, the recovery percentage were 83.00-94.67% in tomato and 81.33-92.00% in 17 18 cabbage head. The half-lives of spiromesifen in tomato and cabbage heads were 2.37 and 3.79 days, respectively. Dietary exposures of the residues were less than maximum permissible 19 intake of 0.48 mg person⁻¹ d⁻¹ on all the sampling days for rural as well as urban. The average 20 matrix effect was less than 20%. Spiromesifen used to control psyllid, aphid and whiteflies in 21 tomato and cabbage. There could be a health risk if its residue stays in the crop. Thus, the 22 validated method was used to study the analysis of spiromesifen residue, its dissipation rate, 23 and safety evaluations in tomato and cabbage. Different household processes were evaluated 24 for removal of the incurred spiromesifen residue in tomato and cabbage. Washing with boiling 25 water could be used as a most effective decontamination strategy for spiromesifen in tomato 26 27 and cabbage.

Keywords: Decontamination, Dissipation kinetics, Spiromesifen residue, Tomato fruit andcabbage head.

1. Introduction

Vegetables contaminated with pesticide residues pose significant health risks to consumers due to potential toxicity, carcinogenicity, and disruption of the endocrine system, among other acute and chronic health concerns. In addition to the direct health implications of pesticide residues on vegetable crops, there are broader environmental and societal considerations to be addressed. Pesticide runoff from agricultural fields can contaminate water sources, leading to ecological imbalances and potentially harming aquatic life. Furthermore, prolonged and indiscriminate use of pesticides can contribute to the development of resistance in pest populations, necessitating

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the use of stronger chemicals or alternative pest management strategies. Hence, it is imperative 39 to conduct thorough pesticide residue analyses in vegetable crops to ensure public health 40 protection, legal compliance, environmental conservation, and promotion of sustainable 41 agricultural practices. Such analyses are integral components of comprehensive strategies for 42 food safety and pesticide management. Tomatoes (Solanum lycopersicum), belonging to the 43 Solanaceae family, represent a crucial cash crop that significantly contributes to the economy. 44 They are cultivated extensively both domestically and internationally, being rich sources of 45 essential nutrients such as potassium, iron, phosphorus, vitamins A, B, and C, as well as 46 47 substantial quantities of lycopene, a potent antioxidant (Khanam et al., 2003). Studies have suggested that tomatoes may have protective effects against certain cancers, including those of 48 49 the head, neck, and prostate (Freedman et al., 2008). India, accounting for 10.4% of global tomato production, is a major producer, with key cultivation regions including Andhra Pradesh, 50 51 Madhya Pradesh, Uttar Pradesh, Karnataka, Orissa, Bihar, and Assam (Razdan and Mattoo, 2007). According to projections, tomatoes are cultivated on 789,000 hectares of land in India, 52 53 yielding 19.7 million tonnes with a productivity of 25.0 t/ha (NHB, 2018).

Cabbage (Brassica oleracea) is another significant vegetable crop with widespread cultivation. 54 This leafy green vegetable is utilized extensively in post-harvest industries, yielding valuable 55 products such as sauerkraut. In India, cabbage production reached 9,095,000 mt in 2018–2019, 56 cultivated across 399,000 hectares of land. Cabbage is rich in phytochemicals like thiocyanate, 57 indole-3-carbinol, lutein, zea-xanthin, and sulforaphane, which are associated with various 58 health benefits, including protection against breast, colon, and prostate cancers. Additionally, 59 cabbage is abundant in beta-carotene, vitamin C, and dietary fiber (http://www.nutrition-and-60 you.com/cabbage.html). 61

Insect pest infestation poses a significant challenge to vegetable yields in India, particularly 62 affecting delicate fruits like tomatoes. Helicoverpa armigera, commonly known as fruit borer, 63 is a major pest that causes substantial damage to tomato crops, reducing marketable yields by 64 22-38% (Dhandapani et al., 2003). Cabbage is also susceptible to various pests such as cabbage 65 whitefly, aphids, and mites, which significantly reduce yields (Trdan and Papler, May 7, 2002). 66 Spiromesifen, a non-systemic insecticidal compound belonging to the spirocyclic phenyl 67 substituted tetronic acid class, is effective against a broad spectrum of pests, including fruit 68 flies. Its mode of action involves inhibition of lipid biosynthesis, particularly triglycerides and 69 free fatty acids (Nauen et al., 2002; Nauen, Schnorbach, & Elbert, 2005). Spiromesifen offers 70 several advantages, such as fast knockdown, residual activity, and minimal impact on beneficial 71 insects, making it a suitable choice for controlling pest infestations. Farmers rely on 72

