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ORIGINAL ARTICLE

Bio-efficacy and dynamic distribution of pymetrozine and cyantraniliprole against *Aphis gossypii* glover, and their residues in cucumber (*Cucumis sativus* l.) fruits using the QuEChERS method and LC-ESI-MS/MS

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Abstract

Mixed pesticides are promising alternative approaches for insect pest management and could reduce the risk to the environment. Therefore, their efficiency against pests and their residues in the environment should be investigated. In this study, the efficacy of pymetrozine, cyantraniliprole, and their mixture against *Aphis gossypii* Glover and their residues in cucumber (*Cucumis sativus* L.) were studied. The results showed that pymetrozine and cyantraniliprole alone or in combination were more effective than acetamiprid insecticide for reducing *A. gosspyii* populations up to 15 days following application. Additionally, a residual analytical method for insecticide determination in cucumber fruits, leaves, and soil was optimized and validated. The tested insecticides' residue extraction was carried out using the QuEChERS method, and the determination was achieved using liquid chromatography-tandem mass spectrometry (LC-MS/MS). The recovery tests were studied at three spiking levels of low concentration (0.01, 0.05, and 0.1 mg · kg^{-1}) with acceptable recovery between 71 and 101% and good precision and expanded uncertainty up to ± 20%. The half-life times of the tested formulations ranged from 8.19 to 10.6 days, while the pre-harvest intervals (PHI) ranged from 8.8 to 23.8 days.

Keywords: aphids, cyantraniliprole, dissipation, efficacy, pymetrozine

Introduction

Cucumber *(Cucumis sativus* L.) is one of the most important cucurbit crops in the world. It is grown in greenhouses, open fields, and other environmental settings for both domestic and international consumption. Over the past several years, its cultivated area has progressively risen in Egypt, particularly in recently reclaimed regions for export to overseas markets and for local consumption (Hanafy 2004). In summer plantations, aphids, namely *Aphis gossypii* Glover, which attack cotton and watermelon, are among the many pests that attack plants throughout their vegetative development (Mohamed *et al.* 2012).

The cotton aphid, or *A. gossypii* Glover, is a damaging pest affecting a wide range of plants globally (Ebert and Cartwright 1997). It is one of the most polyphagous agricultural pests in the world, as it seriously damages a wide range of crops, including vegetables (Ding *et al.* 2024). Apart from directly sucking juice and causing wilt and death, *A. gossypii* spreads over 50 harmful viruses (Farag *et al.* 2024). In certain instances, plant viruses spread by *A. gossypii* can produce indirect injury that is more severe than direct harm. Losses from *A. gossypii*'s direct and indirect harm to different crops typically exceed 10% (Ebert and Cartwright 1997; Heilsnis *et al.* 2023).

Applying chemical or biopesticides has traditionally been the most efficient method of reducing outbreaks of harmful pests (Moustafa *et al.* 2022) including aphids such as *Aphis craccivora* (El-Hefny *et al.* 2024) and *A. gossypii* (Ding *et al.* 2024; El-Shourbagy *et al.* 2024). Unfortunately, resistance to many insecticides has developed by several insect species due to pesticide misuse (Moustafa *et al.* 2024a). New pesticides or new strategies are required to combat such resistance (Awad *et al.* 2024).

Pyrmetrozine, a pyridine azomethine, is a neuroactive pesticide with exceptional selectivity for plant-sucking insects. Aphid feeding behavior observation shows that pymetrozine treatment causes rapid inhibition of sucking followed by delayed death due to starvation. Specifically, sucking aphids remove their stylet from the plant vascular system immediately, and non-feeding aphids are prevented from probing or inserting their stylet when pymetrozine is consumed (Kristinsson 1994; Harrewijn and Kayser 1997; Wyss and Bolsinger 1997).

Cyantraniliprole is a powerful and selective anthranilic diamide ryanodine receptor activator that selectively activates insect ryanodine receptors, leading to their death through the uncontrolled release of calcium ion reserves in muscle cells (Selby *et al.* 2013). In addition, cyantraniliprole has a wide spectrum of insecticidal action.

Recently, acetamiprid has been a commonly employed chemical for the management of *A. gossypii* (Koo *et al.* 2014; Ullah *et al.* 2019). It binds to the nicotinic acetylcholine receptors (nAChRs) in the nervous system of the insect and causes nerve excitation, paralysis, and death. It has been used all over the world to treat sap-sucking insect infestations. In addition, acetamiprid has superior systemic effects and can easily pass through plant tissues (Tomizawa and Casida 2005).

