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Residue determination and decline pattern of abamectin and fenpyroximate in okra fruits: a prelude to risk assessment

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This study developed and validated an LC-MS/MS analytical method for determining abamectin and fenpyroximate residues in okra fruits. The method optimization focused on chromatographic separation and ionization conditions, adding formic acid and ammonium formate to enhance ionization efficiency and signal sensitivity. Validation was performed according to SANTE guidelines, demonstrating good selectivity, linearity ($R^2 > 0.998$), precision, recovery, and minimal matrix effects (14.6% for abamectin and 5.2% for fenpyroximate). The limit of detection (LOD) was set at 0.0006 mg kg^{-1} for abamectin and 0.0002 mg kg^{-1} for fenpyroximate, while the limit of quantification (LOQ) was 0.002 mg kg^{-1} and 0.001 mg kg^{-1}, respectively. Precision was within acceptable limits, with intra-day RSD of 11.4% for abamectin and 7.6% for fenpyroximate. Recovery ranged from 84.2% to 98.6%, meeting the acceptable 70–120% range. Persistence studies indicated that abamectin and fenpyroximate residues dissipated over time, with half-lives of 2.3 and 2.45 days, respectively. The pre-harvest interval (PHI) required for residues to fall below the maximum residue limit (MRL) was estimated to be 2.6 days for abamectin and 6.9 days for fenpyroximate. The risk quotient was assessed based on the Egyptian adult consumers' consumption of okra, ensuring a negligible risk.

1. Introduction

Okra, also known as lady's finger, is a nutritious vegetable with soluble and insoluble dietary fiber, making it an effective natural laxative.[1,2] It is a good source of minerals, such as calcium, magnesium, and iron, and vitamins, including B1, B2, B6, C, and folate, which help manage weight, reduce cancer risk, boost the immune system, lower cholesterol, prevent diabetes, and alleviate asthma symptoms.[3,4] Okra can be eaten raw and is particularly effective for digestive issues, coughs, and excessive sweating.[1] Today, okra is an essential crop in Egypt, thriving in warm summer temperatures. The growing global demand, especially in Europe, drives its exports. As both domestic and international demand rise, Egypt's competitive-quality okra presents promising export opportunities for the future. In modern agriculture, chemical insecticides play a crucial role in cost-effective pest control for essential field crops, revolutionizing the management of insect pests and diseases.[5] One such crop, okra, has a relatively short shelf life and is an annual plant, meaning it completes its lifecycle within a single growing season. Since okra does not regrow after its

lifecycle ends, replanting is necessary each season, especially when harvested fresh.[6]

Fenpyroximate (α-(4-phenoxyphenyl)-α,α-dimethyl-1*H*-pyrazole-3-propanenitrile) is a pyrazole acaricide and insecticide that belongs to the chemical class of sulfonanilides.[7] It possesses acaricidal and insecticidal properties due to inhibiting quinol oxidation in the mitochondria at complex III in its target organisms.[8] Fenpyroximate is used in horticultural crops, indoors, and in ornamental plants. In Egypt, it is registered for use on various crops, including cotton, brassica leafy greens, grapes, head and stem brassica, stone fruit, and pome fruit, specifically for controlling spider mites.[9] Additionally, it is applied to various fruiting vegetables, except for cucurbits, as a selective acaricide against Tetranychidae and Brevipalpidae. The use of pesticides remains the primary means of controlling most insect pests that attack okra crops. Among the various pests that attack okra, fenpyroximate is used in integrated pest management, mainly against fruit-sucking bugs. Concerns regarding fenpyroximate residues and their effects on environmental and food safety have garnered significant attention.

Abamectin is a natural pesticide derived from a product called avermectin.[10] It is highly effective and has low toxicity for mammals and other non-target organisms, making it a promising option for biological pest control. Since its discovery in the 1980s, the use of abamectin has rapidly increased. Avermectins have two main variations—B1a and B1b—that differ in their

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methylation. Abamectin, a chemical derived from the same organism that produces avermectin, has similar effects. It effectively targets a wide range of insects and mites, penetrates leaves easily, and quickly impacts pests. Abamectin is commonly used as an insecticide, acaricide, and nematicide, particularly against caterpillar pests.[10] Regarding safety and environmental impact, abamectin is compelling while protecting the environment.

The objective of this study is to establish and validate an analytical method using LC-MS/MS for detecting abamectin and fenpyroximate residues in okra fruits, optimize chromatographic and ionization conditions to enhance detection sensitivity, assess the persistence and dissipation patterns of abamectin and fenpyroximate in okra fruits, establish preharvest intervals (PHI), and finally conduct a risk assessment to evaluate consumer safety and support safe agricultural practices. The results of this study can benefit farmers, buyers, guideline implementers, lawmakers, and the general public. Furthermore, this study addresses several research gaps in the literature.

2. Materials and methods

2.1. Chemical reagents and standards

The reference standards used in this study included fenpyroximate (99.5% purity) and abamectin (97.2% purity), both of which were obtained from Chem Service Inc. (West Chester, PA, USA). The commercial pesticide formulations Fenpyroximate (Volitan Extra®, 5% suspension concentrate (SC), Fine Seeds International, Egypt) and abamectin (Opaltin®, 5% emulsifiable concentrate (EC), Agrien Serve for Services and Consultants, Egypt) were obtained from a local supplier. HPLC-grade acetonitrile, methanol, and glacial acetic acid were acquired from Fisher Scientific (Loughborough, UK). Additionally, LC-MS grade formic acid and ammonium formate, as well as analytical-grade anhydrous sodium acetate (CH_3COONa) and magnesium sulfate ($MgSO_4$), were sourced from Chem-Lab NV (Zedelgem, Belgium). The primary secondary amine (PSA) was obtained from Macherey-Nagel (Düren, Germany). Multi-walled carbon nanotubes (MWCNT) were acquired from Shilpa Enterprises (Shilpent®, Maharashtra, India). A ceramic homogenizer was purchased from Chrom Tech, Inc. (Copure®, Apple Valley, MN, USA). Ultrapure water was produced using an Evoqua Ultra Clear system (Evoqua Water Technologies LLC, Günzburg, Germany).