spiromesifen for pest management to protect their crops from damage. The Central Insecticide Board and Registration Committee, Ministry of Agriculture and farmer welfare, Government of India, has approved the use of spiromesifen 240 SC on tomatoes. Following a risk assessment, the Food Safety Standard Authority of India, Ministry of Health and Family Welfare, Government of India, set the maximum residual limit (MRL) of spiromesifen on tomatoes at $0.3 \mu g/g$.

The application of pesticides to cabbage presents a unique challenge due to its multilayered 79 structure, which may retain residues for extended periods. Cabbage exhibits resilience to 80 environmental fluctuations, further contributing to the persistence of pesticide residues (Abo-81 El-Seoud et al., 1995). Among various vegetable crops, cabbage has been found to accumulate 82 the highest levels of pesticide residues (Srivastava et al., 2011). This accumulation of pesticide 83 residues in harvested tomatoes and cabbage poses significant concerns during both exportation 84 85 and consumption, potentially impacting human health and increasing environmental burdens (Sharma et al., 2005). Given the potential adverse effects of pesticide residues, it is imperative 86 87 to investigate their persistence on tomato and cabbage following application for crop protection. Gas Chromatography with Electron Capture Detection (GC-ECD) serves as a prominent 88 analytical method for assessing pesticide dissipation. This technique combines gas 89 chromatography separation with electron capture detection, facilitating precise identification 90 and quantification of pesticide compounds (Siddamallaiah and Mohapatra, 2016). To assess the 91 dissipation dynamics of pesticide residues, a field trial involving the application of spiromesifen 92 to tomato and cabbage crops was conducted. This trial aimed to elucidate the dissipation pattern 93 and determine the half-life of spiromesifen on these crops, providing crucial insights into the 94 fate of pesticide residues in agricultural environments. 95

9697 2. MATERIALS AND METHODS

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2.1. Chemicals and Reagents

Spiromesifen (purity 99 %) was procured from Sigma-Aldrich Pvt. Ltd. (Bangalore, India). Acetone, *n*-hexane, magnesium sulfate (MgSO₄), sodium sulfate (Na₂SO₄), and sodium acetate (C₂H₃NaO₂) used were of analytical grade and procured from Thomas Baker, Mumbai, India. MgSO₄ was activated in a muffle furnace for 5 h at 600°C and kept in desiccators prior to use. Primary secondary amine (PSA) of mesh size of 40 μ m was procured from Agilent Technologies (Bangalore, India). The deionized water for the mobile phase was obtained from a Millipore Water Purification System (Sartorius AG, Goettingen, Germany) and filtered using

- Millipore GV filter paper of pore size 0.22 µm. Polytetrafluoroethylene (PTFE) membrane filter
 of pore size 0.2 µm was procured from Phenomenex (Bangalore, India).
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109 2.2. Apparatus

110 The following were used: centrifuge (Kubota, Germany), microcentrifuge (Microfuge Pico,

111 Kendro, D-37,520, Osterode, Germany), mixer and grinder (Bajaj India Pvt. Ltd., Mumbai),

112 precision balance (Vibra, Adair Dutt, Mumbai, India), vortex mixer (Geni 2 T, Imperials

- 113 Biomedicals, Mumbai, India), and ultrasonic bath (Oscar electronics, Mumbai, India).
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115 2.3. Reference Standard

To prepare standard stock solutions, $10 (\pm 0.1)$ mg reference standards were precisely weighed 116 and then dissolved in 10 ml of ethyl acetate, yielding a final concentration of 1000 µg mL⁻¹. 117 The calibration standard solutions at 0.01, 0.02, 0.04, 0.06, 0.08 mg kg⁻¹ were prepared from 118 the working standard mixture of 10 μ g mL⁻¹ that was created by appropriately mixing the 119 individual standard stock solution and further dilution. The tomato and cabbage extract obtained 120 through the sample preparation procedure outlined in the sample preparation and analysis 121 section was used to prepare the matrix matched standards at the concentration (Majumder *et* 122 *al.*, 2022) a. 123

