Residual Effect of the Insecticides Flonicamid and Spiromesifen against *Aphis craccivora* (Hemiptera: Aphididae) and Persistence Dynamics in Faba Bean[1]

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Abstract Field efficacy trials determined that flonicamid was more effective than spiromesifen and the negative control compound acetamiprid against *Aphis craccivora* Koch on faba bean, *Vicia faba* L. Flonicamid and spiromesifen residues in bean tissue and in soil were determined with high-performance liquid chromatography and gas chromatography-mass spectrometry. Using a spike level of 0.1–1 mg/kg, the recovery of flonicamid from bean tissue was 89.2% and from soil 81.4%. Spiromesifen recovery was 99.4% from bean and 90.3% from soil. The relative standard deviations ranged from 2.54 to 8.14%. According to the dissipation kinetics, the half-life of flonicamid residue in beans was 1.93 d and 1.96 d in soil, while that of spiromesifen in beans was 2.35 d and in 2.59 d in soil.

Key Words residual activity, flonicamid, spiromesifen, persistence, half-life

The faba bean (*Vicia faba* L.) is one of the largest legume crops in the world with production yields of up to 700,000 tons annually (Ouda and Zohry 2017). It is a significant source of protein in several parts of the globe, especially in Mediterranean and Middle Eastern cuisines (Crepon et al. 2010, Kirk 2004). El-Defrawi and El-Harty (2009) reported a strong negative linear relationship between *Aphis craccivora* infestations and faba bean crop yield. Aphid feeding causes direct damage to plant stems and foliage of faba bean. Aphids also vector viruses and produce honeydew that accumulates on plant foliage resulting in sooty mold growth that impedes photosynthesis (Swarnalata et al. 2015).

Management of the such pests has typically focused on chemical insecticide applications to minimize outbreaks of economically important pests (Moustafa et al. 2023a). However, this overreliance on pesticides has resulted in the development of resistance (Fouad et al. 2022, Moustafa et al. 2023b) against insecticides in the carbamate, organophosphate, pyrethroid (Foster et al. 2000) and neonicotinoid groups

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(Kilpatrick et al. 2005). Moreover, many pesticides have become restricted in their use or have been banned from many markets (Morita et al. 2007).

Consequently, there is a need for novel methods, including insecticides, that can overcome resistance phenomena (Morita et al. 2007). A novel selective aphicide such as flonicamid (N – cyanomethyl – 4- trifluoromethyl nicotinamide) that belongs to the pyridinecarboxamide group could be a suitable alternative for controlling aphids that are resistant to several insecticides (Hancock 2003). This compound acts as an irreversible inhibitor of aphid feeding (Roditakis et al. 2014). In addition, spiromesifen is a new insecticide that belongs to the chemical class of tetronic derivatives (IRAC 2022) that interfere with lipid biosynthesis (Bielza et al. 2018). Since spiromesifen has good residual values, high selectivity, and minimal activity against predators and pollinators (Nauen and Konanz 2005), it could be a promising new tool for a number of integrated pest management (IPM) programs (Kodandaram et al. 2017).

Given consumer demand for healthy food consumption, reduced persistence of chemical residues in the environment is desired. Further, there have recently been complaints from farmers and consumers regarding the taste and digestive effects of crops due to the possible buildup of pesticides and/or other agricultural inputs (Ikpesu and Ariyo 2013, Otitoju and Lewis 2021). The application of a range of chemicals to combat plant disease and pest infestation on the faba bean could result in the presence of pesticide residues in pods commercially sold for public consumption (Ahmed et al. 2002, Eskenazi et al. 2008, Ismail et al. 2013, Shams EL Din et al. 2015).

Our objectives in this study were (1) to determine the field efficacy flonicamid and spiromesifen against *A. craccivora* on faba bean, and (2) define the residual activity and persistence of the two insecticides in faba bean tissue and in soils. We employed the extraction protocol of Anastassiades et al. (2003) that has since been updated to be more appropriate for the analysis of some pesticides, including those with planar structures, different polarities, and pH-dependent properties. This protocol has produced reliable results and high levels of recovery and effectively replaces earlier extraction techniques that generated hazardous wastes or byproducts or required complicated, time-consuming procedures to recover pesticide residues from fruits and vegetables with high-water content (Hou et al. 2013, Song et al. 2019). In addition, liquid chromatography (LC) with UV and gas chromatography-mass spectrometry (GC-MS) remain as reliable techniques to accurately detect pesticide residues (Kandil et al. 2023).

