

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

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### **ABSTRACT**

Spiromesifen is one of the most popular insecticides used for the chemical control of several insect in many vegetable crops, but its residues may remain in the crops. Residues were extracted using ethyl acetate from tomato and cabbage. Samples were cleaned using graphitized carbon black, primary secondary amine, and magnesium sulfate. At 0.01, 0.02, 0.05, 0.10, and 0.50 mg kg<sup>-1</sup>, the recovery percentage were 83.00–94.67% in tomato and 81.33–92.00% in 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 intake of 0.48 mg person<sup>-1</sup> d<sup>-1</sup> on all the sampling days for rural as well as urban. The average matrix effect was less than 20%. Spiromesifen used to control psyllid, aphid and whiteflies in tomato and cabbage. There could be a health risk if its residue stays in the crop. Thus, the validated method was used to study the analysis of spiromesifen residue, its dissipation rate, and safety evaluations in tomato and cabbage. Different household processes were evaluated for removal of the incurred spiromesifen residue in tomato and cabbage. Washing with boiling water could be used as a most effective decontamination strategy for spiromesifen in tomato and cabbage.

**Keywords:** Decontamination, Dissipation kinetics, Spiromesifen residue, Tomato fruit and cabbage 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

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

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

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

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

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

96

## 97 **2. MATERIALS AND METHODS**

### 98 **2.1. Chemicals and Reagents**

99 Spiromesifen (purity 99 %) was procured from Sigma-Aldrich Pvt. Ltd. (Bangalore, India).  
100 Acetone, *n*-hexane, magnesium sulfate (MgSO<sub>4</sub>), sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>), and sodium acetate  
101 (C<sub>2</sub>H<sub>3</sub>NaO<sub>2</sub>) used were of analytical grade and procured from Thomas Baker, Mumbai, India.  
102 MgSO<sub>4</sub> was activated in a muffle furnace for 5 h at 600°C and kept in desiccators prior to use.  
103 Primary secondary amine (PSA) of mesh size of 40 µm was procured from Agilent  
104 Technologies (Bangalore, India). The deionized water for the mobile phase was obtained from  
105 a Millipore Water Purification System (Sartorius AG, Goettingen, Germany) and filtered using

106 Millipore GV filter paper of pore size 0.22  $\mu\text{m}$ . Polytetrafluoroethylene (PTFE) membrane filter  
107 of pore size 0.2  $\mu\text{m}$  was procured from Phenomenex (Bangalore, India).

## 108 109 **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).

## 114 115 **2.3. Reference Standard**

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

## 124 125 **2.4. Field Experimental Condition**

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

140

## 141 2.5. Sampling

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

## 146 2.6. Sample Preparation and Analysis

148 Tomato and cabbage samples were collected from each treated plot and samples from three  
149 replicates were pooled together to form a sample size of approximately 5 kg. Each sample was  
150 divided into four parts. One part of each sample was taken to make approximately 1-kg  
151 subsample. It was cut into small pieces and homogenized (250 g) homogenized with a silent  
152 crusher and grinder. Tomato and cabbage grown in the experimental field without application  
153 of pesticides was used for spiking. A representative (10 g) sample in three replicates was taken  
154 for analysis and 10 grams of the sample were extracted using 10 mL of 1% acetic acid in ethyl  
155 acetate and 10 g of anhydrous sodium sulphate. The process involved vortexing the sample for  
156 2 minutes and centrifuging it for 5 minutes at 4000 rpm. 75 mg of PSA, 225 mg of MgSO<sub>4</sub>, and  
157 15 mg of GCB were extracted using a dispersive solid phase extraction technique to clean an  
158 aliquot of the supernatant ethyl acetate layer (1.5 mL). After centrifuging the extract for 3  
159 minutes at 5000 rpm and filtering it through a 0.2 µm Nylon 6,6 membrane, 1 milliliter of the  
160 extract was injected into the GC-ECD (Majumder *et al.*, 2023a).