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125 2.4. Field Experimental Condition

The field experiment was carried out at the vegetable research farm, ICAR-Indian Institute of 126 Vegetable Research, Varanasi, Uttar Pradesh, India (longitude 82.52° E and latitude 25.10° N) 127 as per the Food and Agriculture Organisation (FAO) guidelines (Majumder et al. 2022 a) using 128 3 treatments that are duplicated 3 times in a randomised block design. At the fruit formation 129 stage (2 months after transplanting) of tomato crop (open field), spiromesifen (Bayer Oberon 130 240 SC) spray applications were given at the recommended and double doses of 125 and 250 g 131 ai ha⁻¹ for both crops. Spiromesifen was used in tomatoes and cabbage by Knapsack Power 132 Sprayer. The crop was grown using advised agronomic techniques. The area receives an 133 average rainfall of 1000 mm which is distributed over a period of more than 100 days with peak 134 period between July and August. The average maximum and minimum temperatures during the 135 experimental period were 21°C and 24°C for tomato cultivation and the average maximum and 136 minimum temperatures during the experimental period were 15 and 21°C for cabbage 137 cultivation. Row to row and plant to plant spacing were 75-90×45-60 cm for tomato and 45-138 60×30-45 for cabbage, respectively. 139

141 **2.5.** Sampling

At regular intervals on 0 day (2 hours after spraying), 1-day, 3-day, 5-day, 7-day, 10-day, 15day, and 21-days after the final spray, the samples (tomato and cabbage) were zigzag-collected from each replication and control plot separately. The samples were collected in polythene bags and stored at -20° C until analysis to avoid any degradation (Majumder *et al.*, 2023a).

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147 **2.6.** Sample Preparation and Analysis

Tomato and cabbage samples were collected from each treated plot and samples from three 148 149 replicates were pooled together to form a sample size of approximately 5 kg. Each sample was divided into four parts. One part of each sample was taken to make approximately 1-kg 150 151 subsample. It was cut into small pieces and homogenized (250 g) homogenized with a silent crusher and grinder. Tomato and cabbage grown in the experimental field without application 152 of pesticides was used for spiking. A representative (10 g) sample in three replicates was taken 153 for analysis and 10 grams of the sample were extracted using 10 mL of 1% acetic acid in ethyl 154 acetate and 10 g of anhydrous sodium sulphate. The process involved vortexing the sample for 155 2 minutes and centrifuging it for 5 minutes at 4000 rpm. 75 mg of PSA, 225 mg of MgSO₄, and 156 15 mg of GCB were extracted using a dispersive solid phase extraction technique to clean an 157 aliquot of the supernatant ethyl acetate layer (1.5 mL). After centrifuging the extract for 3 158 minutes at 5000 rpm and filtering it through a 0.2 µm Nylon 6,6 membrane, 1 milliliter of the 159 extract was injected into the GC-ECD (Majumder et al., 2023a). 160

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162 **2.7. Extraction and Purification**

The QuEChERS technique was modified to extract the samples. The samples were prepared, 163 164 extracted and purification by following earlier reported method with slight adjustments according to the nature of the pesticide and type of the crop (Majumder *et al.*, 2023b). The 165 complete laboratory subsample was broken up into tiny pieces and completely ground in a 166 mixer grinder. To do an extraction, 10 g of tomato and cabbage samples were weighed into 50 167 mL centrifuge tubes. Then, 10 ml of 1% acetic acid in ethyl acetate and 10 gm of anhydrous 168 sodium sulfate were added. The mixture was vortexed for 2 minutes and then centrifuged for 5 169 minutes at 5000 rpm. The supernatant ethyl acetate layer (1.5 mL) was cleaned using the 170 dispersive solid phase extraction (DSPE) technique with 75 PSA, 15 mg GCB, and 225 mg 171 MgSO₄. After centrifuging this extract for 5 minutes at 10,000 rpm, it was immediately filtered 172 173 through a 0.22 µm Nylon 6,6 membrane filter and subjected to GC-ECD analysis.