Materials and Methods

Field testing. The field experiments were conducted at the Faculty of Agriculture Farm (Giza, Egypt) during two consecutive seasons (2021 and 2022). In both seasons, an area of about 2000 m^2 was sown with faba bean seeds (var 'Giza 716') and divided into 20 plots of 100 m^2 each. Unplanted areas measuring 1 m wide were left as barriers between plots to minimize drift contamination. The planted area received the recommended agricultural practice throughout both growing seasons without any application of insecticides, other than those in the study.

Four treatments (3 insecticides + control) were tested in this area under a randomized complete block design with 4 replications per treatment (Moustafa et al. 2022). The insecticide treatments were commercial formulations of flonicamid (Teppeki 50%

WG, Shoura Chemicals Co., Giza, Egypt), spiromesifen (Oberon 24% SC, Syngenta Agrosciences, Renens, Switzerland), and acetamiprid (Mospilan 20% SP, Shoura Chemicals) at 119.05 g active ingredient (a.i.)/ha of flonicamid, 45.71 g a.i./ha of spiromesifen, and 33.81 g a.i./ha of acetamiprid. The control treatment plots were sprayed with water.

The insecticides were applied with a knapsack sprayer using irrigation water for dilutions. The final volume of the spray solution was 476 L/ha. Applications were made on 15 December 2021 and 20 December 2022.

Adult *A. craccivora* were counted on 25 plants from each plot. The pre- and post-counts were determined as number of adult insects per plant before spraying and 1, 3, 5, 7, 10 and 15 d after application. The percentage reduction in the *A. craccivora* population by treatment was calculated according to Henderson and Tilton (1955) as follows:

Reduction (%) $= [(A \times C)/(B \times D)] \times 100$, where A = number of individuals in treatment after application; B = number of individuals in treatment before application; C = number of individuals in control before application, and; D = number of individuals in control after application.

Residue analysis. Faba bean seeds, pods, leaves, and soil were collected for analysis at 60 d postplanting. Beans (2 kg) and other samples representative of each treated and untreated area were randomly selected for sampling at different intervals. To evaluate pesticide dissipation, samples were taken immediately (2 h) after application and at 1, 3, 5, 7, 10, 15, and 21 d later. Samples were transported on ice to the laboratory where they were homogenized. The homogenate was kept at −4°C while until further preparation and extraction.

The chemicals and reagents used were from several sources. The Central Agricultural Pesticides Laboratory (CAPL) provided certified reference standards from Dr Ehrenstorfer (GmbH, Augsburg, Germany) of spiromesifen and flonicamid (>98% pure). Organic solvents, HPLC grade acetonitrile and methanol, formic acid, anhydrous magnesium sulphate, sodium chloride, and C18 (sorbent used to remove high content of chlorophyll) were obtained from Merck (Darmstadt, Germany). The bulk primary secondary amine (PSA) sorbent (Bondesil-PSA, 40 m) was supplied by Supelco, Sigma Aldrich, Germany. Before usage, anhydrous magnesium sulphate and sodium chloride were heated at 250°C for 4 h in the oven and stored in desiccators. Flonicamid and spiromesifen were prepared as stock solutions (0.1 mg/mL) in acetonitrile (ACN). Stock solutions of each were diluted in ACN to establish standard solutions of 0.01, 0.05, 0.1, 0.5, 1, 5, 10, and 20 μg/mL. When not in use, working standard solutions were kept in the dark at 4°C, and stock solutions were kept at −20°C.