## 161 2.7. Extraction and Purification

163 The QuEChERS technique was modified to extract the samples. The samples were prepared,  
164 extracted and purification by following earlier reported method with slight adjustments  
165 according to the nature of the pesticide and type of the crop (Majumder *et al.*, 2023b). The  
166 complete laboratory subsample was broken up into tiny pieces and completely ground in a  
167 mixer grinder. To do an extraction, 10 g of tomato and cabbage samples were weighed into 50  
168 mL centrifuge tubes. Then, 10 ml of 1% acetic acid in ethyl acetate and 10 gm of anhydrous  
169 sodium sulfate were added. The mixture was vortexed for 2 minutes and then centrifuged for 5  
170 minutes at 5000 rpm. The supernatant ethyl acetate layer (1.5 mL) was cleaned using the  
171 dispersive solid phase extraction (DSPE) technique with 75 PSA, 15 mg GCB, and 225 mg  
172 MgSO<sub>4</sub>. After centrifuging this extract for 5 minutes at 10,000 rpm, it was immediately filtered  
173 through a 0.22 µm Nylon 6,6 membrane filter and subjected to GC-ECD analysis.

174

## 175 2.8. GC- $\mu$ ECD Analysis

176 For the analysis of spiromesifen residue in tomato and cabbage head, the GC with microelectron  
177 capture detector (ECD,  $^{63}\text{Ni}$ ) was used. The injector of the instrument was used in split injection  
178 mode with an injection volume of  $1\ \mu\text{L}$  and a 10:1 ratio at  $250^\circ\text{C}$ . An HP-5 capillary column (30  
179 m in length,  $320\ \mu\text{m}$  in diameter,  $0.25\ \mu\text{m}$  film thickness, and nitrogen gas flowing at  $2\ \text{mL}/\text{min}$ )  
180 was utilized for the separation process. The detector temperature was set to  $300^\circ\text{C}$ , and the  
181 nitrogen gas flow rate was set to  $30\ \text{mL}/\text{min}$ . After holding the temperature at  $90^\circ\text{C}$  for 5  
182 minutes, the oven ramped up to  $200^\circ\text{C}$  at a rate of  $20^\circ\text{C}$  per minute and ramped down to  $240^\circ\text{C}$   
183 at a rate of  $6^\circ\text{C}$  per minute for a further 2 minutes. Under these conditions, it was found that  
184 spiromesifen exhibited a retention time (RT) of 7.845 minutes in these conditions (Figure1).  
185 Total run time for the analysis of one sample was 18 min. An Agilent openlab EZchrom for  
186 acquiring chromatograms.

187 The following formula was used to compute insecticide residue in  $\text{mg kg}^{-1}$ :

$$188 \quad \text{Residue (mg kg}^{-1}\text{)} = (M_1 \times N_1 \times C) / (M_2 \times N_2 \times W)$$

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  $\mu\text{L}$ ,  $C$ =  
191 Concentration of analytical standard in  $\text{mg kg}^{-1}$ , and  $W$ = Weight of the sample in g (Majumder  
192 *et al.*, 2024).

193

## 194 2.9. Method Validation

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

206

207

208

### 209 **2.9.1 Calibration Curves and Linearity**

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

### 215 216 **2.9.2. Selectivity and Sensitivity**

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

### 225 226 **2.9.3. Recovery**

227 Recovery study was carried out at 0.01, 0.02, 0.05, 0.1 and 0.5  $\mu\text{g mL}^{-1}$  levels with six replicates  
228 each. Precision was evaluated in term of repeatability and reproducibility.