175 **2.8. GC- μECD Analysis**

- For the analysis of spiromesifen residue in tomato and cabbage head, the GC with microelectron 176 capture detector (ECD, 63Ni) was used. The injector of the instrument was used in split injection 177 mode with an injection volume of 1µL and a 10:1 ratio at 250°C. An HP-5 capillary column (30 178 m in length, 320 m in diameter, 0.25 m film thickness, and nitrogen gas flowing at 2 mL/min) 179 was utilized for the separation process. The detector temperature was set to 300°C, and the 180 nitrogen gas flow rate was set to 30 mL/min. After holding the temperature at 90°C for 5 181 minutes, the oven ramped up to 200°C at a rate of 20°C per minute and ramped down to 240°C 182 at a rate of 6°C per minute for a further 2 minutes. Under these conditions, it was found that 183 spiromesifen exhibited a retention time (RT) of 7.845 minutes in these conditions (Figure 1). 184 Total run time for the analysis of one sample was 18 min. An Agilent openlab EZchrom for 185
- acquiring chromatograms.
- 187 The following formula was used to compute insecticide residue in mg kg⁻¹:

188 Residue (mg kg⁻¹)=
$$(M_1 \times N_1 \times C)/(M_2 \times N_2 \times W)$$

- 189 Where, M_1 = Area of field sample in the chromatogram, M_2 = Area of analytical standard in the 190 chromatogram, N_1 = Total volume of the sample in mL, N_2 = Injected volume in μ L, C= 191 Concentration of analytical standard in mg kg⁻¹, and W= Weight of the sample in g (Majumder 192 *et al.*, 2024).
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194 **2.9. Method Validation**

Method validation is the process of ensuring an analytical method is appropriate for the intended 195 purpose. Analytical results' consistency, dependability, and quality can all be evaluated using 196 method validation results. The SANTE/12682/2019 guideline (Analytical quality control and 197 method validation procedures for pesticide residues analysis in food and feed) was followed in 198 the evaluation of the recovery percent (% recovery), accuracy, limits of quantification and 199 determination (LOD), and matrix effects (ME) as part of the method validation criteria. A blank 200 sample extract was utilized to ascertain whether there was any interference with the 201 corresponding analytes (selectivity). The linearity range of calibration curves built in solvent or 202 blank matrix was evaluated using the squared coefficient of correlation (R^2) and relative 203 residuals; matrix effects were evaluated by comparing the obtained slopes (Majumder et al., 204 2023b). 205

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209 **2.9.1** Calibration Curves and Linearity

The linear response with respect to the concentration $(mg kg^{-1})$ or the insecticides was evaluated by establishing 6-point calibration curves with calibration standards in the range of 0.01–0.5 mg kg⁻¹ prepared in a solvent, i.e., ethyl acetate, and in the matrix of tomato and cabbage as well as extract for spiromesifen. The linearity graph was obtained by plotting the area of the peak response against the concentration of spiromesifen.

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216 **2.9.2. Selectivity and Sensitivity**

The lowest concentration at which the technique can reliably identify the analyte within the 217 matrix is known as the LOD. It can also mean the lowest concentration that can be reliably 218 219 distinguished from background noise. The smallest measured quantity in the matrix at which the signal to noise ratio (S/N) was 3:1 or 10:1 was determined to be the limit of detection (LOD) 220 and limit of quantification (LOQ), respectively. The smallest quantity or lowest concentration 221 of a pesticide that can be determined using a particular analytical technique with accuracy, 222 precision, recovery, and uncertainty is known as the limit of quantification (LOQ) (Majumder 223 et al., 2024). 224

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226 **2.9.3. Recovery**

Recovery study was carried out at 0.01, 0.02, 0.05, 0.1 and 0.5 µg mL⁻¹ levels with six replicates
each. Precision was evaluated in term of repeatability and reproducibility.

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230 **2.9.4. Matrix Effect**

The Matrix effects were evaluated by comparing the peak area of the solvent standard with that of matrix matched standard at 0.1 μ g mL⁻¹. The matrix effect was calculated by spiking postextraction at 0.005, 0.01, 0.02, 0.06, 0.1, and 0.5 μ g mL⁻¹. The formula was used to determine the matrix effect (Majumder *et al.*, 2022c):

235 ME (%) = (Peak area of matrix matched standard – Peak area of solvent standard) \times 100 236 Peak area of matched standard

238 2.9.5. Dissipation Kinetics

The rate at which the pesticide's active ingredient leaves the portion of the plant being measured as a result of several processes working together, such as volatilization, hydrolysis, photolysis, chemical and microbial degradation, etc., is known as the dissipation rate. The first-order kinetic equation was applied to the data in order to study the dissipation of spiromesifen (Majumder *et al.*, 2024).

