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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^{-1}, 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 $person^{-1}$ d^{-1} 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

the use of stronger chemicals or alternative pest management strategies. Hence, it is imperative to conduct thorough pesticide residue analyses in vegetable crops to ensure public health protection, legal compliance, environmental conservation, and promotion of sustainable agricultural practices. Such analyses are integral components of comprehensive strategies for food safety and pesticide management. Tomatoes (*Solanum lycopersicum*), belonging to the Solanaceae family, represent a crucial cash crop that significantly contributes to the economy. They are cultivated extensively both domestically and internationally, being rich sources of essential nutrients such as potassium, iron, phosphorus, vitamins A, B, and C, as well as 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 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, 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, 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. This leafy green vegetable is utilized extensively in post-harvest industries, yielding valuable products such as sauerkraut. In India, cabbage production reached 9,095,000 mt in 2018–2019, cultivated across 399,000 hectares of land. Cabbage is rich in phytochemicals like thiocyanate, indole-3-carbinol, lutein, zea-xanthin, and sulforaphane, which are associated with various health benefits, including protection against breast, colon, and prostate cancers. Additionally, cabbage is abundant in beta-carotene, vitamin C, and dietary fiber (http://www.nutrition-and-you.com/cabbage.html).

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

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 µg/g.

The application of pesticides to cabbage presents a unique challenge due to its multilayered structure, which may retain residues for extended periods. Cabbage exhibits resilience to environmental fluctuations, further contributing to the persistence of pesticide residues (Abo-El-Seoud *et al*., 1995). Among various vegetable crops, cabbage has been found to accumulate the highest levels of pesticide residues (Srivastava *et al*., 2011). This accumulation of pesticide residues in harvested tomatoes and cabbage poses significant concerns during both exportation 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 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 analytical method for assessing pesticide dissipation. This technique combines gas chromatography separation with electron capture detection, facilitating precise identification and quantification of pesticide compounds (Siddamallaiah and Mohapatra, 2016). To assess the dissipation dynamics of pesticide residues, a field trial involving the application of spiromesifen to tomato and cabbage crops was conducted. This trial aimed to elucidate the dissipation pattern and determine the half-life of spiromesifen on these crops, providing crucial insights into the fate of pesticide residues in agricultural environments.

2. MATERIALS AND METHODS

2.1. Chemicals and Reagents

Spiromesifen (purity 99 %) was procured from Sigma-Aldrich Pvt. Ltd. (Bangalore, India). Acetone, *n*-hexane, magnesium sulfate ($MgSO_4$), sodium sulfate (Na_2SO_4), and sodium acetate ($C_2H_3NaO_2$) used were of analytical grade and procured from Thomas Baker, Mumbai, India. $MgSO_4$ 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 µm 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).

2.2. Apparatus

The following were used: centrifuge (Kubota, Germany), microcentrifuge (Microfuge Pico, Kendro, D-37,520, Osterode, Germany), mixer and grinder (Bajaj India Pvt. Ltd., Mumbai), precision balance (Vibra, Adair Dutt, Mumbai, India), vortex mixer (Geni 2 T, Imperials Biomedicals, Mumbai, India), and ultrasonic bath (Oscar electronics, Mumbai, India).

2.3. Reference Standard

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

2.4. Field Experimental Condition

The field experiment was carried out at the vegetable research farm, ICAR-Indian Institute of Vegetable Research, Varanasi, Uttar Pradesh, India (longitude 82.52° E and latitude 25.10° N) as per the Food and Agriculture Organisation (FAO) guidelines (Majumder *et al*. 2022 a) using 3 treatments that are duplicated 3 times in a randomised block design. At the fruit formation stage (2 months after transplanting) of tomato crop (open field), spiromesifen (Bayer Oberon 240 SC) spray applications were given at the recommended and double doses of 125 and 250 g ai ha^{-1} for both crops. Spiromesifen was used in tomatoes and cabbage by Knapsack Power Sprayer. The crop was grown using advised agronomic techniques. The area receives an average rainfall of 1000 mm which is distributed over a period of more than 100 days with peak period between July and August. The average maximum and minimum temperatures during the experimental period were 21^0C and 24^0C for tomato cultivation and the average maximum and minimum temperatures during the experimental period were 15 and 21°C for cabbage cultivation. Row to row and plant to plant spacing were 75-90×45-60 cm for tomato and 45-60×30-45 for cabbage, respectively.