### 229 230 **2.9.4. Matrix Effect**

231 The Matrix effects were evaluated by comparing the peak area of the solvent standard with that  
232 of matrix matched standard at 0.1  $\mu\text{g mL}^{-1}$ . The matrix effect was calculated by spiking post-  
233 extraction at 0.005, 0.01, 0.02, 0.06, 0.1, and 0.5  $\mu\text{g mL}^{-1}$ . The formula was used to determine  
234 the matrix effect (Majumder *et al.*, 2022c):

$$235 \text{ME (\%)} = \frac{(\text{Peak area of matrix matched standard} - \text{Peak area of solvent standard}) \times 100}{236 \text{Peak area of matched standard}}$$

### 237 238 **2.9.5. Dissipation Kinetics**

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

$$244 C_t = C_0 e^{-kt} \quad (1)$$

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.

### 247 248 **2.9.6. Half Life**

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

$$251 \quad t_{1/2} = \ln 2/k \quad (2)$$

### 252 **2.9.7. Consumer risk assessment:**

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

### 262 263 **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  
265 cabbage. The plots of tomato and cabbage were sprayed with spiromesifen 22.9 SC@96 g ai  
266 ha<sup>-1</sup> during fruiting and head formation, and samples were taken 1 hour later. These were  
267 immediately brought to the laboratory for testing. To decontaminate spiromesifen from tomato  
268 and cabbage, 5 treatments were replicated 3 times. T<sub>1</sub> - Washing with running water for 5  
269 minutes, T<sub>2</sub> - Treating with warm water (50°C), T<sub>3</sub> - Treating with 1% sodium chloride (NaCl)  
270 solution, T<sub>4</sub> - Treating with Vinegar solution, T<sub>5</sub> – Washing with boiling water (blanching) for  
271 5 minutes. The residues in the control samples (untreated) were assumed to be 100% of the  
272 residue, and the residues remaining after treatment were computed in comparison to the control  
273 sample.

## 274 275 **3. Result and Discussion**

### 276 **3.1. Sample Preparation**

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



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

287

### 288 **3.2. Method Validation**

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

304

### 305 **3.3. Dissipation Kinetics**

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

314 days, the residues from DAA fell below the detectable limit (BDL) (Table 2). Over time, the  
315 dissipation behaviour changed from being faster at first to slower. This revealed an exponential  
316 pattern of degradation and implied that the degradation followed a simple first-order kinetics  
317 that is adequate to explain the dissipation behaviour of the residues. Tomato and cabbage  
318 regression equations were  $y = 0.2532e^{-0.292x}$  and  $y = 0.1699e^{-0.183x}$ , respectively.  
319 Overall residue degradation on the plant occurs at a rate determined by several processes, such  
320 as volatilization, photolysis, washing off, leaching, hydrolysis, and degradation (Sardar *et al.*,  
321 2022).

### 322 323 **Half-lives**

324 Pesticide dissipation is commonly expressed as the half-life ( $t_{1/2}$ ), which is the amount of time  
325 required for the 50% dissipation of pesticide residue from its initial concentration. The residue  
326 dissipation of the spiromesifen followed the first-order kinetics, which could be expressed in  
327 the form,  $C_t = C_0 e^{-kt}$ . Spiromesifen dissipation pattern on tomato and cabbage are presented  
328 in Figure 3; Figure 4 and Figure 5. The half-lives of spiromesifen in tomato and cabbage were  
329 2.37 and 3.79 days respectively, (Table 2) with good linearity. The half-lives of spiromesifen  
330 from treatment at 96 g ai ha<sup>-1</sup> varied from 5.5 to 6.2 days on apple, 2.18 to 2.4 days on chilli,  
331 5.0 to 8.5 days on tea, and 0.93 to 1.38 days on tomato from multi-locational field studies carried  
332 out earlier (Sharma *et al.*, 2007; Sharma *et al.*, 2007; Sharma *et al.*, 2014). Spiromesifen's  
333 dissipation at the dose of application took only a short time to reach the maximum residue limit,  
334 making it safe to use in tomato and cabbage crops to control insect infestations in the fruits of  
335 those plants.

### 336 337 **3.4. Consumer Risk Assessment**

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

348

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

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

369

### 370 **4. Conclusions**

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

382 residue exposures were less than the estimated MPI. Among the household method, blanching  
383 could be used as a potential decontamination process for spiromesifen from tomato and cabbage  
384 head. The technique could be used to quickly analyse of spiromesifen in actual samples.