2.2. Pesticide standard preparation

Primary stock solutions of fenpyroximate and abamectin were prepared at concentrations of 1000 μg mL^{-1} by dissolving 0.0503 g of fenpyroximate and 0.0514 g of abamectin, respectively, in 50 mL of HPLC-grade acetonitrile. An intermediate 50 μg mL^{-1} solution was prepared from the primary stock using HPLC-grade acetonitrile. A working standard mixture of fenpyroximate and abamectin at 10 μg mL^{-1} was prepared by diluting the intermediate stock solution with acetonitrile. The standard solutions were kept refrigerated at −20 °C.

2.3. Preparation of calibration standards

The blank okra samples were processed using the proposed extraction and purification method to create matrix blank extracts. These extracts and acetonitrile were then used to serially dilute a standard working solution mixture (10 μg mL^{-1}) of fenpyroximate and abamectin. Serial dilutions were prepared at concentrations of 0.5, 0.25, 0.1, 0.05, 0.025, 0.01, and 0.005 μg mL^{-1} to create both in-solvent and matrix-matched calibration curves.

2.4. LC-MS/MS

A Dionex Ultimate 3000 RS Ultra-High-Performance Liquid Chromatography (UHPLC) separation module was coupled with a TSQ (Triple Stage Quadrupole) Altis tandem mass spectrometer (Thermo Fisher Scientific, Austin, TX, USA) for chromatographic analysis. The electrospray ionization (ESI) interface operated in selective reaction monitoring (SRM) and positive ionization modes. The interface conditions were set: capillary voltage at 3.8 kV, source temperature at 275 °C, and desolvation temperature at 325 °C. Sheath and auxiliary gas flows were adjusted to 40 and 10 Arb, respectively.

An Accucore Reversed-Phase Mass Spectrometry (RP-MS) C18 column (2.6 μm, 2.1 × 100 mm) maintained at 40 °C was used for analyte separation. The mobile phase consisted of two solutions: mobile phase A (methanol and water, 95 : 5 v/v, with 0.1% formic acid and 10 mM ammonium formate) and mobile phase B (water and methanol, 95 : 5 v/v, also containing 0.1% formic acid and 10 mM ammonium formate). The flow rate and injection volume were set at 0.3 mL min^{-1} and 5 μL, respectively. Gradient elution was programmed as follows: 0–1 min at 2% B, 1–5 min at 35% A, 5–10 min at 98% B, 10–14 min at 98% B, and 14.1–20 min returning to 2% B. Initial tuning was performed using a Harvard infusion pump (Harvard Apparatus, South Natick, MA, USA), with a total run time of 20 minutes. Quantification and confirmation were performed using multiple reaction monitoring modes, with data acquisition and system control handled by Trace Finder software v4.1 (Thermo Fisher Scientific Inc., Waltham, MA, USA).

2.5. Field experiment

The field experiments were conducted in the Belbies region of El-Sharkia Governorate, Egypt, during the spring season in April 2024. The experiment utilized a completely randomized block design, comprising three replicates on 100 m^2 plots (10 m × 10 m) each. Untreated control plots were positioned at an adequate distance from those treated with fenpyroximate and abamectin to minimize pesticide drift.

2.6. Dissipation experiment

For the dissipation study, abamectin (5% EC) and fenpyroximate (5% SC) were applied in okra following the guideline of the Ministry of Agriculture in Egypt,[11] at the recommended doses of 10 g a.i. ha^{-1} and 25 g a.i. ha^{-1}, respectively. The applications were made using a manual backpack sprayer with a 20 liter capacity, with water used for formulation dilution at

a rate of 1000 L ha^{-1}. Representative random samples (1 kg) were collected from each treated plot at 2 hours (initial residue) and 1, 3, 7, 10, 14, and 21 days following application. All samples were promptly transported to the laboratory, processed immediately, and stored at −20 °C until analysis.

2.7. Terminal residue experiment

To evaluate the terminal residues of the tested pesticides, abamectin and fenpyroximate were uniformly applied to okra two or three times. The recommended rates were 25 g a.i. ha^{-1} for fenpyroximate and 10 g a.i. ha^{-1} for abamectin, with treatments also applied at double the recommended doses of 50 g a.i. ha^{-1} and 20 g a.i. ha^{-1}, respectively. These treatments were executed at 14 day intervals during the 2024 farming season. Samples were analyzed 4, 7, and 14 days after the final treatment. The okra samples were packed in labeled, vented polyethylene bags, stored at low temperatures, transported to the laboratory, and stored at −20 °C until analysis.

2.8. Extraction and cleanup

A 10 ± 0.1 g portion of the finely ground frozen sample was weighed into a 50 mL centrifuge tube. For extraction, 10 mL of acidified acetonitrile (1% acetic acid) and a ceramic homogenizer were added, then the tube was vortexed for 2 minutes. To the extraction tube, 4 g of anhydrous $MgSO_4$ and 1 g of CH_3-COONa were added, followed by vortexing and centrifugation at 5000 rpm for 5 minutes. After centrifugation, 1 mL of the clear supernatant was transferred to a 2 mL tube containing 150 mg of anhydrous $MgSO_4$, 25 mg of PSA, and 2.5 mg of Multi-Walled Carbon Nanotubes (MWCNTs). The mixture was vortexed for 1 min, centrifuged for 5 min at 10 000 rpm, and filtered through a 0.22 μm syringe filter into an LCMS/MS vial for analysis. When necessary, diluted solutions of real samples were made up using blank extracts (Fig. 1).

2.9. Method validation

The method was validated according to the SANTE guideline[9] for linearity, limits of detection (LOD) and quantification (LOQ), recovery, and precision. Blank okra samples collected from untreated fields were used to validate the method. Linearity was studied using a six-point standard calibration graph by plotting the detector response against standard concentration within the 0.001 to 0.5 μg mL^{-1} range. The LOD was estimated at a signal-to-noise ratio of 3 : 1. The LOQ was estimated by

considering a value of 3.3 times the LOD and then confirmed by calculating the recovery and repeatability,[12] which should be within 70–120% and <20%, respectively.

The method recovery study was assessed at four spiking concentrations of 0.005, 0.01, 0.1, and 1 mg kg^{-1}, with five replications. The spiked samples were equilibrated and processed using the above extraction and clean-up procedure. The method's repeatability was estimated through the relative standard deviation (RSD%) at the LOQ level in one day (intraday repeatability, RSD$_r$, $n = 6$) and three different days (interdays repeatability, RSD$_R$, $n = 18$).