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

245 Where, C_t is the concentration at time t, C_0 is the initial concentration, k is the rate constant 246 for insecticide dissipation, and t is the time.

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248 **2.9.6.** Half Life

For calculating the half-life $(t_{1/2})$ of the parent compounds, the residue data were subjected to statistical analysis as per the following equation 2 (*Majumder et al.*, 2024).

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

252 **2.9.7. Consumer risk assessment:**

253 The food safety of spiromesifen was evaluated by comparing the dietary exposure [theoretical maximum daily intake (TMDI)] against the maximum permissible intake (MPI). An average 254 255 child's bodyweight (16 kg) was multiplied by the Acceptable Daily Intake (ADI) to determine the MPIs. The ADI of spiromesifen was 0.03 mg kg⁻¹ bodyweight day. Dietary exposures were 256 calculated by taking into account the residue levels in each sample (mg kg⁻¹). The food safety 257 of spiromesifen was evaluated by analysing the dietary exposure TMDI i.e. (Theoretical 258 maximum daily intake) to determine if it is within the Maximum Permissible Intake (MPI). The 259 MPIs were derived by multiplying the ADI by the bodyweight of an average child (16 kg). The 260 MPI of spiromesifen were estimated to be $0.48 \text{ mg person}^{-1} \text{ d}^{-1}$. 261

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263 **2.9.8.** Decontamination of spiromesifen residues from tomato and cabbage:

264 A second field trial was conducted to investigate spiromesifen decontamination in tomato and cabbage. The plots of tomato and cabbage were sprayed with spiromesifen 22.9 SC@96 g ai 265 ha⁻¹ during fruiting and head formation, and samples were taken 1 hour later. These were 266 immediately brought to the laboratory for testing. To decontaminate spiromesifen from tomato 267 268 and cabbage, 5 treatments were replicated 3 times. T1 - Washing with running water for 5 minutes, T₂ - Treating with warm water (50^oC), T₃ - Treating with 1% sodium chloride (NaCl) 269 solution, T_4 - Treating with Vinegar solution, T_5 – Washing with boiling water (blanching) for 270 5 minutes. The residues in the control samples (untreated) were assumed to be 100% of the 271 residue, and the residues remaining after treatment were computed in comparison to the control 272 273 sample.

275 **3. Result and Discussion**

3.1. Sample Preparation

Tomato fruits samples were crushed without any external addition of water because it contains
more water. Cabbage heads were crushed with water. An addition of water at 1:1 (sample:
water) ensured that there was also an increase in the recoveries of spiromesifen in cabbage. The

recoveries of were within tomato, 83 to 94% and cabbage, 81.33 to 92% (Table 1), respectively.
Addition of distilled increased precision, which might be due to the separation of matrix
material from water. The ethyl acetate extract of tomato fruit was red in colour and cabbage
was dark green in colour, and higher matrix-induced signal enhancement was recorded for
spiromesifen when the analysis was performed without cleanup or with only 50 mg of PSA.
Cleanup with 75 mg of PSA and GCB could reduce the matrix effect to < 20%. Hence, cleanup
of 1.5 ml of ethyl acetate extract was performed with 75 mg of PSA and 15 gr GCB.

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288 **3.2. Method Validation**

QuEChERS method used for the extraction of spiromesifen in tomato and cabbage was 289 290 validated by studying various parameters of method validation. The parameters studied were accuracy, precision, limit of detection (LOD), limit of quantification (LOQ), linearity, range, 291 selectivity and measurement uncertainty. Accuracy and precision of the analytical method was 292 carried out by conducting the percentage recovery at the concentration of 0.01, 0.02, 0.05, 0.10 293 and 0.50 mg kg⁻¹ was 83.00 to 94.67% in tomato and 81.33% to 92.00 in Cabbage (Table 1). 294 Control samples of cabbage and tomato were spiked with spiromesifen at 5 concentrations. The 295 coefficients of determination (R^2) were 0.996, 0.999, 0.999, and the regression equations were 296 y=3E+08x-2E+06, y=3E+08x-1E+0.6 and y=2E+08x+79856 for solvent standard (Figure 2), 297 Tomato and Cabbage matrix, respectively, within the calibration range of 0.01 to 0.1 mg kg⁻¹. 298 299 The average matrix effect (ME) percentages were less than 20%. The LOQ was established to be 0.01 mg kg⁻¹ for both the matrices (tomato and cabbage). The method optimised data in the 300 present study satisfied the EU protocols for method validation and are considered appropriate 301 for the determination of trace amounts of spiromesifen residue in matrices of tomato and 302 303 cabbage.