385

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389

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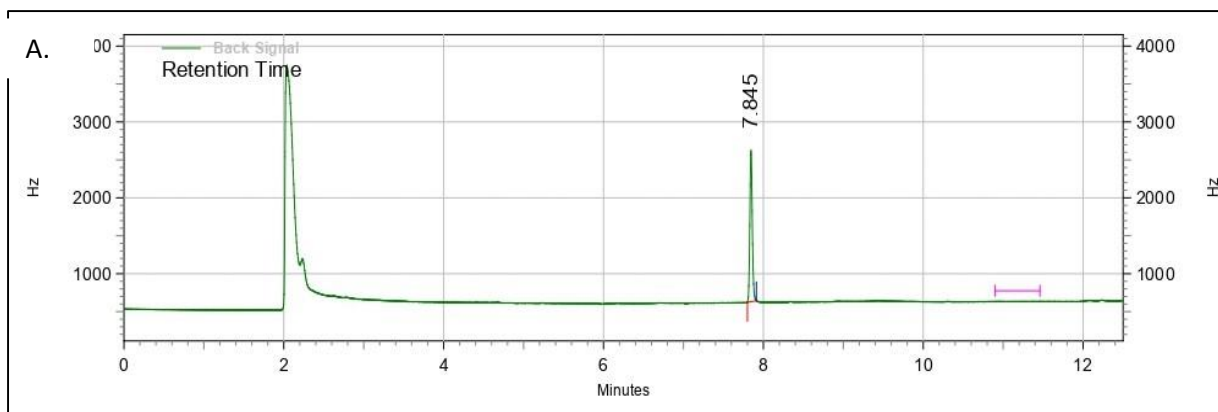
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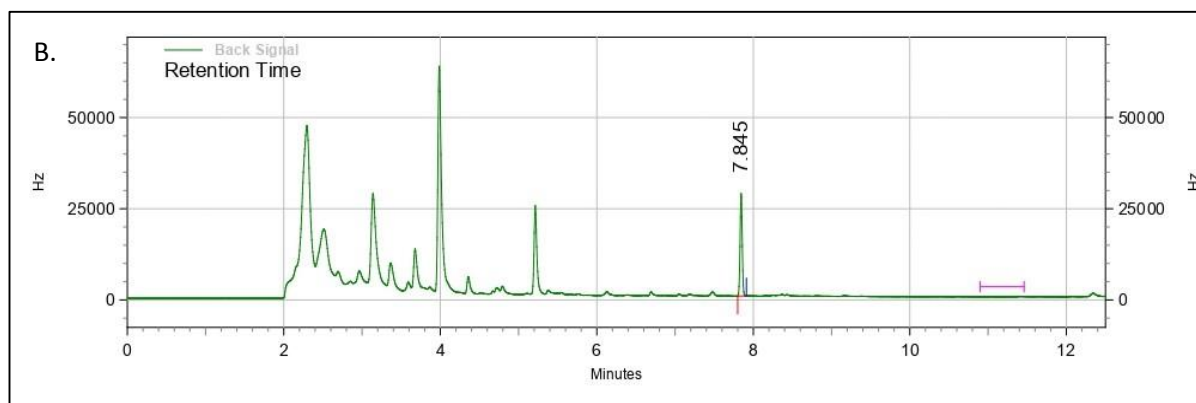