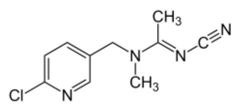
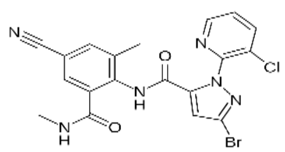
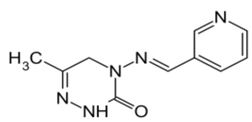
The current study aimed to investigate the efficacy of cyantraniliprole and pymetrozine insecticides, either alone or in combination, as alternatives for traditional insecticides for controlling *A. gossypii* on cucumbers in field settings. In addition, the dissipation of these chemicals in cucumber was investigated using the QuEChERS and LC-ESI-MS/MS techniques.

Materials and Methods

Insecticides and chemicals

Table 1 lists the tested pesticides and their application rates. Pymetrozine and cyantraniliprole reference standards with >99% purity were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). The study used HPLC grade Merck acetonitrile and methanol, Riedel-de Haen ammonia solution (33%), and formic acid (98–100%). De-ionized water of LC-MS quality was created using a millipore device. The extraction reagents (magnesium sulfate, sodium chloride, sodium

Table 1. Tested insecticides and their rates of application

Common name	Trade name	Formulation [a.i. %]	Application rates	Chemical structure
Acetamprid	Mosplian	20% SP	23.8 g · hectare^{-1}	
Cyantraniliprole	Benivia	10% OD	35.7 g · hectare^{-1}	
Pymetrozin	Chess	50% WG	285.6 g · hectare^{-1}	
Pymetrozin 50% + Cyantraniliprole 10%	Plycivia star	60% WG	299.88 g · hectare^{-1}	

a.i. – active ingredient; SP – soluble powder; OD – oil water-dispersal; WG – wettable granule citrate and citric acid disodium salt) were purchased from Agilent Technologies QuEChERS (Kandil *et al.* 2023; El-Hefny *et al.* 2024; Moustafa *et al.* 2024b). In addition, a millipore 0.45 µm syringe filter was employed.

Greenhouse trials

The efficacy of the tested pesticides against *A. gossypii* was investigated over two consecutive summer seasons (2022 and 2023) in the greenhouse at the experimental farm of the Faculty of Agriculture, Cairo University, Giza, Egypt. In the first week of June, four replicates of the *Cucumis sativus* L. variety "Al Nafis" were planted in a randomized full-block configuration. The crops were grown using standard horticultural techniques, and each plot (16 m^2) had four rows that were 5 meters long and 0.8 broad, with plants positioned 0.4 meters apart within the rows. When the aphid infection rate reached around 10 adults/leaf, chemical treatments began (Agriculture Protocol for Evaluating Pesticides Efficiency, 2013). A knapsack sprayer with an adjustable cone nozzle to dispense 200 $l \cdot feddan^{-1}$ of the diluted spray was used for the application. Only water was sprayed on the control plots. Pre-treatment and 3, 5, 7, 10, and 15 days after spraying, the numbers of adult aphid apterus were counted on 25 randomly selected leaves (old, young, and fresh) from each plot. Handerson's formula was used to compute the reduction for each treatment (Handerson and Tilton 1955).

LC-MS/MS analysis

A Phenomenex Kinetex C18 column (4.6 × 150 mm, 3.5 µm particle size) was used for separation, coupled with a Vanquish HPLC system linked to a TSQ Altis triple quadrupole mass spectrometer. Using an electrospray ionization (ESI) interface, LC-MS/MS was developed. Starting with 100% bottle A and a flow rate of 0.4 $ml \cdot min^{-1}$, liquid-solid separation was carried out. Then, 95% bottle B was used, with a flow rate of 0.5 $ml \cdot min^{-1}$ until minute 6, after which 100% bottle A was used again, with a flow rate of 0.4 $ml \cdot min^{-1}$ from minute 6.2 to minute 8. Bottle B contained methanol while bottle A contained ammonium formate solution (pH 4) in water-methanol (9:1). The quantification by confirmation ion method utilizing positive ionization was supported by the SRM (Selected Reaction Monitoring) separation and detection system. Nitrogen gas was utilized for nebulizing while argon gas was used for fragmentation.

Method validation

Method validation is a crucial first step in guaranteeing the precision and dependability of analytical results. Therefore, the parameters and acceptance criteria for the method used in this study were chosen following the Magnusson and Örnemark (2014) Guidance Document on Analytical Quality Control and Method Validation Procedures for Pesticide Residues Analysis in Food and Feed.

Pesticide standards preparation

Pymetrozine and cyantraniliprole stock solutions (1000 $\mu g \cdot ml^{-1}$) were made in Toluene. The stock solution was diluted in acetonitrile to a concentration of 10 $\mu g \cdot ml^{-1}$ to create an intermediate solution. The intermediate solution was serially diluted to create calibration mixes with acetonitrile concentrations of 0.005, 0.01, 0.05, 0.1, and 0.5 $\mu g \cdot ml^{-1}$.