2.5. Sampling

At regular intervals on 0 day (2 hours after spraying), 1-day, 3-day, 5-day, 7-day, 10-day, 15-day, 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^{0}C until analysis to avoid any degradation (Majumder *et al*., 2023a).

2.6. Sample Preparation and Analysis

Tomato and cabbage samples were collected from each treated plot and samples from three 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 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 of pesticides was used for spiking. A representative (10 g) sample in three replicates was taken for analysis and 10 grams of the sample were extracted using 10 mL of 1% acetic acid in ethyl acetate and 10 g of anhydrous sodium sulphate. The process involved vortexing the sample for 2 minutes and centrifuging it for 5 minutes at 4000 rpm. 75 mg of PSA, 225 mg of $MgSO_4$, and 15 mg of GCB were extracted using a dispersive solid phase extraction technique to clean an aliquot of the supernatant ethyl acetate layer (1.5 mL). After centrifuging the extract for 3 minutes at 5000 rpm and filtering it through a 0.2 µm Nylon 6,6 membrane, 1 milliliter of the extract was injected into the GC-ECD (Majumder *et al*., 2023a).

2.7. Extraction and Purification

The QuEChERS technique was modified to extract the samples. The samples were prepared, 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 complete laboratory subsample was broken up into tiny pieces and completely ground in a mixer grinder. To do an extraction, 10 g of tomato and cabbage samples were weighed into 50 mL centrifuge tubes. Then, 10 ml of 1% acetic acid in ethyl acetate and 10 gm of anhydrous sodium sulfate were added. The mixture was vortexed for 2 minutes and then centrifuged for 5 minutes at 5000 rpm. The supernatant ethyl acetate layer (1.5 mL) was cleaned using the dispersive solid phase extraction (DSPE) technique with 75 PSA, 15 mg GCB, and 225 mg $MgSO_4$. After centrifuging this extract for 5 minutes at 10,000 rpm, it was immediately filtered through a 0.22 µm Nylon 6,6 membrane filter and subjected to GC-ECD analysis.

2.8. GC- µECD Analysis

For the analysis of spiromesifen residue in tomato and cabbage head, the GC with microelectron capture detector (ECD, $_{63}Ni$) was used. The injector of the instrument was used in split injection mode with an injection volume of 1µL and a 10:1 ratio at 250˚C. An HP-5 capillary column (30 m in length, 320 m in diameter, 0.25 m film thickness, and nitrogen gas flowing at 2 mL/min) was utilized for the separation process. The detector temperature was set to 300˚C, and the nitrogen gas flow rate was set to 30 mL/min. After holding the temperature at 90˚C for 5 minutes, the oven ramped up to 200^0C at a rate of 20˚C per minute and ramped down to 240˚C at a rate of 6˚C per minute for a further 2 minutes. Under these conditions, it was found that spiromesifen exhibited a retention time (RT) of 7.845 minutes in these conditions (Figure1). Total run time for the analysis of one sample was 18 min. An Agilent openlab EZchrom for acquiring chromatograms.

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

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

Where, M_1= Area of field sample in the chromatogram, M_2= Area of analytical standard in the chromatogram, N_1= Total volume of the sample in mL, N_2= Injected volume in µL, C= Concentration of analytical standard in mg kg^{-1}, and W= Weight of the sample in g (Majumder *et al*., 2024).

2.9. Method Validation

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

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.

2.9.2. Selectivity and Sensitivity

The lowest concentration at which the technique can reliably identify the analyte within the matrix is known as the LOD. It can also mean the lowest concentration that can be reliably 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) and limit of quantification (LOQ), respectively. The smallest quantity or lowest concentration of a pesticide that can be determined using a particular analytical technique with accuracy, precision, recovery, and uncertainty is known as the limit of quantification (LOQ) (Majumder *et al*., 2024).

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.