Calibration curves for the tested analytes, constructed in pure solvent and matrix-matched solutions, were used to assess the matrix effect (ME) by comparing their slopes using eqn (1).

$$ME\ (\%) = (S_{matrix} - S_{solvent})/S_{solvent} \times 100 \quad (1)$$

Here, S_{matrix} and $S_{solvent}$ represent the slopes of the matrix-matched and solvent calibration curves, respectively.

An ME value between −20% and 20% indicates no significant matrix effect. Values from −20% to −50% or 20% to 50% suggest a moderate effect, while values below −50% or above 50% indicate a strong effect.[13]

2.10. Calculations

2.10.1. Dissipation kinetics. To determine the dissipation kinetics of abamectin and fenpyroximate, the experimental data were fitted to three typical models: zero-order, first-order, and second-order. The goodness of fit for each model was assessed using the regression coefficient (R^2), with a model considered more suitable when R^2 was closer to 1.0.

The dissipation kinetics of abamectin and fenpyroximate residues in okra were best described by a first-order kinetic model, represented by the equation: $C_t = C_0 \times \exp^{-kt}$, where C_t is the concentration (mg kg^{-1}) of abamectin or fenpyroximate at time t (days), C_0 is the initial concentration (mg kg^{-1}), and k is the dissipation rate constant (per day). The goodness of fit was evaluated based on the correlation coefficient (R^2).

The half-life ($t_{1/2}$) was calculated using: $t_{1/2} = \ln(2)/k$, while the pre-harvest interval (PHI), or safe waiting period, was determined using: PHI $= (\ln C_0 - \ln MRL)/k$.

2.10.2. Chronic dietary risk assessment. The chronic dietary risk associated with fenpyroximate and abamectin intake was evaluated by calculating the national estimated daily intake (NEDI) and the chronic hazard quotient (HQc) using eqn (1) and (2), respectively:[14,15]

$$NEDI = \Sigma(STMRi \times Fi) \quad (2)$$

$$HQc = NEDI/ADI \times bw \quad (3)$$

Here, STMRi represents the median residue from supervised trials, Fi is the average daily intake of okra (1.57 g per day),[16] and bw denotes the average adult body weight (60 kg).[17] The acceptable daily intake (ADI) values are 0.01 mg per kg bw per day for fenpyroximate[18] and 0.0012 mg per kg bw per day for abamectin.[19]

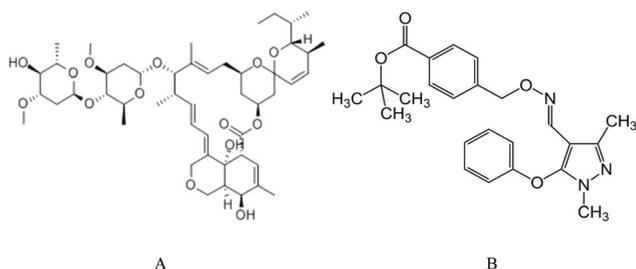

Fig. 1 Chemical structure of abamectin (A) and fenpyroximate (B).

3. Results and discussion

3.1. Optimization of LC-MS/MS conditions

Data acquisition parameters for the analytes in selective reaction monitoring (SRM) mode were automatically optimized using Trace Finder software v4.1. Each analyte was directly infused at a concentration of 0.5 mg L^{-1}. Optimal precursor ions, fragment voltages, precursor-product ion pairs, and collision energies were selected for the target compounds (Fig. 2). Two product ions were chosen for each analyte: one with a higher abundance for quantification and another with a lower abundance for confirmation (Table 1).
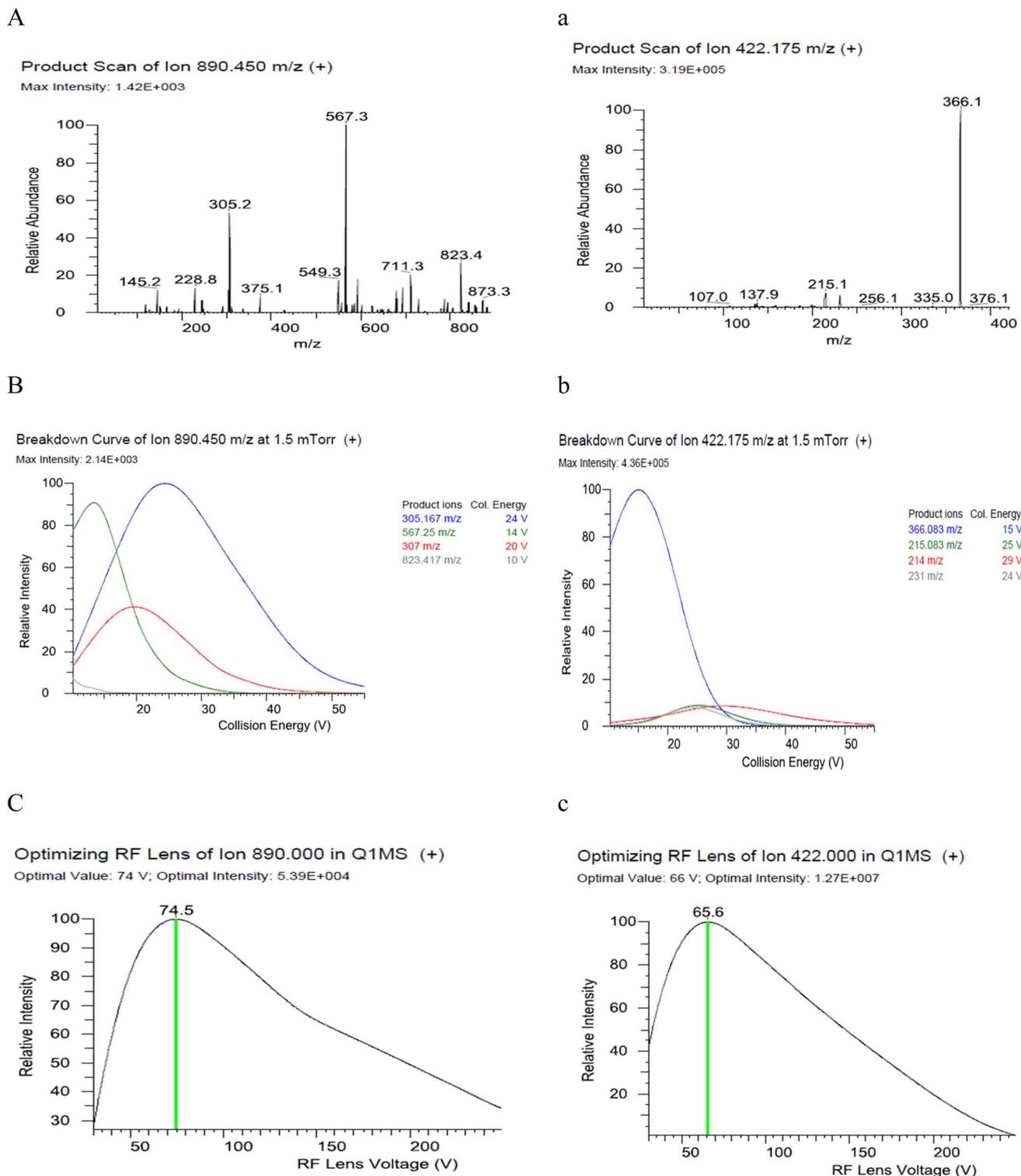