LC mobile phase

900 mL of deionized water was mixed with 1.73 ml of formic acid. After that, an ammonia solution was used to bring the mixture's pH down to 4 and, methanol was used to raise the volume to 1 liter.

Cucumber sample extraction

A 50 ml polyethylene (PFTE) tube was filled with 10 g of the leaf or fruit sample. Ten milliliters of acetonitrile were then added. A Geno shaker was used to homogenize the mixture for 5 minutes at 700 rpm. After that, the tube was filled with a buffer-salt combination, and homogenization was carried out once again. After centrifuging the mixture for 5 minutes at 4000 rpm, an aliquot from the top layer was filtered through a 0.45 µm syringe filter, and 2 µl of the mixture was then injected into the LC system. The Sample Prep 2010–230 Geno/Grinder horizontal shaker was utilized with a 15- and 50-ml tube holder.

Soil sample extraction

After adding a 10 g sample and 10 ml of deionized water to a 50 ml polyethylene (PFTE) tube, the mixture was sonicated for 10 minutes. After adding 10 milliliters of acetonitrile, a Geno shaker was used to homogenize the mixture at 700 rpm for 5 minutes. After adding the buffer-salt combination a second time, centrifugation was done for 5 minutes at 4000 rpm. Before adding 2 µl to the LC system, an aliquot from the top layer was filtered using a 0.45 µm syringe filter. A horizontal shaker (Sample Prep 2010-230 Geno/ Grinder) with a 15 and 50 ml tube holder, manufactured by SPEX Sample pre (UK) was used.

Data analysis

Data entry and coding were performed using SPSS V.22. Data were examined to ensure that the assumptions for parametric tests were met. Continuous variables were assessed for normality using the Shapiro-Wilk and Kolmogorov-Smirnov tests. To normalize data on probabilities and percentiles, the arcsine square root transformation was applied. The mean and standard deviation of the data were calculated. For each experimental group (control, acetamiprid, pymetrozine, cyantraniliprole, and cyantraniliprole+pymetrozine), an ANOVA analysis was performed to calculate the percentage reduction in *A. gossypii* after the application of insecticides. Analysis was conducted using a minimum of four replicates per group, with Tukey's pairwise comparison employed for post-hoc analysis. P-values were considered significant if less than 0.05. MiniTab V. 14 and R studio V. 2022.02.4 were used for data assessment and visualization.

A first-order kinetic model, $C_t = C0e^{-kt}$, was used to simulate the degradation of pymetrozine and cyantraniliprole. In this model, C_t denotes the concentration at time t, and C0 is the initial concentration. Insecticide dissipation over time was assessed using the dissipation rate constant k.

Results

Efficacy of pymetrozine and cyantraniliprole in *Aphis gossypii*

The data in Table 2 and Fig. 1 demonstrated how the tested pesticides affected the quantity of *A. gossypii* infesting cucumber plants. Aphid counts varied from 26.75 to 33.5 individuals/100 leaves before a single spraying day. However, in season 2022, there was no discernible difference in the populations of *A. gossypii* between treatments (Table 2). The plot treated with acetamiprid had the highest number of aphids/100 leaves (15) after 1 day of spraying. In contrast, the plot treated with pymetrozine+ cyantraniliprole had the lowest number (1), followed by cyantraniliprole (3.33) and pymetrozine (7.5). Additionally, the number of aphids/100 leaves for pymetrozine + cyantraniliprole, cyantraniliprole, pymetrozine, and acetamiprid, respectively, were 0, 2.5, 3.75, and 11.25 aphids after 3 days of application. Except for acetamiprid treatment, all treatments showed a decline in the aphid population during the time intervals following spraying (Fig. 1). Table 2 displays the trend of the results obtained in the 2023 season.

Furthermore, Table 3 and Figure 2 display the percentage reduction of *A. gossypii* after pymetrozine and cyantraniliprole application, either individually, or in combination. The results demonstrated that the most effective insecticides against aphids were pymetrozine + cyantraniliprole, with the largest initial mortality occurring after 24 h of treatment (99.35) and a continual decrease in the aphid population up to 15 days following application (Table 3 and Fig. 2).