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 µg mL^{-1}. The matrix effect was calculated by spiking post-extraction at 0.005, 0.01, 0.02, 0.06, 0.1, and 0.5 µg mL^{-1}. The formula was used to determine the matrix effect (Majumder *et al*., 2022c):

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

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).

$$C_t = C_0\, e^{-kt} \qquad (1)$$

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

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).

$$t_{1/2} = \text{In } 2/k \quad (2)$$

2.9.7. Consumer risk assessment:

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 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 calculated by taking into account the residue levels in each sample (mg kg^{-1}). The food safety of spiromesifen was evaluated by analysing the dietary exposure TMDI i.e. (Theoretical maximum daily intake) to determine if it is within the Maximum Permissible Intake (MPI). The MPIs were derived by multiplying the ADI by the bodyweight of an average child (16 kg). The MPI of spiromesifen were estimated to be 0.48 mg $person^{-1}$ d^{-1}.

2.9.8. Decontamination of spiromesifen residues from tomato and cabbage:

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 ha^{-1} during fruiting and head formation, and samples were taken 1 hour later. These were immediately brought to the laboratory for testing. To decontaminate spiromesifen from tomato and cabbage, 5 treatments were replicated 3 times. T_1 - Washing with running water for 5 minutes, T_2 - Treating with warm water (50^0C), T_3 - Treating with 1% sodium chloride (NaCl) solution, T_4 - Treating with Vinegar solution, T_5 – Washing with boiling water (blanching) for 5 minutes. The residues in the control samples (untreated) were assumed to be 100% of the residue, and the residues remaining after treatment were computed in comparison to the control sample.

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.

3.2. Method Validation

QuEChERS method used for the extraction of spiromesifen in tomato and cabbage was validated by studying various parameters of method validation. The parameters studied were accuracy, precision, limit of detection (LOD), limit of quantification (LOQ), linearity, range, selectivity and measurement uncertainty. Accuracy and precision of the analytical method was carried out by conducting the percentage recovery at the concentration of 0.01, 0.02, 0.05, 0.10 and 0.50 mg kg^{-1} was 83.00 to 94.67% in tomato and 81.33% to 92.00 in Cabbage (Table 1). Control samples of cabbage and tomato were spiked with spiromesifen at 5 concentrations. The coefficients of determination (R^2) were 0.996, 0.999, 0.999, and the regression equations were y= 3E+08x-2E+06, y= 3E+08x-1E+0.6 and y= 2E+08x+79856 for solvent standard (Figure 2), Tomato and Cabbage matrix, respectively, within the calibration range of 0.01 to 0.1 mg kg^{-1}. 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 present study satisfied the EU protocols for method validation and are considered appropriate for the determination of trace amounts of spiromesifen residue in matrices of tomato and cabbage.

3.3. Dissipation Kinetics

The spray application of spiromesifen was given to tomato and cabbage at the recommended and double doses of 125 and 250 g ai ha^{-1}, respectively. The structural makeup of cabbage is composed of tightly packed layers of stiff leaves arranged in clusters, which gives the vegetable 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-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 a quicker rate of degradation; at that point, about 90% of the residues evaporated, and after ten

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).

Half-lives

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 dissipation of the spiromesifen followed the first-order kinetics, which could be expressed in the form, $C_t = C_0 e^{-kt}$. Spiromesifen dissipation pattern on tomato and cabbage are presented in Figure 3; Figure 4 and Figure 5. The half-lives of spiromesifen in tomato and cabbage were 2.37 and 3.79 days respectively, (Table 2) with good linearity. The half-lives of spiromesifen 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, 5.0 to 8.5 days on tea, and 0.93 to 1.38 days on tomato from multi-locational field studies carried out earlier (Sharma *et al*., 2007; Sharma *et al*., 2007; Sharma *et al*., 2014). Spiromesifen's dissipation at the dose of application took only a short time to reach the maximum residue limit, making it safe to use in tomato and cabbage crops to control insect infestations in the fruits of those plants.

3.4. Consumer Risk Assessment

There isn't much information available regarding the safety assessment of spiromesifen residues in vegetables, particularly in tomato and cabbage, despite the fact that almost identical patterns of dissipation were observed in the doses for spiromesifen in tomato and cabbage. Hence, food safety evaluation of this insecticides was required to be assessed. The acceptable daily intake (ADI) of spiromesifen 0.03 mg kg^{-1} body weight d^{-1} (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 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 the residue levels in each sample (mg kg^{-1}) (Table 3).