Purification and extraction protocols were those of Anastassiades et al. (2003). Ten g of the homogenized plant samples were combined with 10 mL of 1% acetic acid in a 50-mL Teflon centrifuge tube. The salt extraction mixture was then vortexed for 1 min and centrifuged for 5 min at 4,000 rpm. Two mL of the supernatant was transferred to 15-mL centrifuge tubes containing clean-up sorbents which was then vortexed again for 1 min and centrifuged for 5 min. A 2-mL aliquot of that supernatant was filtered a 0.22 μm filter. For soil samples, 5 g of each sample were combined with 5 mL of water and 10 mL of 1% acetic acid to which ACN was added in a 50-mL Teflon centrifuge tube.

Analyses of flonicamid in samples were performed on an Agilent HPLC 1260 infinite series HPLC system equipped with a quaternary pump, a variable wavelength diode array detector (DAD), and an auto-sampler with an electric sample valve (Agilent Technologies). A 150 mm × 4.6 mm × 5 m ODS analytical column was used. The injection volume was 20 μL, the mobile phase (90% ACN in HPLC grade water) flow rate was 1 mL/min, and the detection wavelength was set at 210 nm. The retention period for flonicamid was 3.4 min in the 8 min isocratic run.

Analyses of samples for spiromesifen performed on a HP 6890 GC-MS unit equipped with an HP7673 auto-sampler equipped with a 30 m × 0.32 mm capillary column with a 0.25-m thick coating of 5% phenylmethyl polysiloxane (HP-5) from Hewlett and Packard. The oven temperature program was 200°C (2 min), 10°C/min to 220°C (2 min), and then 10°C/min to 260°C (5 min), and finally 10°C/min to 280°C (10 min). The carrier gas (He) flow rate was in constant flow mode at 1.5 mL/min. Splitless injection of 1 μL volume was carried out at 300°C. The mass spectrometer was operated in electron ionization mode with transfer line temperature of 230°C and SIM mode. Data analyses were assured by software ChemStation (Agilent Technologies).

According to SANTE/12682/2019, laboratory technique verification was performed to demonstrate that the method is suitable for the extraction and quantitative assessment of the tested pesticide in beans and soil. For GC-MS and HPLC analyses, the determined pesticide residues in soil and beans were serially diluted with pure solvent to yield 0.01, 0.05, 0.1, 0.5, 1, 5, 10, and 20 μg/mL. The Matrix effects were assessed by contrasting the response produced from the determined pesticide residue in pure solvent solution with extracted samples spiked with the determined pesticide in the same solvent at the same concentration level. Selectivity and sensitivity were determining the limit of quantification (bias). Recovery at 1, 0.5, and 0.1 mg/kg and the repeatability accuracy (RSD%) were examined across 5 replicates. The lowest concentration with a precision of between 70% and 120% was determined to be the limit of quantification (LOQ).

Statistical analysis. Data from the field efficacy tests were subjected to analysis of variance (ANOVA) with a completely randomized design using MSTAT-C software package (Freed et al. 1989). The least significance difference (LSD) was performed to detect statistical differences among treatments when the F-test was significant at a 5% probability level. In addition, the dissipation rate constant (k) and half-life of flonicamid and spiromesifen in bean, seeds, and leaves were calculated using the first-order kinetic model, $C_t = C_0\ e^{-kt}$. The starting and residual concentrations (mg/kg), respectively, at time t (days), are denoted by the letters C_0 and C_t in the formula. Using regression analysis, the rate constant (k) was deduced from the C_0/C_t, and t curves $t_{1/2}$ were determined according to formula, $t_{1/2} = \ln 2/k$ (Hoskins 1961).

Results

Efficacy tests. Based upon the mean percentage reduction in the numbers of *A. craccivora* in the insecticide treatments, efficacy of the treatments from highest to lowest was flonicamid > spiromesifen > acetamiprid at 1 and 3 d postspraying in both years (Tables 1 and 2) and was established as initial kill, while the reduction in aphid density at 5, 7, 10, and 15 d as a residual effect (Table 1). By 5 d after application,

Table 1. Mean (±SD) percentage reduction in numbers of *A. craccivora* aphids on faba bean after insecticide application in 2021.