During season 2022, after 3 days of treatment, the percentage reduction in *A. gossypii* was 100%, demonstrating the extraordinary residual activity of pymetrozine + cyantraniliprole. Furthermore, cyantraniliprole's findings were similar to those of pymetrozine + cyantraniliprole, with a percentage reduction of 82.87 and 92.55, respectively. Pymetrozine alone and combined with cyantraniliprole resulted in 78.75 and 91.58% initial mortality, respectively. On the other hand, pymetrozine alone resulted in 99.33, 100, 100, and 100% reduction after 5, 7, 10, and 15 days,

Table 2. *Aphis gosspyii* infestation (no. of aphids · 100 plants^{-1}) after field application of pymetrozine and cyantraniliprole alone or combined during the 2022 and 2023 seasons

Season	Treatment	Before treatment	1 day	3 days	5 days	7 days	10 days	15 days
Season 2022	control	26.75 ± 3.96 a	28 ± 3.46 a	32.5 ± 3.64 a	39.5 ± 3.64 a	45 ± 9.35 a	55 ± 6.12 a	67.5 ± 4.27 a
	acetamprid	30.5 ± 4.15 a	15 ± 3.08 c	11.25 ± 3.41 b	8.25 ± 1.08 b	11.25 ± 3.03 b	17.5 ± 4.15 b	25 ± 3.08 b
	pymetrozine	37.5 ± 8.29 a	7.5 ± 1.8 c	3.75 ± 0.82 c	1 ± 0 b	0.00	0.00	0.00
	cyantraniliprole	33.5 ± 5.85 a	3.33 ± 0.94 c	2.5 ± 0.5 c	0.00	0.00	0.00	0.00
	cyantraniliprole+ pymetrozine	28.25 ± 5.3 a	1 ± 0 c	–	0.00	0.00	0.00	0.00
Season 2023	Control	29.5 ± 2.95 a	31.25 ± 1.08 a	34.5 ± 3.04 a	41.25 ± 7.66 a	50.5 ± 7.79 a	62 ± 9.51 a	76.25 ± 3.56 a
	acetamprid	35 ± 7.03 a	12.5 ± 3.5 b	10 ± 2.12 b	7.25 ± 1.92 b	9.5 ± 0.5 b	16.25 ± 4.02 b	25 ± 5.78 b
	pymetrozine	24.5 ± 3.84 a	9.5 ± 1.5 bc	5 ± 2.23 bc	2.5 ± 0.5 b	1 ± 0 b	0.00	0.00
	cyantraniliprole	28.75 ± 4.76 a	5 ± 1.22 cd	2.66 ± 0.47 c	1.5 ± 0.5 b	0.00	0.00	0.00
	cyantraniliprole+ pymetrozine	36.25 ± 4.6 a	1 ± 0 d	0.00	0.00	0.00	0.00	0.00

Means in a column that do not share a letter are significantly different

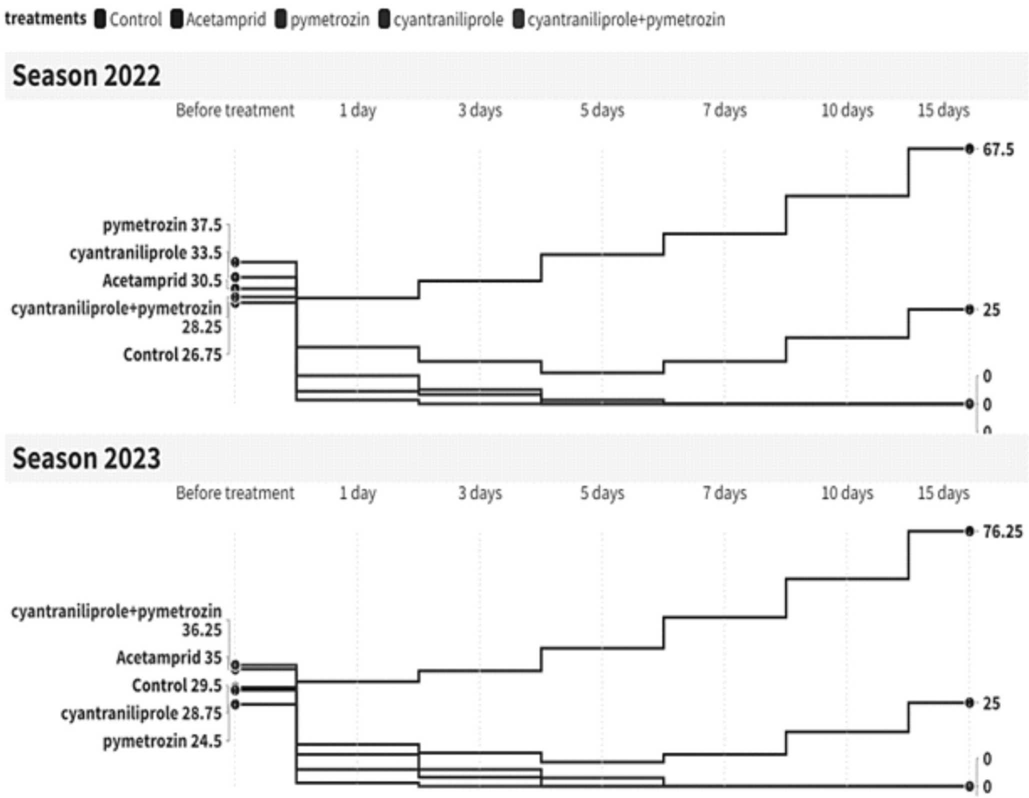


Fig. 1. Step slope chart representing the mean (±SD) number of infestation (no. of aphids · 100 leaves^{-1}) in *Aphis gossypii* after field application of pymetrozine and cyantraniliprole alone or combined during the 2022 and 2023 seasons