Fig. 2 Product ions scan, product ion collision energy, and RF lens optimization of abamectin (A)–(C) and fenpyroximate (a)–(c).

Table 1 LC-MS/MS parameters[a]

Pesticide	t_R (min)	Precursor ion (m/z)	Product ion (m/z)	Collision energy (v)	RF lens (v)
Abamectin	14.77	890.4	305.1	24	75
			567.2	14	75
Fenpyroximate	14.53	422.1	366	15	66
			231	24	66

[a] The underlined ions were used for quantitation.

Optimizing chromatographic separation and ionization conditions is essential to ensure accuracy and sensitivity in analysis. This study evaluated different gradient elution programs using water and methanol as the mobile phase. Adding formic acid to the water/methanol phase enhanced ionization, particularly for fenpyroximate. Ammonium formate was added to enhance abamectin detection during electrospray ionization (ESI). It promoted the formation of ammonium adducts $[M + NH_4]^+$, which improved ionization efficiency, leading to high signal intensity and greater detection sensitivity.[20] In this study, adding 10 mM ammonium formate improved the chromatographic peak shape and sensitivity for abamectin without significantly affecting fenpyroximate detection. Adding 0.1% formic acid to the water/methanol mobile phase enhanced the signal response of fenpyroximate considerably.

This improvement contributed to a lower limit of detection (LOD) and limit of quantification (LOQ) for abamectin. The mass transitions m/z 890.4 > 305.1 for abamectin and 422.1 > 366 for fenpyroximate were used for quantification, as they showed higher intensities and stability than other transitions. Fenpyroximate and abamectin were eluted under standardized chromatographic conditions at 14.53 min and 14.77 min, respectively (Fig. 3).

3.2. Method validation

The validation process assessed linearity, limit of quantification (LOQ), matrix effect (ME), precision, and recovery. Results are provided in Tables 2 and 3.

3.2.1. Selectivity, linearity, and matrix effect. Control and spiked okra samples ($n = 3$ each) were compared at 0.001 mg kg^{-1}. The method showed selectivity, as no peaks were observed in the retention times for abamectin and fenpyroximate in the control samples. In contrast, clear peaks were detected in the spiked samples under the given instrumental conditions.

A linear correlation between detector response (y) and analyte concentration (x) in mg kg^{-1} was determined from calibration curves prepared for abamectin and fenpyroximate standards. The signal responses of the target analytes were
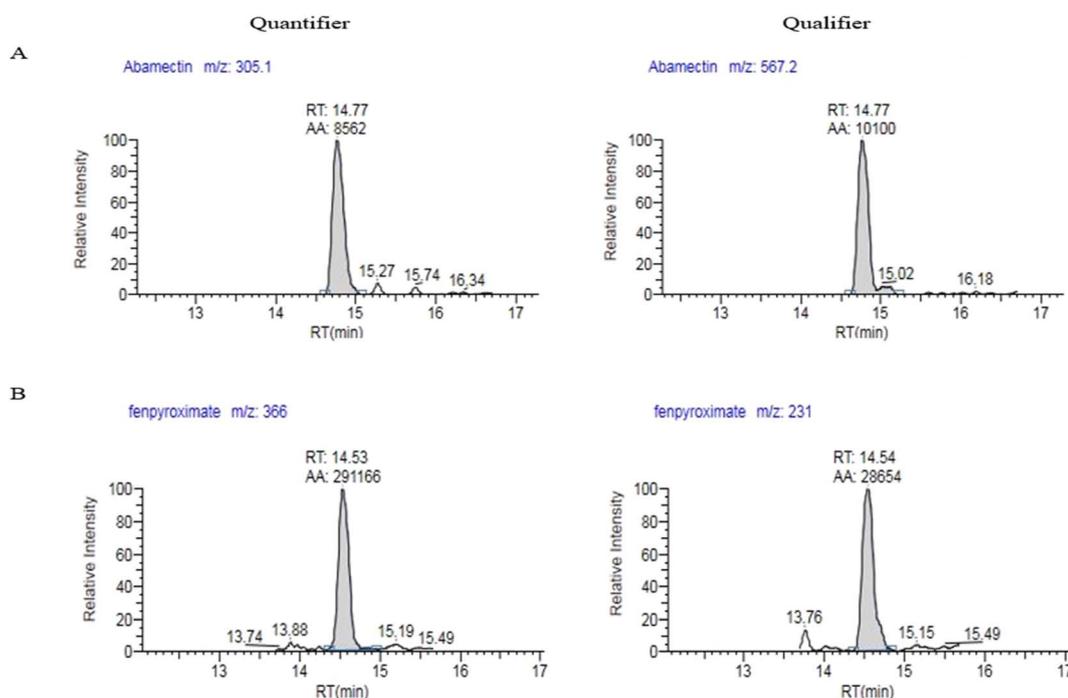

Fig. 3 Product ion chromatograms (m/z) for abamectin (A) and fenpyroximate (B) in the spiked okra matrix at 0.005 mg kg^{-1}.

Table 2 Validation results

	Abamectin	Fenpyroximate
Range (mg kg^{-1})	0.002–0.1	0.001–0.1
Regression equation	$Y = 1.401 \times 10^3 + 1.797 \times 10^3$	$Y = 3.03 \times 10^5 + 1.855 \times 10^4$
R^2	0.9971	0.9984
RSD$_r$ ($n = 6$)^a	11.4	7.6
RSD$_R$ ($n = 18$)^b	16.8	10.3
ME (%)	−14.6	−5.2
LOD (mg kg^{-1})	0.0006	0.0002
LOQ (mg kg^{-1})	0.002	0.001

^{a} RSD$_r$: the relative standard deviation (intra-day repeatability). ^{b} RSD$_R$: the relative standard deviation (inter-days repeatability).