	Initial		Residual			
Insecticides	**1 d**	**3 d**	**5 d**	**7 d**	**10 d**	**15 d**
Acetamiprid	86.1 b ± 2.8	77.7 c ± 2.3	73.5 b ± 3.9	62.0 b ± 7.5	56.8 b ± 6.2	39.2 b ± 7.2
Flonicamid	97.6 a ± 1.7	99.0 a ± 0.9	99.3 a ± 0.8	98.0 a ± 0.5	98.0 a ± 1.2	96.2 a ± 1.0
Spiromesifen	91.7 b ± 4.1	95.9 b ± 0.7	97.1 a ± 1.4	97.2 a ± 1.0	94.8 a ± 0.7	89.0 a ± 3.6
LSD 5%	5.65	2.90	4.23	7.94	6.85	7.31

Means within a column followed by different letters are significantly different ($P < 0.05$).

Table 2. Mean (±SD) percentage reduction in numbers of *A. craccivora* on faba bean after insecticide application in 2022.

	Initial		Residual			
Insecticides	**1 d**	**3 d**	**5 d**	**7 d**	**10 d**	**15 d**
Acetamiprid	86.3 b ± 4.2	84.6 c ± 4.1	76.2 b ± 7.5	63.7 b ± 11.9	59.9 b ± 12.4	60.8 b ±10.6
Flonicamid	97.3 a ± 1.2	98.7 a ± 1.3	99.7 a ± 0.5	100.0 a ± 0.0	98.5 a ± 0.5	98.6 a ± 0.5
Spiromesifen	88.0 b ± 1.3	93.7 b ± 3.6	95.7 a ± 1.9	95.2 a ± 2.2	93.0 a ± 3.4	91.7 a ± 1.0
LSD 5%	5.23	4.67	7.28	11.52	12.02	10.95

Means within a column followed by different letters are significantly different ($P < 0.05$).

the effect of flonicamid and spiromesifen did not differ significantly, but both proved more effective than acetamiprid.

Method validation. The analytical performance of the HPLC and GC-MS methods utilized was evaluated under optimized conditions. Calibration curves were created by triple injection (n = 3) for each of the 8 tested insecticide concentrations. The average recovery percentages of the tested insecticides in beans and soil were adjusted based on the recovery percentages (Table 3). The LOD and LOQ were calculated to be 0.01 and 0.1 mg/kg, respectively. To account for matrix effects, matrix-matched calibration curves ($R^2 > 0.98$) were employed for quantification of the 2 chemicals, which ranged from 0.01 to 20 μg/mL. The matrix effect for the tested insecticides ranged from 8.92–12.33%, indicating the absence of a potential interfering endogenous peak that neither significantly suppressed nor increased the response of the instrument. Possible matrix effect outcomes have been defined based on Saber et al. (2016) and Ferrer et al. (2011) as no effect (between −20% and 20%), medium effect (between −50% and −20%), and strong effect (< −50% or > 50%).

Dissipation of spiromesifen and flonicamid in bean pods, seeds, leaves and soil. Residual spiromesifen and flonicamid in beans pods, seeds, leaves, and soil at different sampling times (0, 1, 3, 5, 7, 10, 15, and 21 d) is summarized in Tables 4 and 5. Spiromesifen and flonicamid in bean leaves were initially 14.36 and 13.64 mg/kg (Fig. 1). The concentration decreased 10.10 and 8.07 mg/kg with a loss of 29.66% (spiromesifen) and 40.83% (flonicamid) at 1 d posttreatment. At 5 d posttreatment, the concentrations were 6.29 mg/kg (spiromesifen) and 3.54 mg/kg (flonicamid), which correspond to losses of 56.19% and 74.04%. At 21 d posttreatment, spiromesifen was 0.81 mg/kg, whereas flonicamid was undetectable.

For bean pods, spiromesifen and flonicamid were initially at 4.59 and 3.35 mg/kg, respectively (Fig. 2). Both decreased over time and, by 15 d postapplication, spiromesifen was barely detectable at 0.15 mg/kg, while flonicamid was below the determination limit. At 21 d postapplication the residual for both pesticides was below the LOQ.

Neither insecticide persisted for long in bean pods. Spiromesifen was below the detection limit at all sampling times, while flonicamid quickly dissipated (day 1 - 0.12 mg/kg; day 3 - 0.05 mg/kg; day 5 - 0.01 mg/kg) to levels below the determination limit by day 7.