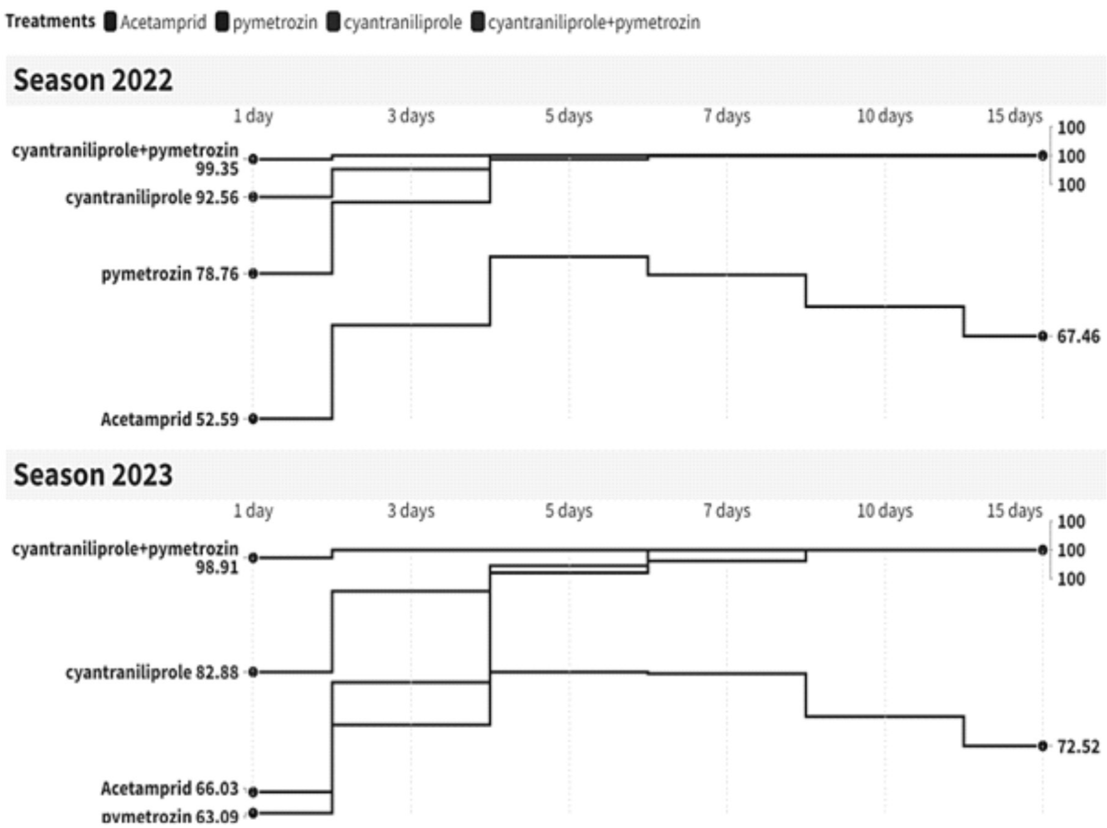


Fig. 2. Step slope chart representing the mean (±SD) percentage reductions in *Aphis gossypii* after field application of pymetrozine and cyantraniliprole alone or combined during the 2022 and 2023 seasons

Table 3. Percentage reduction of *Aphis gosspyii* after field application of pymetrozine and cyantraniliprole alone or combined during the 2022 and 2023 seasons

Season	Treatment	1 day	3 days	5 days	7 days	10 days	15 days
Season 2022	acetamprid	52.59 ± 9.84 c	69.44 ± 10.62 b	81.76 ± 2.78 b	78.51 ± 3.11 b	72.78 ± 4.32 b	67.45 ± 6.39 b
	pymetrozine	78.75 ± 10.65 b	91.58 ± 2.16 a	99.33 ± 0.67 a	100 ± 0 a	100 ± 0 a	100 ± 0 a
	cyantraniliprole	92.55 ± 5.04 ab	97.56 ± 2.44 a	100 ± 0 a	100 ± 0 a	100 ± 0 a	100 ± 0 a
	cyantraniliprole + pymetrozine	99.35 ± 1.12 a	100 ± 0 a	100 ± 0 a	100 ± 0 a	100 ± 0 a	100 ± 0 a
Season 2023	acetamprid	66.03 ± 7.24 c	75.48 ± 2.87 b	82.86 ± 9.04 b	82.64 ± 6.34 b	76.63 ± 8.37 b	72.51 ± 2.96 b
	pymetrozine	63.09 ± 5.72 c	81.43 ± 8.44 b	96.8 ± 3.53 a	98.47 ± 1.62 a	100 ± 0 a	100 ± 0 a
	cyantraniliprole	82.87 ± 5.71 b	94.21 ± 4.14 a	97.76 ± 2.32 a	100 ± 0 a	100 ± 0 a	100 ± 0 a
	cyantraniliprole + pymetrozine	98.9 ± 1.1 a	100 ± 0 a	100 ± 0 a	100 ± 0 a	100 ± 0 a	100 ± 0 a