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

Non-systemic insecticides typically act on pests through direct contact or ingestion and do not 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 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 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%. 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 it is a non-systemic insecticide. Thus, it is established that boiling water removes spiromesifen residues from tomato and cabbage more effectively than cold water. Comparative results for elimination in different crops have been conducted for fipronil and its metabolites in okra, as well as similar findings for profenophos in eggplant, sweet pepper, and hot pepper (Radwan *et al*. 2005). According to food safety, the consumers must know the health hazards and take precautionary steps to reduce the residue impact before consumption. Our decontamination treatment according to the findings, consumers can lower the risk of residue from the farm to their table by blanching and treating tomato and cabbage heads with 1% NaCl before consumption.

4. Conclusions

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 on the same day. Therefore, this insecticide can be used safely on the crops as it doesn't appear to be harmful to human health or the environment. The risk of residues can be further decreased by processing the fruits at home with low-cost, simple methods; for complete consumer safety, these procedures should be followed before use and consumption. Using GC-ECD method, it 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 81.33–92% 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 heads, spiromesifen half-lives were 2.37 and 3.79 days, respectively. Dietary spiromesifen

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

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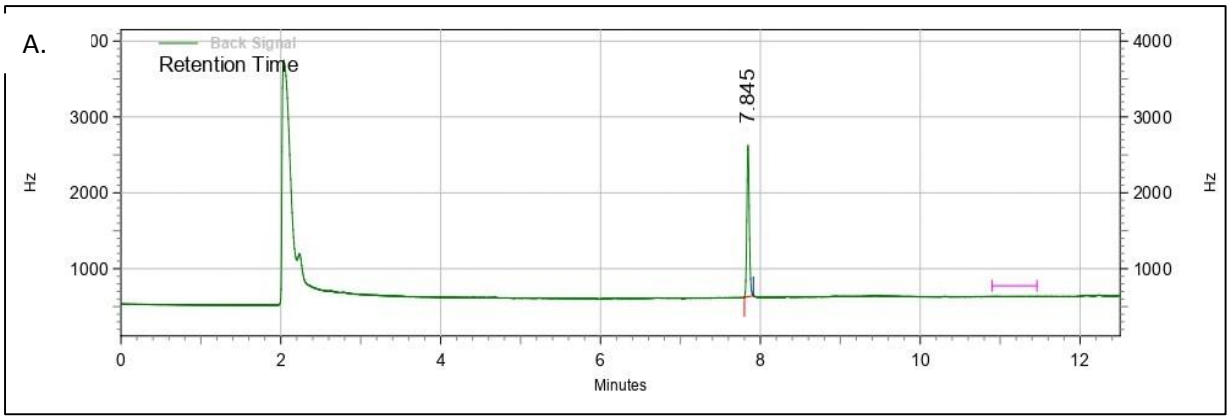

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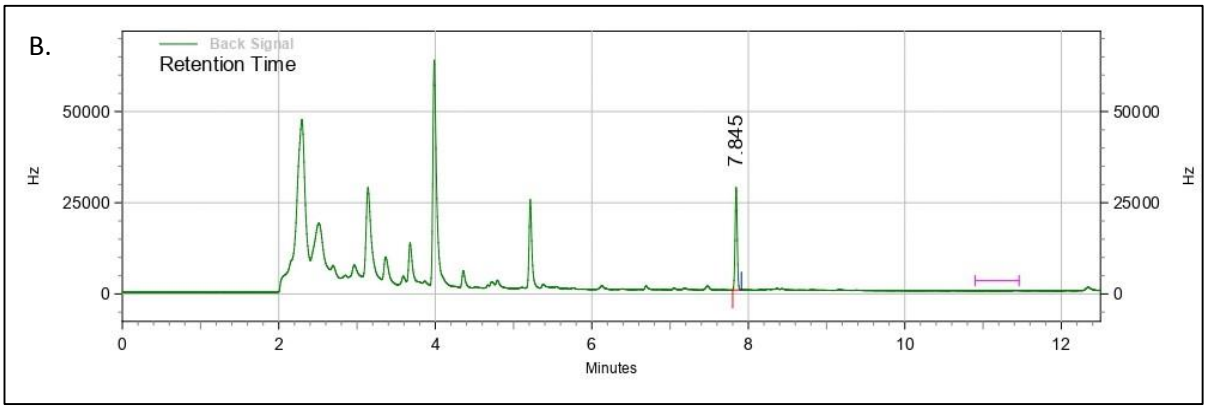