Initial deposits of spiromesifen and flonicamid in soil were 0.80 mg/kg and 1.05 mg/kg, respectively (Fig. 3), but were below the detection limit within 3 (spiromesifen) and 7 d (flonicamid) postapplication.

The waiting period for when residual spiromesifen was below the MRL of 1 mg/kg (codex, 2017 database) at 10 d after the last application and was 7 d for flonicamid to < 0.7 mg/kg (codex, 2018 database). The half-life values for spiromesifen in pods and leaves were 2.35 d and 2.59 d, whereas for flonicamid the values ranged from 1.66 d to 1.96 d across pods, seeds, leaves, and soil.

Discussion

Despite potential adverse ecological effects, chemical control is still considered the preferred method for quick relief from insect pests. However, indiscriminate application of these compounds can yield questionable outcomes as their efficacy can be impacted by a number of extrinsic factors such as sunlight, UV light, and photolysis in

Table 3. Mean (±SD) percentage recovery and repeatability precision of spiromesifen and flonicamid from spiked samples of faba beans and soil.

	Spiromesifen				Flonicamid			
	Beans		Soil		Beans		Soil	
Level	Recovery	*RSDr	Recovery	RSDr	Recovery	RSDr	Recovery	RSDr
0.1	89.22 ± 1.88	2.54	81.41 ± 2.74	4.22	92.05 ± 1.28	3.49	82.43 ± 2.00	3.97
0.5	92.94 ± 1.32	4.21	85.49 ± 2.12	6.55	95.24 ± 2.01	3.55	86.82 ± 1.52	3.25
1	98.65 ± 1.21	6.43	88.19 ± 3.01	8.14	99.35 ± 2.42	2.92	90.33 ± 1.55	2.97

*RSDr is repeatability accuracy.

Table 4. Residual flonicamid in bean pods, seeds, leaves and soil samples.

	Beans			Pods			Leaves			Soil		
Days after application	Residues	% Loss	% Persistence	Residues	% Loss	% Persistence	Residues	% Loss	% Persistence	Residues	% Loss	% Persistence
0	*ND	—	—	3.35 ± 2.04	0.00	100.0	13.64 ± 2.51	0.00	100.0	1.05 ± 1.11	0.00	100.0
1	0.12 ± 1.23	0.00	100.0	2.10 ± 2.55	37.31	62.69	8.07 ± 2.33	40.83	59.17	0.88 ± 2.01	16.19	83.81
3	0.05 ± 1.62	58.33	41.67	1.27 ± 1.96	62.08	37.92	6.62 ± 2.41	51.46	48.46	0.12 ± 1.25	88.57	11.43
5	0.01 ± 0.97	91.66	8.34	0.72 ± 2.22	78.50	21.50	3.54 ± 1.99	74.04	25.96	0.04 ± 0.85	96.19	3.81
7	ND	—	—	0.31 ± 3.40	90.74	9.26	1.59 ± 2.02	88.34	11.66	ND	—	—
10	ND	—	—	0.08 ± 1.67	97.61	2.39	0.61 ± 2.41	95.52	4.48	ND	—	—
15	ND	—	—	ND	—	—	0.04 ± 0.52	99.70	0.30	ND	—	—
21	ND	—	—	ND	—	—	ND	—	—	ND	—	—
$t_{1/2}$		1.96			1.93			1.96			1.66	
**MRL	0.7 (codex, 2018)											
***PHI	7 d											

* ND is not detected.
** MRL is maximum residual limits.
*** PHI is preharvest interval.

Table 5. Residual spiromesifen in bean pods, seeds, leaves and soil samples.