Means in a column that do not share a same letter are significantly different

respectively. The residual impact of pymetrozine and cyantraniliprole was demonstrated by a significant reduction in the aphid population 15 days after treatment. In contrast, acetamiprid had a moderate impact on the aphid population for the same post-treatment period. The initial mortality rate was 52.59% followed by 69.44, 81.76, 78.51, 72.78, and 67.45% after 3, 5, 7, 10, and 15 days, respectively. As shown in Table 3 and Figure 2, the impact of the tested insecticides during season 2023 were comparable to those of season 2022.

Optimization and validation of the residue analysis

LC-ESI-MS/MS

In LC-ESI-MS/MS analysis, the sensitivity of pymetrozine and cyantraniliprole increased when an ESI source in positive mode coupled with direct continuous infusion was used. The best possible quantitation and confirmation were obtained by optimizing the SRM parameters. Therefore, two multiple reaction monitoring (MRM) transitions were chosen. Before examining pesticide recovery, the HPLC separation process was preconditioned, and the acquisition technique was adjusted. The injection volume was adjusted to 2 μl to lessen the matrix impact.

Matrix effect

All findings were calculated using the matrix standard to guarantee that the presence of sample components would not affect the analytical signal's correctness in the finished extract.

Method linearity

For quantitative analysis, a six-point calibration curve (ranging from 0.001 to 0.1 μg · ml^{-1}) was used to assess the linearity of the technique. Pymetrozine and cyantraniliprole had correlation values of 0.9982 and 0.9997, respectively.

Limit of quantitation

Limit of quantitation (LOQ) is the lowest concentration of the analyte in the test sample that can be accurately identified under certain test circumstances with acceptable accuracy (repeatability) and recovery. Multiple spiking samples were evaluated at the anticipated lowest quantitation level of 0.01 mg · kg^{-1} to determine the lowest practicable limit of quantification. Table 4

Table 4. Evaluation of recovery and determination method for pymetrozine and cyantraniliprole

Insecticide	Mean% ± RSD% (0.01, 0.05 and 0.1) [mg · kg^{-1}]			Q_{type}	RSD_{pooled}
Pymetrozine	79 ± 0.03	101 ± 7.8	87 ± 1.3	89.0%	4.00%
Cyantraniliprole	71 ± 16	76 ± 7.3	84 ± 3.4	77.0%	9.00%
Selected reaction monitoring for pymetrozine					
Mass resolution	RT [min]	CID Gaz	precursor	fragments	CE
Q1 (0.7 Dalton)	1.11	1.5 mTorr	218.1	77.9	38.4
Q3 (0.7 Dalton)				104.9	20.24
Selected reaction monitoring for cyantraniliprole					
Mass resolution	RT [min]	CID Gaz	precursor	fragments	CE
Q1 (0.7 Dalton)	6.44	1.5 mTorr	475.1	286	18
Q3 (0.7 Dalton)				444	27

RT – retention time; CE – collision energy voltage; CID – collision-induced dissociation displays the recovery and relative standard deviation (RSD%) at the LOQ.

Recovery test and uncertainty evaluation

Six duplicates of blank cucumber samples were spiked at three doses (0.01, 0.05, and 0.1 mg · kg^{-1}) and subjected to LC-MS/MS analysis to evaluate the method's performance. As shown in Table 6 a reasonable recovery with a relative standard deviation (RSD) of less than 16% and a range of 71% to 101% were obtained.

Analysis of many spiking samples at various levels allowed for the determination of the precision investigation, which is represented by the relative standard uncertainty $u_r(y)$. It was discovered that the $u_r(y)$ values were 0.9%, 0.5%, and 1%. The tabulated t-value (t_tab) for 5 degrees of freedom was 2.45, but the calculated t-value (t_calc) was 6.63. The lowest mean recovery of 71 ±16% was used to assess the bias in the analytical technique.

An error of 0.7% resulted from the uncertainties related to the fabrication of the reference standard, which included elements like the purity of the analyte standard, balance, pipettes, micropipettes, solvents, and volumetric flasks.