Table 3 Average recoveries ($n = 5$) and relative standard deviations (RSDs) of abamectin and fenpyroximate in okra at four spiked levels

Pesticides	Spiked levels (mg kg^{-1})	Average recoveries (%)	RSDs (%)
Abamectin	0.005	84.2	5.8
	0.01	91.4	3.8
	0.1	93.7	4.1
	1	96.2	6.5
Fenpyroximate	0.005	89.4	8.7
	0.01	96.3	5.8
	0.1	98.6	7.1
	1	97.1	8.4

evaluated by injecting 5 μL of the analytical solution prepared in acetonitrile across nine concentration levels (0.001, 0.002, 0.005, 0.01, 0.02, 0.05, 0.1, 0.2, and 0.5 mg kg^{-1}). Calibration curves for abamectin and fenpyroximate demonstrated strong linearity within the ranges of 0.002–0.1 mg kg^{-1} and 0.001–0.1 mg kg^{-1}, with correlation coefficients (R^2) of 0.9971 and 0.9984, respectively (Fig. 4). Back-calculating the area (y) for each concentration level (x) resulted in deviations from the ideal response of ≤13.8%, well within the acceptable deviation limit of ±20%.[12]

The matrix effect (ME) was assessed by comparing the calibration curve slopes for abamectin and fenpyroximate in a pure solvent with those in okra extracts, and they showed weak signal suppression with ME values of 14.6% and 5.2%, respectively. The ME values were <20%, indicating no significant effect on the current analysis. Nevertheless, the analytes tested were quantified with matrix-matched calibration curves by an external standard method to mitigate possible matrix effects (Table 4).

3.2.2. Limit of detection (LOD) and limit of quantification (LOQ). The limit of detection (LOD) was established as the lowest pesticide concentration detectable in the matrix with a signal-to-noise ratio of 3 : 1. LOD values were determined to be 0.0006 mg kg^{-1} for abamectin and 0.0002 mg kg^{-1} for fenpyroximate. The limit of quantification (LOQ) represented the lowest concentration quantifiable with an acceptable recovery of 70–120% and precision of ≤20%. LOQ values were 0.002 mg kg^{-1} for abamectin and 0.001 mg kg^{-1} for fenpyroximate, yielding mean recoveries ($n = 3$) of 74 ± 8% and 81 ± 6%, respectively. LOD and LOQ values were below the maximum residue limit (MRL) of 0.01 mg kg^{-1} set by the European Commission Regulation (EU MRL) for the tested pesticides in okra.

3.2.3. Precision. Blank okra samples were spiked with abamectin and fenpyroximate at LOQ levels of 0.002 mg kg^{-1} and 0.001 mg kg^{-1}, respectively. The recovered amounts relative
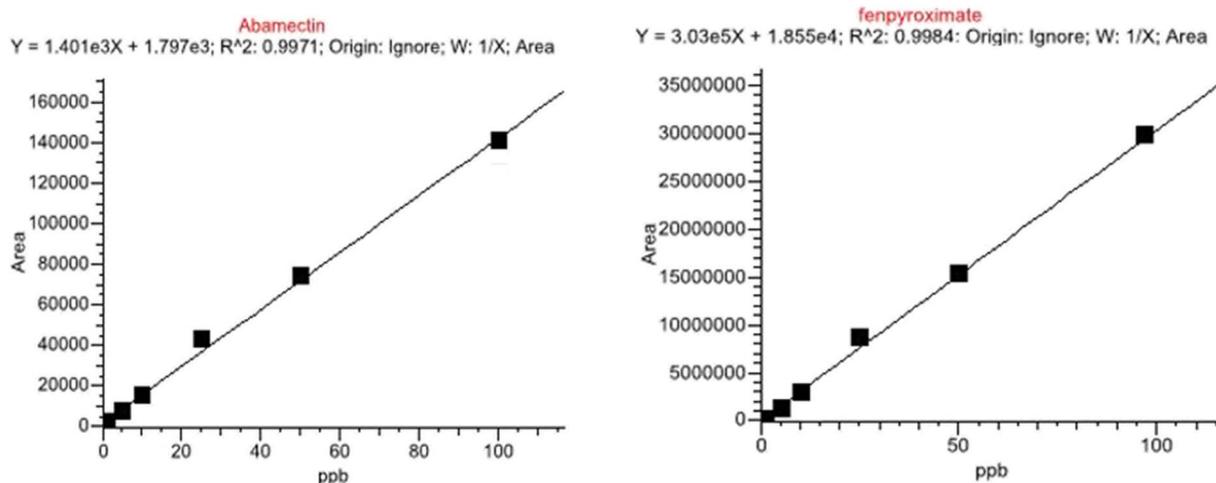

Fig. 4 Calibration curves for abamectin and fenpyroximate in the spiked okra matrix.

Table 4 Comparison of extraction, cleanup, and analytical performance of abamectin and fenpyroximate in different matrices using various analytical methods

Analyte	Matrix	Instrument	Sample weight (g)	Extraction solvent	Salts	Cleanup	LOQ (mg kg^{-1})	Recovery (%)	Precision (RSD%)	Reference
Abamectin	Perilla leaves	HPLC-FLD (derivatization)	10	Acetonitrile (30 mL)	MgSO$_4$ (6 g)	Silica cartridge (SPE)	0.01	82.11–93.03	≤8	21
Abamectin	Apples Pears Tomatoes	HPLC-FLD (derivatization)	5	Acetonitrile (20 mL)	—	C18 cartridge (SPE)	0.002–0.005	88–106	Satisfactory	23
Abamectin[a]	Eggplant	LC-MS/MS	10	Acidified (1%), acetonitrile (10 mL)	MgSO$_4$ (4g), CH$_3$COONa (1g)	2× dilution	0.02	88.6–94.8	≤14.8%	20
Fenpyroximate	Grapes	HPLC-UV	10	Acidified (1%), acetonitrile (10 mL)	MgSO$_4$ (4g), NaCl (1g)	MgSO$_4$ (150 mg), PSA (25 mg), GCB (5 mg)	0.05	88.5–100.4	≤8	22
Fenpyroximate	Apple Citrus Grape	HPLC-UV	10	Acidified (1%), acetonitrile (15 mL)	MgSO$_4$ (4g), NaCl (1g), sodium citrate Dehydrate (1g), disodium hydrogen citrate sesquihydrate (0.5 g)	MgSO$_4$ (166.6 mg), PSA (25 mg)	0.003	92–103	≤9	24
Fenpyroximate	Guava Orange Eggplant	LC-MS/MS	10	Acetonitrile (10 mL)	MgSO$_4$ (4g), NaCl (1g)	20× dil	0.01	92.4–107.3	≤15.4	9
Abamectin Fenpyroximate	Okra	LC-MS/MS	10	Acidified (1%), acetonitrile (10 mL)	MgSO$_4$ (4g), CH$_3$COONa (1g)	MgSO$_4$ (150 mg), PSA (25 mg), MWCNTs, (2.5 mg)	0.002 0.001	84.2–96.2 89.4–98.6	≤16.8 ≤10.3	This study