	Beans			Pods			Leaves			Soil		
Days after application	Residues	% Loss	% Persistence	Residues	% Loss	% Persistence	Residues	% Loss	% Persistence	Residues	% Loss	% Persistence
0	*ND	—	—	4.59 ± 1.22	—	100	14.36 ± 2.33	—	100	0.80 ± 2.21	—	100
1	ND	—	—	3.12 ± 1.25	32.02	67.98	10.10 ± 2.14	29.66	70.34	0.74 ± 1.54	7.50	92.50
3	ND	—	—	2.60 ± 1.74	43.35	56.65	9.38 ± 1.95	34.67	65.33	ND	—	—
5	ND	—	—	1.63 ± 1.62	64.48	35.52	6.29 ± 1.52	56.19	43.81	ND	—	—
7	ND	—	—	1.02 ± 1.28	77.77	22.23	4.43 ± 0.98	69.15	30.85	ND	—	—
10	ND	—	—	0.66 ± 1.65	85.62	14.38	2.59 ± 1.41	81.96	18.04	ND	—	—
15	ND	—	—	0.15 ± 1.98	96.73	3.27	1.21 ± 1.51	91.57	8.43	ND	—	—
21	ND	—	—	ND	—	—	0.81 ± 1.69	94.35	5.65	ND	—	—
$t_{1/2}$		—			2.35			2.59			—	
**MRL	1 (codex, 2017)											
***PHI	10 d											

* ND is not detected.
** MRL is maximum residual limits.
*** PHI is preharvest interval.

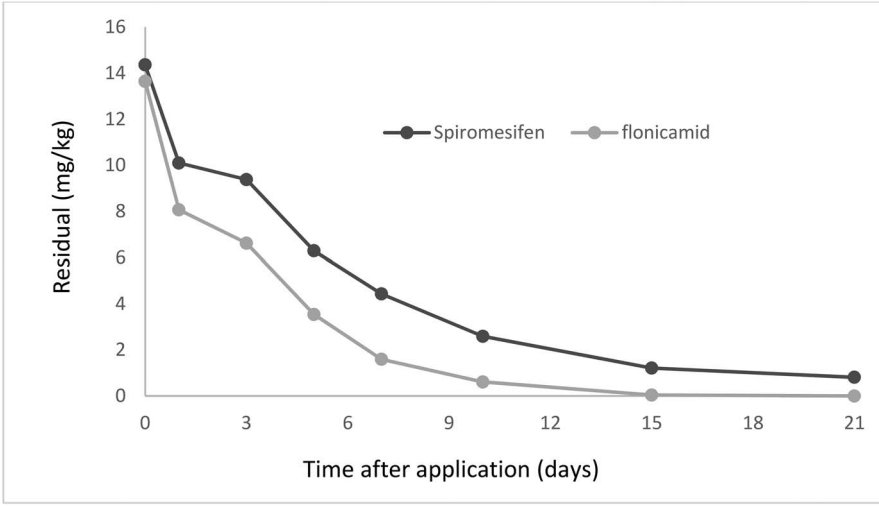

Fig. 1. Residual spiromesifen and flonicamid in faba leaves. Dissipation pattern of spiromesifen and flonicamid (n = 3) in faba bean leaves when the pesticide formulations were sprayed at the recommended dosage on sampling days 0, 1, 3, 5, 7, 10, 15, and 21.

water (Moustafa et al. 2018). Therefore, it would be ideal to use pesticides within defined applications, the specificity of which would provide better pest management with reduced disturbance to the ecosystem and environment (Kumar et al. 2010). Therefore, the aim of the present study was to investigate the efficacy of flonicamid and spiromesifen for *A. craccivora*, as well as to determine the persistence of their residuals in leaves and pods of faba beans and in associated soil samples, with the goal of enhancing productivity.

In this study, flonicamid and spiromesifen provided significantly better protection against *A. craccivora* than the control compound (i.e., acetamiprid). These findings are consistent with the observations of Morita et al. (2014) who also reported that flonicamid was effective for aphid control and (Kodandaram et al. 2017) who reported 91% mortality after flonicamid treatment. The flonicamid mode of action, which triggers an immediate cessation of feeding at exposure, is particularly effective against sucking pests, which experience starvation-induced mortality (Kodandaram et al. 2017). In addition, the activity of spiromesifen against the greenhouse whitefly, *Trialeurodes vaporariorum* Westwood (Liu 2004, Nauen et al. 2002) and *A. craccivora* (Patil et al. 2018) suggest that it might be useful as a new component for sucking insect IPM (Bi and Toscano 2007). The relatively limited effectiveness that we found for acetamiprid on *A. craccivora* indicates the possible development of resistance. Field populations of *Aphis gossypii* Glover have evolved resistance against several insecticides including acetamiprid (Koo et al. 2014, Ullah et al. 2020, Wang et al. 2007), and *Myzus persicae* Sulzer resistance to acetamiprid likely involves mechanisms other than P450 activity and target site mutations (Berber et al. 2022).