The square root of the sum of squares of the several uncertainty components was computed to get the combined uncertainty (U_C). At a 95% confidence level, the final enlarged uncertainty was ±20%. This was derived by multiplying the combined uncertainty by a coverage factor (k = 2).

Dissipation study

Figures 1 and 2 show the residue amounts of cyantraniliprole and pymetrozine in cucumber fruits, cucumber leaves, and soil. The data show a typical dissipation pattern in the fruits for both pesticides. The half-lives of pymetrozine alone were 10.6, 4, and 9.7 days for fruits, leaves, and soil, respectively, compared to 8.88, 8.19, and 8.28 days for the combination. Similarly, the half-lives of cyantraniliprole alone were 8.8, 23.8, and 16.3 days for fruits, leaves, and soil, respectively, compared to 8.81, 19.45, and 11.51 for the combination.

Pre-harvest intervals (PHI) for the insecticides were computed using their dissipation rates. The PHI for cyantraniliprole was calculated using the maximum residue limit (MRL) of the Codex Alimentarius Commission (0.05 mg · kg^{-1}) and the EU (0.5 mg · kg^{-1}). The PHIs for cyantraniliprole alone were 16.8 and 2.5 days, as calculated using codex and EU MRL, respectively, compared to 17.6 and 3 days for the combination. On the other hand, the PHI was 52.6 and 37.8 for pymetrozine alone and the combination, respectively.

Discussion

Chemical insecticides are still widely used as an essential tool for pest management. Nevertheless, several factors, including the pesticides' chemical and physical

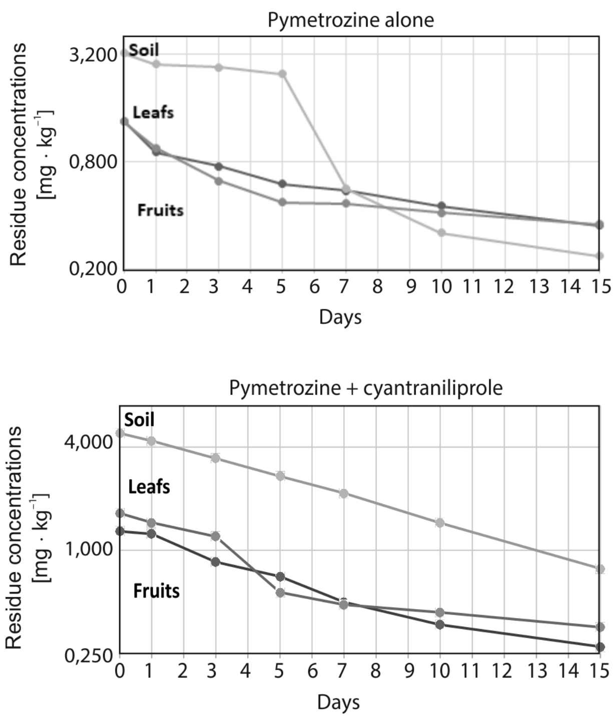


Fig. 3. Dissipation rates for pymetrozine

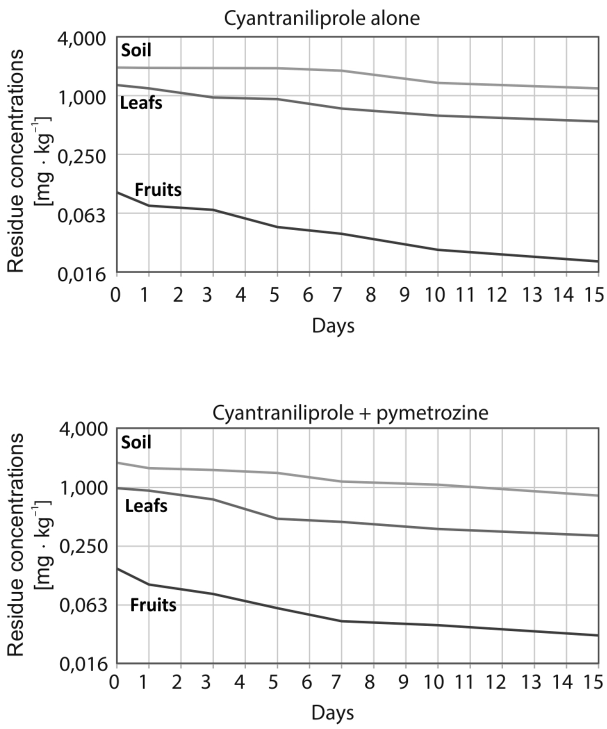


Fig. 4. Dissipation rates for cyantraniliprole

qualities, the frequency of administration, and the growth dilution factor, affect their efficacy and destiny (Malhat and Abdallah 2019). There has also been a development of resistance to *A. gossypii* due to years of heavy pesticide usage (Ullah *et al*. 2019). Furthermore, resistance to many insecticides, including acetamiprid, has been observed in the field population of *A. gossypii* (Wang *et al.* 2007; Koo *et al.* 2014). Thus, to investigate alternatives to conventional pesticides, novel formulation methods or pesticide-active chemicals may be employed (Zhang and Kothalawala 2023). In light of this, the current study aimed to evaluate the effectiveness of pymertozine and cyantraniliprole against *A. gossypii* and to determine their residues.