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3.3. Dissipation Kinetics

The spray application of spiromesifen was given to tomato and cabbage at the recommended 306 and double doses of 125 and 250 g at ha^{-1} , respectively. The structural makeup of cabbage is 307 composed of tightly packed layers of stiff leaves arranged in clusters, which gives the vegetable 308 309 a rounded or globular form. Because of the way the vegetable is structured, cabbage may have retained residue for up to 21 days (Table 2). Following the final spraying (2 hours post-310 311 application), the initial residue deposition in tomato and cabbage was determined to be 0.254 and 0.343 mg kg⁻¹ for dosage, respectively. Up to five days after application (DAA), there was 312 a quicker rate of degradation; at that point, about 90% of the residues evaporated, and after ten 313

days, the residues from DAA fell below the detectable limit (BDL) (Table 2). Over time, the
dissipation behaviour changed from being faster at first to slower. This revealed an exponential
pattern of degradation and implied that the degradation followed a simple first-order kinetics
that is adequate to explain the dissipation behaviour of the residues. Tomato and cabbage

regression equations were $y=0.2532e^{-0.292x}$ and $y=0.1699^{-0.183x}$, respectively.

Overall residue degradation on the plant occurs at a rate determined by several processes, such as volatilization, photolysis, washing off, leaching, hydrolysis, and degradation (Sardar *et al.*, 2022).

323 Half-lives

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324 Pesticide dissipation is commonly expressed as the half-life $(t_{1/2})$, which is the amount of time required for the 50% dissipation of pesticide residue from its initial concentration. The residue 325 dissipation of the spiromesifen followed the first-order kinetics, which could be expressed in 326 the form, $C_{t} = C_{0} e^{-kt}$. Spiromesifen dissipation pattern on tomato and cabbage are presented 327 in Figure 3; Figure 4 and Figure 5. The half-lives of spiromesifen in tomato and cabbage were 328 2.37 and 3.79 days respectively, (Table 2) with good linearity. The half-lives of spiromesifen 329 from treatment at 96 g ai ha⁻¹ varied from 5.5 to 6.2 days on apple, 2.18 to 2.4 days on chilli, 330 5.0 to 8.5 days on tea, and 0.93 to 1.38 days on tomato from multi-locational field studies carried 331 out earlier (Sharma et al., 2007; Sharma et al., 2007; Sharma et al., 2014). Spiromesifen's 332 dissipation at the dose of application took only a short time to reach the maximum residue limit, 333 making it safe to use in tomato and cabbage crops to control insect infestations in the fruits of 334 335 those plants.

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337 **3.4. Consumer Risk Assessment**

There isn't much information available regarding the safety assessment of spiromesifen residues 338 in vegetables, particularly in tomato and cabbage, despite the fact that almost identical patterns 339 of dissipation were observed in the doses for spiromesifen in tomato and cabbage. Hence, food 340 safety evaluation of this insecticides was required to be assessed. The acceptable daily intake 341 d⁻¹ spiromesifen 0.03 kg⁻¹ body 342 (ADI) of mg weight (https://www.ncbi.nlm.nih.gov/pmc/articles/PMC8933456/#:~:text=The%20ADI%20of%20s 343 piromesifen%20set,and%200.2556%25%20in%20perilla%20leaves). Multiplying the ADI by 344 345 the body weight of an average child (16 kg), the MPI of spiromesifen were estimated to be 0.48 mg person⁻¹ d⁻¹. Dietary exposures for rural and urban peoples were calculated by multiplying 346 the residue levels in each sample $(mg kg^{-1})$ (Table 3). 347

349 3.5. Decontamination of spiromesifen residues from tomato and cabbage head by 350 household process