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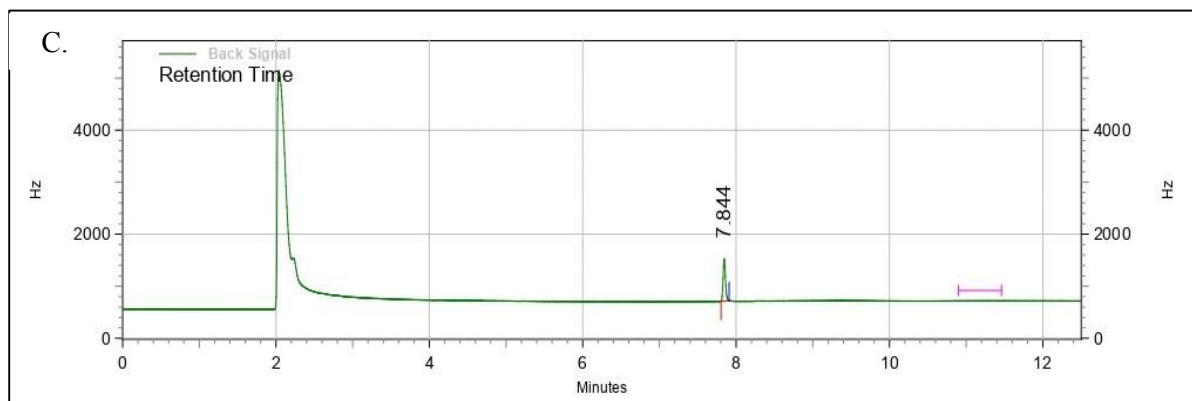
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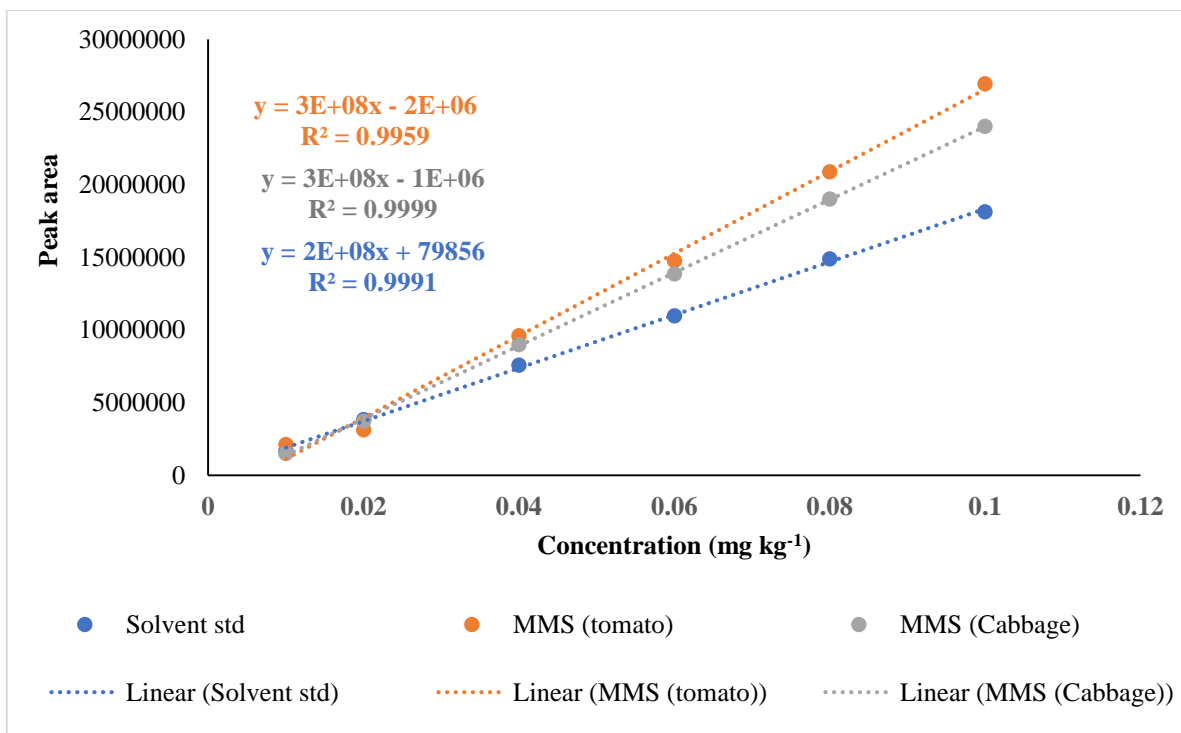