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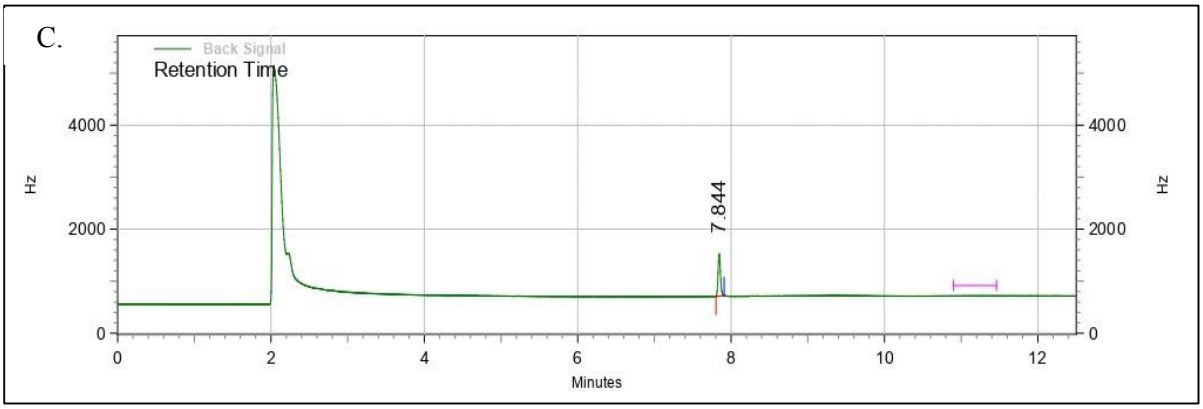

533
534 **Figure 1.** Chromatogram for A) spiromesifen standard B) tomato sample C) cabbage sample.
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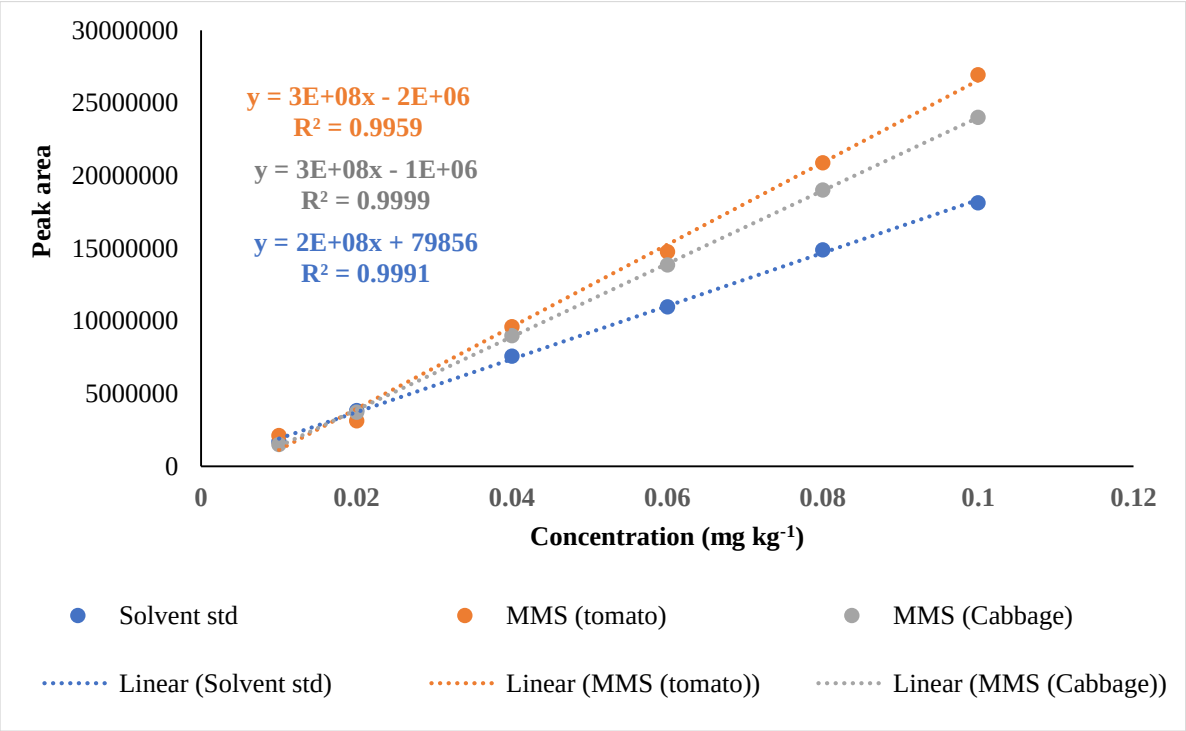