Non-systemic insecticides typically act on pests through direct contact or ingestion and do not 351 352 move within the plant's vascular system. Therefore, the efficacy and persistence of these insecticides can be influenced by various factors related to household treatment practices such 353 354 as washing, boiling, blanching etc. due to low adherence of such chemicals to fruits and vegetables surface it is easy to break down surface tension and thereby reducing significant 355 356 portion of such insecticides. The experiment demonstrated that blanching, or washing with hot water, reduced the amount of spiromesifen residues from tomato and cabbage heads by 77.02%. 357 358 With all other treatments, however, residue removal was only achieved to a degree of 58.51-69.26% (Table 4). Take out spiromesifen residue from tomato and cabbage heads are because 359 it is a non-systemic insecticide. Thus, it is established that boiling water removes spiromesifen 360 residues from tomato and cabbage more effectively than cold water. Comparative results for 361 elimination in different crops have been conducted for fipronil and its metabolites in okra, as 362 well as similar findings for profenophos in eggplant, sweet pepper, and hot pepper (Radwan et 363 al. 2005). According to food safety, the consumers must know the health hazards and take 364 precautionary steps to reduce the residue impact before consumption. Our decontamination 365 treatment according to the findings, consumers can lower the risk of residue from the farm to 366 their table by blanching and treating tomato and cabbage heads with 1% NaCl before 367 consumption. 368

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370 4. Conclusions

371 The method of spiromesifen residue analysis in cabbage and tomato samples showed that the pesticide residue levels in cabbage and tomato samples were below the necessary MRL even 372 on the same day. Therefore, this insecticide can be used safely on the crops as it doesn't appear 373 to be harmful to human health or the environment. The risk of residues can be further decreased 374 by processing the fruits at home with low-cost, simple methods; for complete consumer safety, 375 these procedures should be followed before use and consumption. Using GC-ECD method, it 376 377 was possible to successfully find spiromesifen residues in tomato and cabbage. The recoveries were in the range of 83.00-94.67% with the RSD of 2.199-4.695% of tomato fruit and 81.33-378 379 92% with the RSD of 1.878 – 4.804 of cabbage head. The limit of quantification (LOQ) of the analytical method for the analysis of spiromesifen was 0.01 mg kg⁻¹. In tomato and cabbage 380 heads, spiromesifen half-lives were 2.37 and 3.79 days, respectively. Dietary spiromesifen 381

residue exposures were less than the estimated MPI. Among the household method, blanching 382 could be used as a potential decontamination process for spiromesifen from tomato and cabbage 383 head. The technique could be used to quickly analyse of spiromesifen in actual samples. 384 385 Acknowledgements 386 The authors are thankful to Director, ICAR-Indian Institute of Vegetable Research, Varanasi, 387 388 for financial and other support to carry out this research. 389 References 390 391 Abo-El-Seoud, M. A., Shams-El-Din, A. M., Danial, L. N., and Ahmed, S. M. 1995. Residues and persistence of some organophosphorus insecticides applied to cabbage 392 plants. Food Chem. 54(2), 137-140. 393 394 Dhandapani, N., Umeshchandra, S. R. and Murugan, M. 2003. Biointensive pest 395 management (BIPM) in major vegetable crops An Indian perspective. J. Food Agric. 396 397 Environ. 1:333-339. Freedman, N. D., Park, Y., Subar, A. F., Hollenbeck, A. R., Leitzmann, M. F., Schatzkin, 398 A., and Abnet, C. C. 2008. Fruit and vegetable intake and head and neck cancer risk in 399 400 a large United States prospective cohort study. Int. J. Cancer, 122(10), 2330-2336. 401 http://www.nutrition-and-you.com/cabbage.html 402 403 https://www.ncbi.nlm.nih.gov/pmc/articles/PMC8933456/#:~:text=The%20ADI%20of 404 %20spiromesifen%20set,and%200.2556%25%20in%20perilla%20leaves. 405 406 Khanam, U. K. S., Hossain, M., Ahmed, N., Uddin, M. M., and Hossain, M. S. 2003. 407 Varietal screening of tomato to tomato fruit borer, Helicoverpa armigera (Hub.) and 408 associated tomato plant characters. Pak. J. Bio.l Sci. 6(4), 413-421. 409 410 Majumder, S., Verma, C. K., Rani, V., Rani, A. T., Pandey, K. K., and Singh, J. 2022a. 411 Residue dynamics and food safety evaluation of fungicide kresoxim-methyl in green 412 chilli (Capsicum annum L.). Int. J. Environ. Anal. Chem. 102(19), 7433-7443. 413 414 Majumder, S., Rani, A. T., Divekar, P. A., Halder, J., Pandey, K. K., and Behera, T. K. 415 2023a. Field bioefficacy and residue dynamics of chlorantraniliprole (18.50% sc) in 416 okra (Abelmoschus esculentus). Indian J. Agric. Sci. 93(3), 314-317. 417 418 Majumder, S., Singh, S., Divekar, P. A., Pandey, K. K., and Behera, T. K. 2022b. Residue 419 dissipation kinetics, safety evaluation and decontamination of hexaconazole in green 420 chilli. Int. J. Environ. Anal. Chem. 1-13. 421 422 Majumder, S., Pandey, J., Divekar, P. A., Ali, E. O., Pandey, K. K., and Behera, T. K. 423 2023b. Dissipation kinetics, food safety evaluation and decontamination of 424 chlorantraniliprole in cowpea. J. Environ. Health, Part B, 58(5), 389-398. 425 426 Majumder, S., Mandal, S., Majumder, B., Paul, A., Paul, T., Sahana, N., and Mondal, P. 427 428 2022c. A liquid chromatographic method for determination of acetamiprid and