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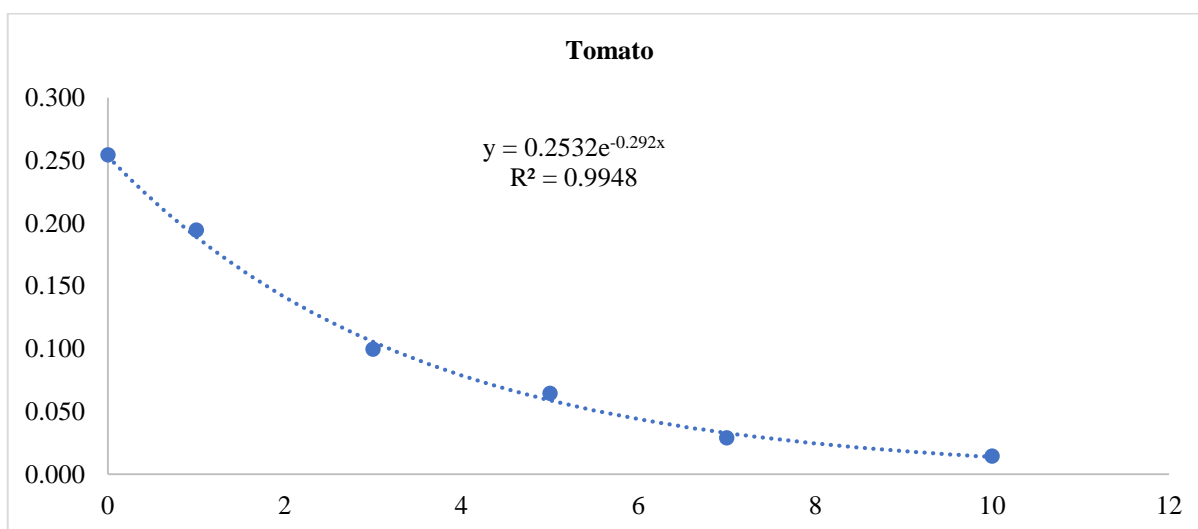
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**Figure 1.** Chromatogram for A) spiromesifen standard B) tomato sample C) cabbage sample.



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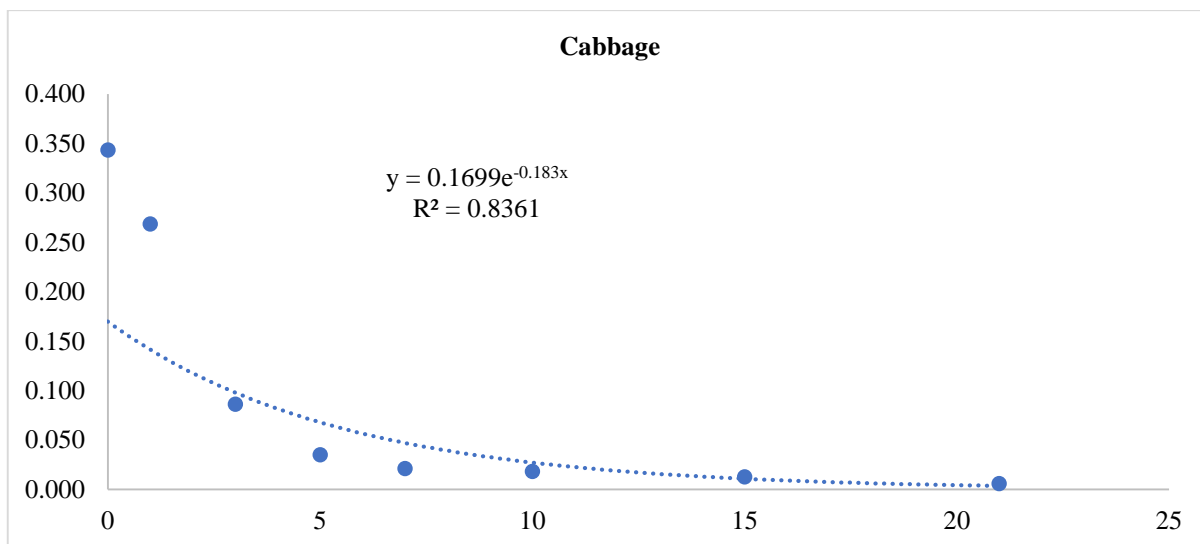
**Figure 2.** Linearity graph for solvent standard and Matrix Matched Standard (MMS).