Figure 2. Linearity graph for solvent standard and Matrix Matched Standard (MMS).

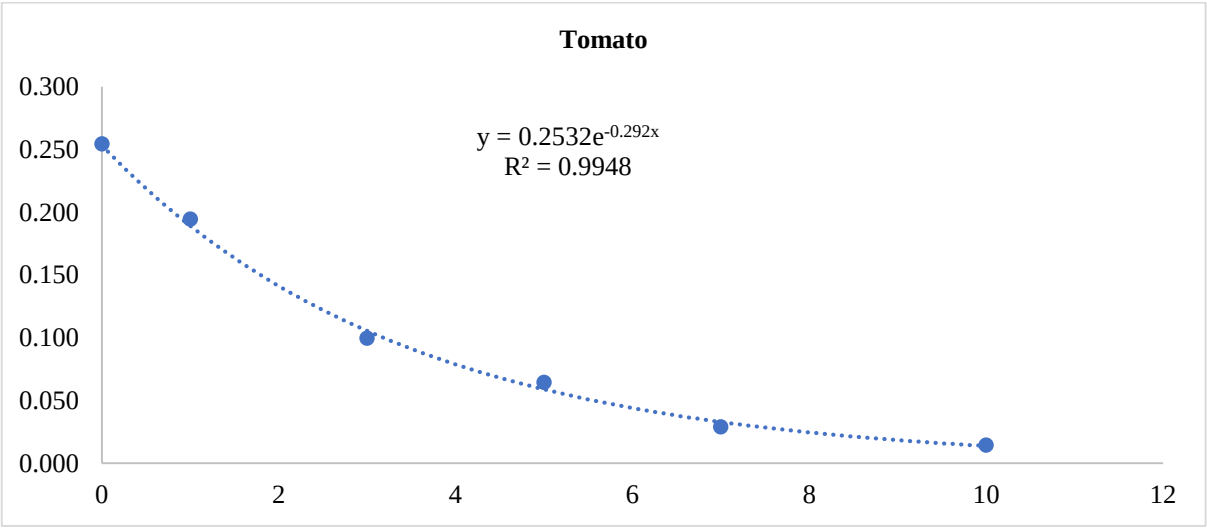
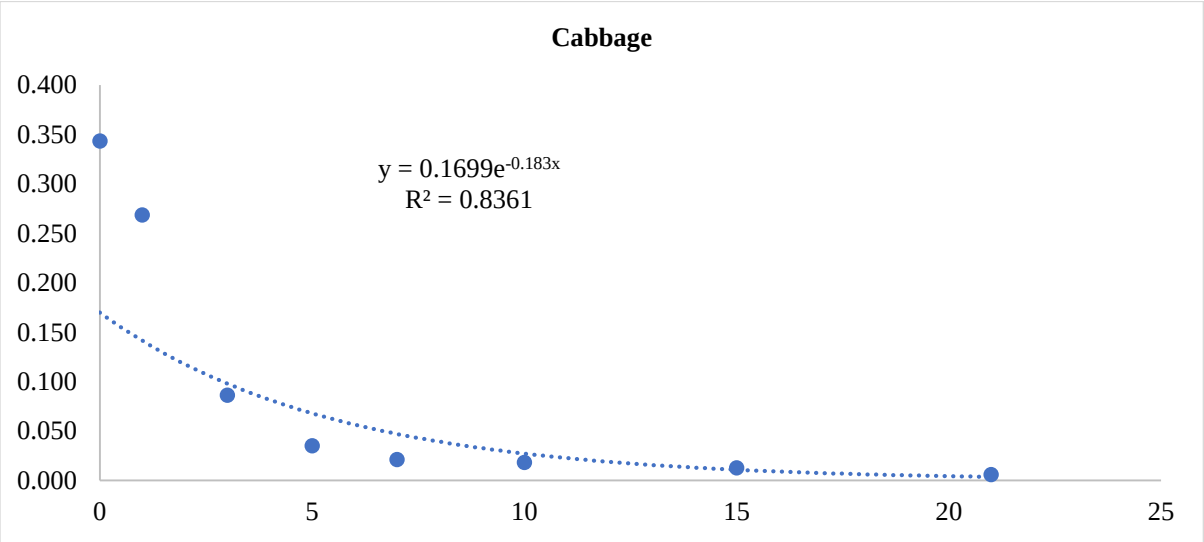