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Figure 1. Chromatogram for A) spiromesifen standard B) tomato sample C) cabbage sample.





Figure 3. Dissipation curves of studied pesticide in tomato.





Figure 4. Dissipation curves of studied pesticide in cabbage head sample.



Figure 5. Degradation pattern of spiromesifen in tomato and cabbage head.

Level of fortification	% Recovery	% Relative Standard Deviation
$(mg kg^{-1})$		(RSD)
	Tomato fruit	
0.01	83.00	3.188
0.02	86.67	3.331
0.05	88.67	4.695
0.1	94.67	2.199
0.5	90.67	4.592
	Cabbage head	
0.01	81.33	1.878
0.02	88.33	3.268
0.05	88.00	4.545
0.1	92.00	2.174
0.5	86.67	4.804

Table 1. Percentage recovery of spiromesifen in tomato fruits and cabbage head

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	1401		meren uays.		
	Conc. (1	ng kg ⁻¹)	Decrease	% of residue	
Days	Tomato	Cabbage	Tomato	Cabbage	
0	0.254	0.343	0.000	0.000	
1	0.194	0.269	19.393	16.447	
3	0.100	0.086	67.801	72.674	
5	0.065	0.035	90.603	89.165	
7	0.029	0.021	94.252	95.424	
10	0.014	0.018	96.476	97.270	
15	0.000	0.013		97.966	
21	0.000	0.006		98.219	
Half life	2.37	3.79			

Table 2. Residue on the different days.

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Table 3. Safety evaluation of day wise residue of spiromesifen in tomato and cabbage head.

	Tomato			Tomato Cabbage		
Sampling days	Residue	Dietary exposure		Residue	Dietary	exposure
	(mg kg ⁻¹)	$(mg person^{-1} d^{-1})$		(mg kg ⁻¹)	(mg pe	erson ⁻¹)
		Rural	Urban		Rural	Urban
0	0.254	0.0048	0.0069	0.343	0.0026	0.0031
1	0.194	0.0037	0.0053	0.269	0.0020	0.0024
3	0.100	0.0019	0.0027	0.086	0.0007	0.0008
5	0.065	0.0012	0.0017	0.035	0.0003	0.0003
7	0.029	0.0005	0.0008	0.021	0.0002	0.0002
10	0.014	0.0003	0.0004	0.018	0.0001	0.0002
15	0.000	0.0000	0.0000	0.013	0.0001	0.0001
21	0.000	0.0000	0.0000	0.006	0.0000	0.0001

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556 Table 4. Effect of different household preparation in the removal of spiromesifen residue from tomato and cabbage.

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Decontamination treatment	% Reduction	SD
Without washing	0	0.00
Washing with running tap water	58.51	2.62
1% NaCl	69.26	0.74
Warm water (50°C)	61.46	0.88
Vinegar solution	64.08	2.03
Washing with Boiling water (Blanching)	77.02	1.46