[a] Abamectin was determined among other analytes.

standard deviation (RSD) was calculated to assess intra-day and inter-day repeatability. Intra-day repeatability (RSD$_r$, $n = 6$) was 11.4% for abamectin and 7.6% for fenpyroximate, while inter-day repeatability (RSD$_R$, $n = 18$) was 16.8% and 10.3%, respectively. All values were within the acceptable limit of $\leq$20%, aligning with SANTE guidelines.

3.2.4. Recovery. Blank okra samples were spiked at four concentration levels: 0.005 mg kg^{-1} (0.5$\times$ MRL), 0.01 mg kg^{-1} (MRL), 0.1 mg kg^{-1} (10$\times$ MRL) and 1 mg kg^{-1} (100$\times$ MRL). The spiked samples were processed using the proposed procedure, and the percentage recoveries were calculated. Satisfactory recoveries ranged from 84.2% to 98.6% with RSD values of 3.8–8.7% (Table 3). The mean recoveries were within the acceptable range of 70–120%.[12]

The validation results demonstrate the method's reliability for determining abamectin and fenpyroximate in okra samples.

3.3. Comparison of extraction, cleanup, and analytical performance with previous studies

This study optimized the determination of abamectin and fenpyroximate in okra using LC-MS/MS, achieving improved sensitivity, precision, and cleanup efficiency compared to previous methodologies (Table 1). The limit of quantification (LOQ) achieved was 0.002 mg kg^{-1} for abamectin and 0.001 mg kg^{-1} for fenpyroximate, lower than previous methods such as 0.01 mg kg^{-1} in perilla leaves,[21] 0.02 mg kg^{-1} in eggplant,[20] and 0.05 mg kg^{-1} in grapes.[22] This highlights the enhanced sensitivity of our method. The recovery rates, 84.2–96.2% for abamectin and 89.4–98.6% for fenpyroximate (in this study), are comparable to or better than previous studies, including 82.11–93.03% for abamectin in perilla leaves[21] and 88.6–94.8% in eggplant.[20] Precision (RSD%) was $\leq$16.8% for abamectin and $\leq$10.3% for fenpyroximate (in this study), aligning with values reported in other studies, such as $\leq$14.8% for eggplant[20] and $\leq$8% for grapes.[22]

This study extraction and cleanup procedures reduced matrix interference and improved method robustness. Acidified (1%) acetonitrile with MgSO$_4$ (4 g) and CH$_3$COONa (1 g) was used for extraction, improving analyte solubilization over methods relying solely on acetonitrile and MgSO$_4$, such as perilla leaves.[21] Cleanup included MgSO$_4$ (150 mg), PSA (25 mg), and multi-walled carbon nanotubes (MWCNTs, 2.5 mg), which enhanced matrix removal compared to PSA alone or C18 cartridges.[23,24] MWCNTs improved selectivity, reducing background noise and enhancing sensitivity. LC-MS/MS provided superior specificity and lower detection limits than HPLC-FLD[21,23] or HPLC-UV,[22,24] making it more suitable for trace pesticide detection. The combined improvements in LOQ, extraction efficiency, and cleanup selectivity make this method highly effective for determining abamectin and fenpyroximate residues.

3.4. Persistence and dissipation kinetics

The persistence of abamectin and fenpyroximate residues in okra fruits was investigated over the experimental time (Fig. 5). The initial residue of abamectin after applying the
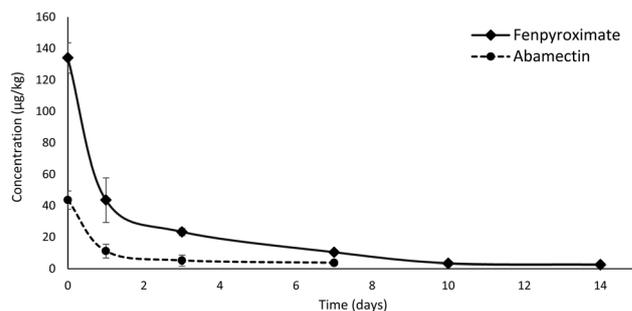

Fig. 5 Dissipation curves of abamectin and fenpyroximate residue in/on okra fruits.

recommended dose of 10 g a.i. ha^{-1} was 0.0437 mg kg^{-1}, which gradually decreased to 0.0111 mg kg^{-1} after 1 day (74.56% reduction), 0.0051 mg kg^{-1} after 3 days (88.28% reduction), and 0.0037 mg kg^{-1} after 7 days (91.60% reduction). By day 10, abamectin residues had fallen below the detection limit (BDL) of 0.0006 mg kg^{-1}. Fenpyroximate had a higher initial residue of 0.134 mg kg^{-1} after applying the recommended dose of 25 g a.i. ha^{-1}. It decreased after 1 day to 0.044 mg kg^{-1} (67.41% reduction), after 3 days to 0.0233 mg kg^{-1} (82.59% reduction), and after 7 days to 0.0103 mg kg^{-1} (92.31% reduction). By day 10, the residue had fallen further to 0.0033 mg kg^{-1} (97.51% reduction) and reached 0.0025 mg kg^{-1} (98.12% reduction) after 14 days. On day 21, the residues of fenpyroximate were below the detection limit of 0.0003 mg kg^{-1}. The results showed that both pesticides degraded over the experimental period, with residues of abamectin falling below the detection limit within 10 days, while fenpyroximate persisted for up to 21 days.