Figure 3. Dissipation curves of studied pesticide in tomato.



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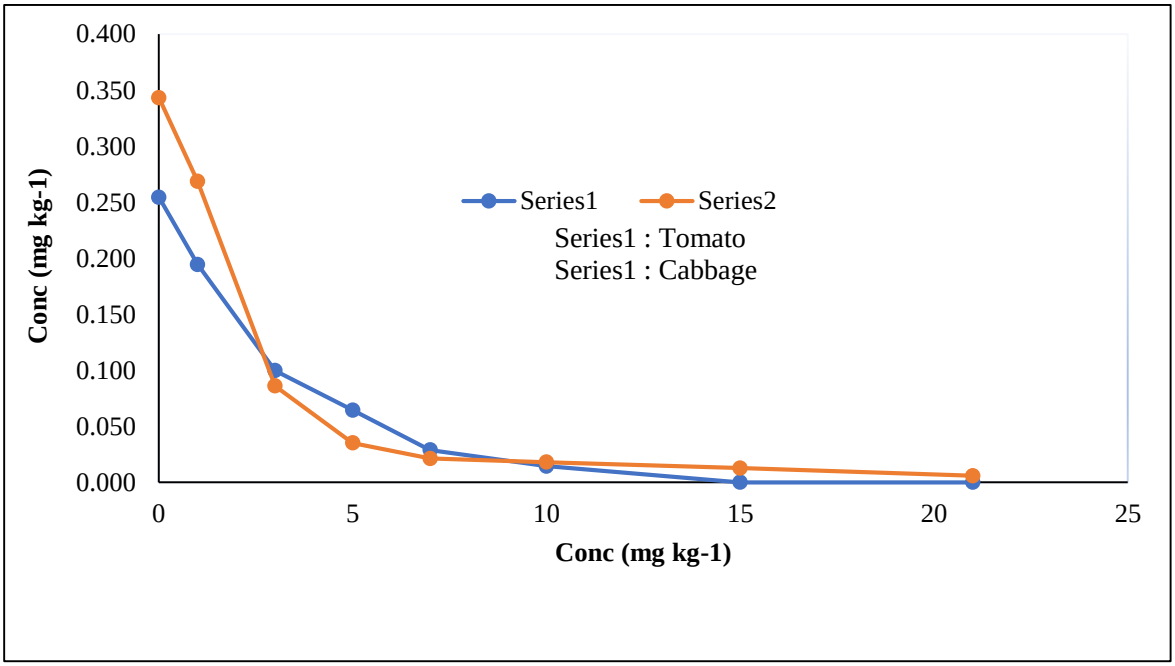

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548 **Figure 5.** Degradation pattern of spiromesifen in tomato and cabbage head.
549
550 **Table 1.** Percentage recovery of spiromesifen in tomato fruits and cabbage head.

Level of fortification (mg kg^{-1})	% 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

551

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

	Conc. (mg 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		

553

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

	Tomato			Cabbage		
Sampling days	Residue (mg kg^{-1})	Dietary exposure (mg person^{-1} d^{-1})		Residue (mg kg^{-1})	Dietary exposure (mg person^{-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

555

556 **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

557