Based on these findings regarding the efficacy of the tested insecticides at various intervals, it was evident that pymetrozine, cyantraniliprole, and pymetrozine + cyantraniliprole exhibited long effects and reduced the aphid population until the 15th day following application. After 10 days of application, acetamiprid was the least effective against the *A. gossypii* population. On the other hand, the combined application of pymetrozine and cyantraniliprole significantly reduced the *A. gossypii* population, demonstrating a synergistic effect (Tables 2 and 3). Pymetrozine generally modifies the neuronal regulation of the pump in Hemiptera (Talebi-Jahromi 2007) while cyantraniliprole depends on the insects' ryanodine receptors, which are essential for muscular contraction, being activated (Sattelle *et al.* 2008). Cyantraniliprole activates ryanodine receptors (RyRs), which play a critical role in muscle function. It binds to the RyRs, causing uncontrolled release and depletion of calcium from muscle cells, thus preventing further muscle contraction and ultimately leading to death (Sattelle *et al.* 2008). The combination's elevated mortality rate may be primarily attributed to the different modes of action of the two chemicals. Synergism can be attained by activating one of the mixture's pesticides or blocking the detoxifying enzyme that works well (Talebi-Jahromi 2007).

When several pesticide classes with distinct modes of action are combined, the amount of insecticide that enters the environment is reduced, control is increased, costs are decreased, and resistant insect populations are prevented (Somar *et al.* 2019). For the early phases of *A. gossypii* control, imidacloprid and pymetrozine together are advised (Somar *et al.* 2019). When the combined use of imidacloprid and pymetrozine was assessed on *A. gossypii*, the findings indicated that the two insecticides work compatibly. Pyrethrin is an effective pesticide for insects that feed through piercing and sucking. Its use is crucial in integrated pest management strategies. (Talebi-Jahromi 2007).

Furthermore, Ferguson *et al.* (1999) observed that within 7 days of administration, pymetrozine demonstrated 90% control of cotton aphids. Thus, according to Kim *et al.* (2024), cyantraniliprole and pymetrozine may help control the density of *A. gossypii*. Based on the results of this study, the practical use of these insecticides against *A. gossypii* in greenhouses is suggested.

The analytes, such as their log octanol-water values (−0.18 for pymetrozine and 4.63 for cyantraniliprole according to OECD 107), indicated that pymetrozine was polar and cyantraniliprole was moderately polar. Furthermore, the dissociation constants (pKa = 4.4 for pymetrozine and 10.03 for cyantraniliprole at 20°C) played an important role in ionization. A mobile phase with a pH lower than the pKa of the analyte was favored to enhance sensitivity (Krishnan 2009). In addition, there was less migration from fruits to other sections of the plant when cyantraniliprole showed more active translocation into the xylem versus phloem tissues. This shows that foliar-applied insecticides tend to concentrate in fruit tissue with limited mobility to other parts of the plant. Moreover, cyantraniliprole does not move from the sprayed leaves to new leaves at any stage of treatment (Pes *et al.* 2020).

The half-lives of cyantraniliprole and pymetrozine are mostly affected by environmental factors and crop type. A study on the urea herbicide linuron – a chemically-related compound – reported a half-life range of 40 to 70 days (Hong *et al.* 2011) while the present results reported a half-life time of 10.6 and 8.9 in cucumber fruits, with PHI of 52.6 and 57.8 for both pymetrozine alone and the combination, respectively, as calculated using EU MRL.

It was reported that cyantraniliprole had a half-life of 2.6 days on spinach (Abd-Alrahman and Kotb 2020). However, the present results revealed that cyantraniliprole, alone or combined, had a half-life of 8.8 days in cucumber fruits. For single and combined cyantraniliprole, PHIs of 16.8 and 17.6 days were obtained using Codex standards, compared to 2.5 and 3 days using EU MRL. These findings are consistent with previous reports on grapes (Hong *et al.* 2011) (PHI = 39 days) and beetroot (PHI = 37.98 days) (Registration data sheet, 2000).

In conclusion, pymetrozine and cyantraniliprole insecticides can be effectively and safely used for managing aphid populations on cucumbers.

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