Abamectin and fenpyroximate dissipation patterns in okra fruits were evaluated by fitting the experimental data to zero-order, first-order, and second-order kinetic models to identify the best-fitting model (Table 5).

The zero-order model was unsuitable for analyzing abamectin, yielding an R^2 value of only 0.4937. In contrast, the first-order model provided a considerably better fit, with an R^2 value of 0.7186. The second-order model, however, achieved the highest accuracy, producing an optimal R^2 value of 0.9217, indicating the best fit to the data. For fenpyroximate, the first-order model provided the best fit, with an R^2 value of 0.9389. The zero-order model had an R^2 value of 0.5351, while the second-order model had an R^2 value of 0.9144. Simpler models are generally preferred when they minimize overfitting and enhance interpretability, provided they offer reasonable accuracy. Consequently, we selected the first-order model. The experimental results indicated an exponential decay pattern consistent with first-order kinetics, showing a sharp reduction in concentration between days 0 and 1, followed by a gradual, steady decline.

The results indicate that the calculated half-life of abamectin was 2.30 days, whereas fenpyroximate has a slightly longer half-life of 2.45 days. Abamectin dissipates at a rate of 0.3014 per days compared to 0.2832 per days for fenpyroximate. A higher dissipation rate indicates a faster decline, which means that

Table 5 The comparison of fitting models for abamectin and fenpyroximate in okra fruits

Pesticide	Kinetic model	Model equation	Half-life ($t_{1/2}$)	Intercept (C_0)	Rate constant (k)	R^2	$t_{1/2}$ (days)
Abamectin	Zero-order	$C_t = C_0 - kt$	$\dfrac{[C_0]}{2k}$	0.0437	0.0043	0.4937	5.12
	First-order	$C_t = C_0 e^{-kt}$	$\dfrac{0.693}{k}$	0.0224	0.3014	0.7186	2.30
	Second-order	$C_t = \dfrac{C_0}{1 + kC_0 t}$		0.0197	34.3088	0.9217	0.67
Fenpyroximate	Zero-order	$C_t = C_0 - kt$	$\dfrac{[C_0]}{2k}$	0.134	0.0067	0.5351	9.96
	First-order	$C_t = C_0 e^{-kt}$	$\dfrac{0.693}{k}$	0.07367	0.2832	0.9389	2.45
	Second-order	$C_t = \dfrac{C_0}{1 + kC_0 t}$	$\dfrac{1}{k[C_0]}$	−0.0267	35.2029	0.9144	0.21

abamectin is dissipated more quickly than fenpyroximate in okra fruits. Fenpyroximate achieved a significantly higher initial deposition on okra fruits (0.134 mg kg^{-1}) than abamectin (0.0437 mg kg^{-1}). This impressive difference in initial deposition indicates that fenpyroximate adheres very effectively or deposits more efficiently on the okra surface. Fenpyroximate has a higher log P value (5.7) than abamectin (4.4),[25] which evaluates the high lipophilicity of fenpyroximate compared to abamectin, which will facilitate the binding of fenpyroximate to the waxy surface of okra and increases its persistence. This increased binding affinity could explain the higher initial deposition observed for fenpyroximate, as it is less likely to be washed off or rapidly degraded.

Abamectin and fenpyroximate are formulated as 5% EC and 5% SC, respectively. The formulation type of a pesticide can influence how long the active ingredient persists on plants.[26] In the case of abamectin, the EC formulation, which involves dissolving the active ingredient in a solvent with an emulsifier, may lead to higher and more persistent residues on okra surfaces compared to the SC formulation of fenpyroximate due to the solvent's penetration properties in the EC formulation. However, abamectin is also highly susceptible to rapid photodegradation[27] and enzymatic breakdown[28] within plants, leading to a faster metabolism and quicker dissipation. In contrast, fenpyroximate in its SC form is more resistant to plant metabolic degradation.[18] The lipophilic nature of fenpyroximate[25] allows it to adhere longer to plant surfaces, making it less prone to rapid metabolic breakdown and, therefore, more

persistent within plant tissues. The vapor pressure is critical in determining a pesticide's tendency to volatilize. Fenpyroximate has a higher vapor pressure (0.00921 mPa) than abamectin (0.0037 mPa),[25] indicating that fenpyroximate may be more likely to volatilize under favorable climatic conditions. Temperature and humidity significantly influence vapor pressure on volatilization but may not significantly affect the overall dissipation rate in this context. Another critical factor influencing persistence and dissipation is the chemical structure. Fenpyroximate is photostable,[29] *i.e.*, it is more resistant to sunlight degradation than abamectin,[30] increasing its persistence on the plant surface.[25]

The half-life of abamectin determined in this study was 2.3 days, slightly longer than the documented values of 1.0, 1.06, 1.02, and 1.75 days for green beans, tomatoes, strawberries, and tomatoes, respectively.[31–34] However, it is similar to the half-lives of 2.38 days in cucumbers and 2.1 to 2.4 days in eggplants reported by other studies.[20,35] The half-life of fenpyroximate was 2.45 days, longer than the previously reported values of 1.7, 2.2, and 1.9 days for eggplants, guavas, and oranges[9] but within the range of 1.56 to 2.75 days observed for other crops.[24] However, it was shorter than the longer half-life of 3.5 days in grapes.[22]

The differences in dissipation rates across crops are influenced by morphological factors, including surface structure, wax content, and transpiration rates, which affect pesticide retention and absorption since okra's higher trichome density and cuticle thickness than strawberries or tomatoes might slow the penetration and breakdown of pesticide residues, leading to

Table 6 Terminal residues, National estimated Dietary Intake (NEDI), and hazard quotient (HQc) of abamectin in okra fruits

Dosage (g a.i. ha^{-1})	Number of times sprayed	Days after spraying	Mean residues (mg kg^{-1})	SD	NEDI (mg kg^{-1} bw)	HQc (%)
10	2	3	0.0073	0.0006	1.92×10^{-7}	0.016
		7	0.0022	0.0010	2.36×10^{-8}	0.002
	3	3	0.0083	0.0021	2.19×10^{-7}	0.018
		7	0.0028	0.0001	7.41×10^{-8}	0.006
20	2	3	0.0170	0.0010	4.45×10^{-7}	0.037
		7	0.0021	0.0000	2.62×10^{-8}	0.002
	3	3	0.0120	0.0017	3.14×10^{-7}	0.026
		7	0.0043	0.0006	1.13×10^{-7}	0.009