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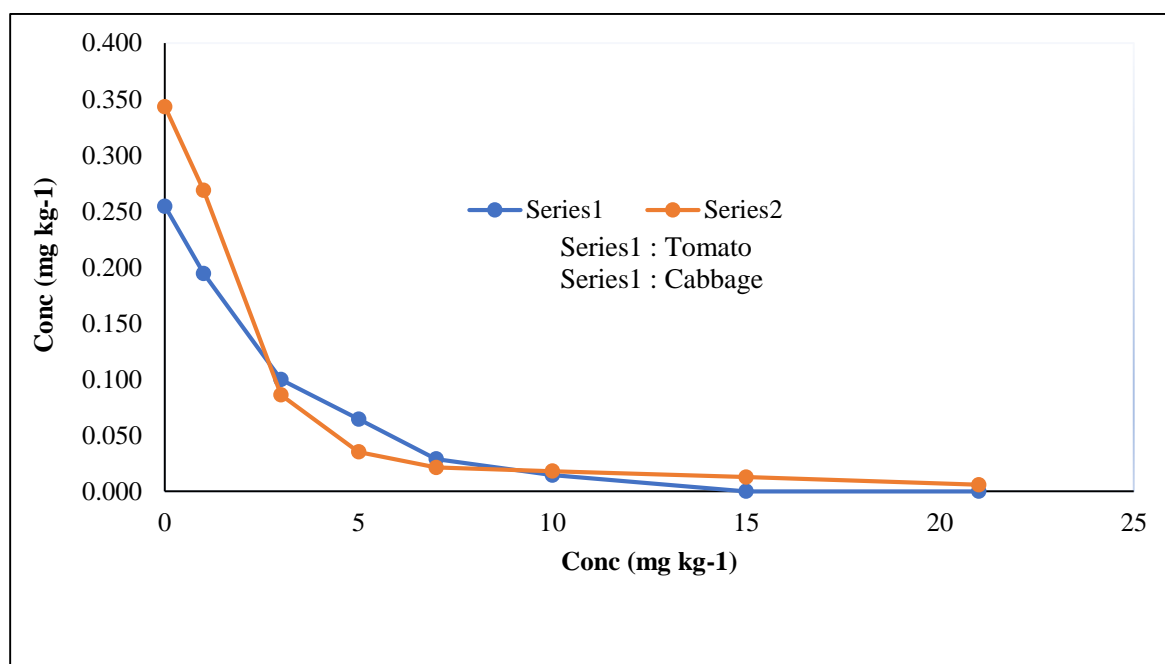
**Figure 3.** Dissipation curves of studied pesticide in tomato.





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



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

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

Level of fortification (mg kg <sup>-1</sup> )	% Recovery	% Relative Standard Deviation (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

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**Table 2.** Residue on the different days.

Days	Conc. (mg kg <sup>-1</sup> )		Decrease % of residue	
	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		

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

Sampling days	Tomato			Cabbage		
	Residue (mg kg <sup>-1</sup> )	Dietary exposure (mg person <sup>-1</sup> d <sup>-1</sup> )		Residue (mg kg <sup>-1</sup> )	Dietary exposure (mg person <sup>-1</sup> )	
		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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**Table 4.** Effect of different household preparation in the removal of spiromesifen residue from tomato and cabbage.

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

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