Table 7 Terminal residues, National estimated Dietary Intake (NEDI), and chronic hazard quotient (HQ) of fenpyroximate in okra fruits

Dosage (g a.i. ha^{-1})	Number of times sprayed	Days after spraying	Mean residues (mg kg^{-1})	SD	NEDI (mg kg^{-1} bw)	HQ (%)
25	2	3	0.040	0.002	1.05×10^{-3}	10.47
		7	0.011	0.001	2.70×10^{-4}	2.70
		14	0.002	0.001	6.11×10^{-5}	0.61
	3	3	0.042	0.005	1.09×10^{-3}	10.86
		7	0.009	0.002	2.46×10^{-4}	2.46
		14	0.002	0.000	5.74×10^{-5}	0.57
50	2	3	0.060	0.003	1.58×10^{-3}	15.79
		7	0.022	0.000	5.76×10^{-4}	5.76
		14	0.004	0.000	1.05×10^{-5}	0.10
	3	3	0.097	0.006	2.53×10^{-3}	25.25
		7	0.027	0.006	7.07×10^{-4}	7.07
		14	0.003	0.000	6.63×10^{-5}	0.66

a slightly extended persistence. Environmental conditions such as temperature, humidity, and UV exposure are crucial in pesticide dissipation. Additionally, microbial degradation is another critical factor influencing pesticide dissipation. The presence of pesticide-degrading bacteria and fungi in soil and plant surfaces can contribute to faster degradation in warmer climates with higher microbial activity. The climatic conditions in Egypt, characterized by med-high temperatures and intense solar radiation in the spring-summer seasons, likely enhanced the dissipation rates of both compounds compared to studies conducted in cooler environments. The formulation type significantly affects pesticide adherence, penetration, and persistence on plant surfaces. Furthermore, $\log P$ (partition coefficient) values influence the solubility and persistence of pesticides.[36]

The pre-harvest interval (PHI), defined as the time required for abamectin and fenpyroximate residue levels to decrease below the established maximum residue limit (MRL) of 0.01 mg kg^{-1} (as per the EU-MRL database), was calculated to be 2.6 days for abamectin and 6.9 days for fenpyroximate.

3.5. Terminal residues and risk assessment

The results of fenpyroximate and abamectin terminal residues in okra fruits are shown in Tables 6 and 7. Various doses, spraying frequencies, and residue measurements at varied intervals were used to evaluate the associated risk. Abamectin dosages of 10 and 20 g a.i. ha^{-1} showed residue levels ranging from 0.0020 mg kg^{-1} to 0.0170 mg kg^{-1}, with concentrations decreasing significantly between day 3 and day 7. This trend highlights the fast dissipation of abamectin terminal residues in okra fruits.

The estimated national daily intake (NEDI) values for abamectin, ranging from 2.36×10^{-8} to 4.45×10^{-7} mg kg^{-1} body weight, and the corresponding chronic hazard quotient (HQc) values, all well below the 100% threshold, provide reassurance of the minimal health risk from abamectin residues in okra fruits.

For fenpyroximate, 25 and 50 g a.i. ha^{-1} dosages showed terminal residue levels between 0.002 mg kg^{-1} and 0.097 mg kg^{-1}, decreasing over time. The highest residue (0.097 mg kg^{-1})

was observed at 50 g a.i. ha^{-1} with three sprays three days after application. NEDI values ranged from 6.11×10^{-5} to 2.53×10^{-3} mg kg^{-1} body weight, while HQc values ranged from 0.10% to 25.25%, all remaining below the 100% threshold, indicating a low risk associated with fenpyroximate-treated okra.

Both abamectin and fenpyroximate residues consistently decreased concentrations over time, influenced by dosage and spraying frequency. Nevertheless, the HQc values remained below 100%, which means a negligible risk for the adults, even with high dosages and repeated applications. The dissipation pattern underlines the importance of appropriate pre-harvest intervals to reduce residue levels before consumption. Our results provide essential insights for safely using these acaricides in okra cultivation.

4. Conclusion

The validated QuEChERS (Quick, Easy, Cheap, Effective, rugged, and Safe) method combined with LC-MS/MS was developed in this study for determining abamectin and fenpyroximate residues in okra fruits. The method was successfully validated according to SANTE guidelines and was characterized by high accuracy and reliability and excellent selectivity, linearity, and sensitivity. The optimized chromatographic conditions significantly improved the ionization efficiency and, thus, the detection sensitivity for both pesticides. Persistence studies showed that fenpyroximate has higher initial residues and longer persistence than abamectin due to its greater lipophilicity and UV photostability, with half-lives of 2.3 and 2.45 days, respectively. The estimated pre-harvest intervals (PHI) of 2.6 days for abamectin and 6.9 days for fenpyroximate ensured residue levels below the MRL, supporting consumer safety. The study found that the risk to consumers from abamectin and fenpyroximate application in okra was negligible when used at approved and double approved rates. The risk assessment for both compounds at all intervals demonstrated an acceptable level of dietary risk. These findings provide important insights into the safe use of these pesticides on okra. However, this study is limited to a specific climatic region (Egypt), which may affect its applicability to other environments. It also focuses only on

two pesticides without considering interactions with other agrochemicals. Additionally, long-term monitoring is needed to assess cumulative exposure and environmental persistence. Future research should explore the effects of environmental factors on pesticide degradation, compare dissipation across different crops, and evaluate long-term dietary risks.

Abbreviations

QuEChERS	Quick, easy, cheap, effective, rugged, and safe
MRL	Maximum residue limit
ADI	Acceptable daily intake
NEDI	National estimated daily intake
LOQ	The limit of quantitation
ME%	Matrix effect percent
STMRi	The median final residue obtained from the supervised trials (mg kg^{-1})
Fi	The average daily per capita consumption (kg per day)
SRM	Selective reaction monitoring
EC	Emulsifiable concentrate
SC	Suspension concentrate
PHI	Pre-harvest interval
HQc	Chronic hazard quotient

Data availability

The data associated with this article have been included in the manuscript.

Author contributions

Farag Malhat and Osama I. Abdallah: conceptualization, methodology, investigation, formal analysis, data curation, writing– original draft, writing review & editing, visualization, supervision, project administration. El-Sayed Saber and Nevein S. Ahmed: investigation, resources, data curation. Shokr Abel Salam Shokr: editing, funding acquisition, project administration.

Conflicts of interest

The authors have no conflicts of interest to declare.

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