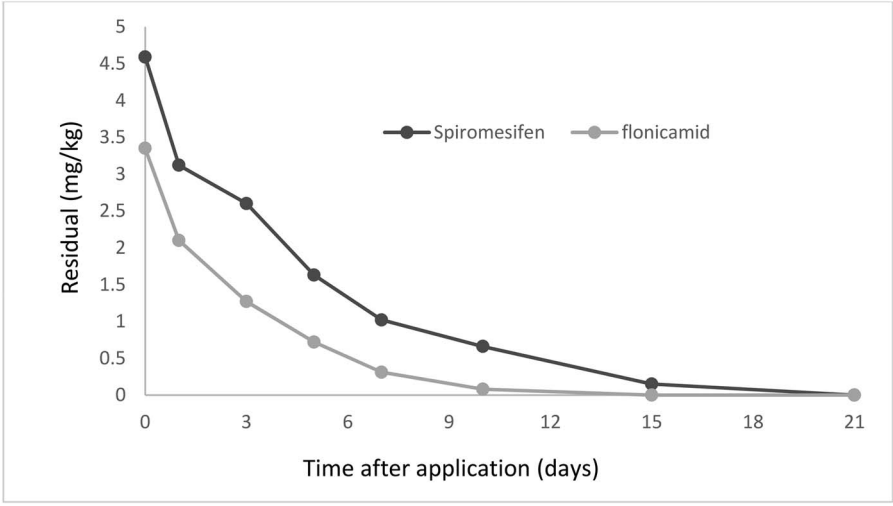

Fig. 2. Residual spiromesifen and flonicamid in faba bean pods. Dissipation pattern of spiromesifen and flonicamid (n = 3) in faba bean pods when the pesticide formulations were sprayed at the recommended dosage on sampling days 0, 1, 3, 5, 7, 10, 15, and 21.

The lack of interference from either the bean or soil matrix coupled with high selectivity and sensitivity, good linearity, and satisfactory accuracy and precision, support utilization of our residue analysis method for monitoring trace amounts of flonicamid and spiromesifen in complex matrices. The LOD was determined to be the

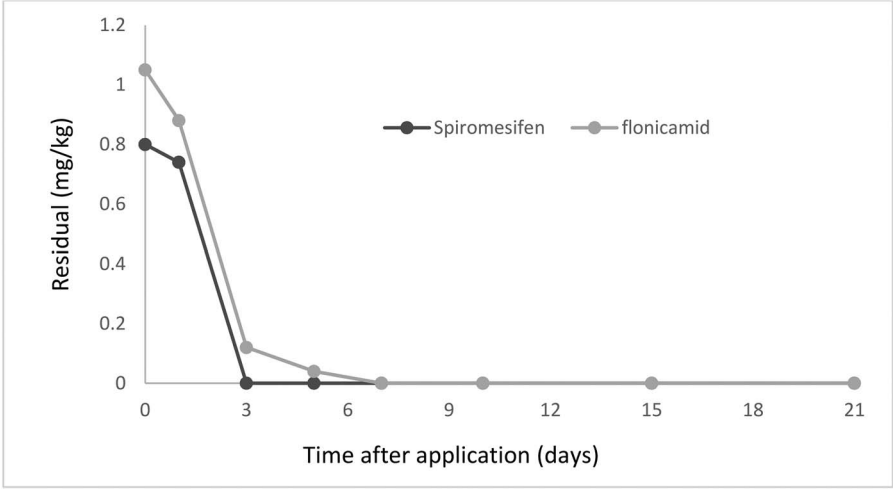

Fig. 3. Residual spiromesifen and flonicamid in soil. Dissipation behavior of spiromesifen and flonicamid (n = 3) in soil samples.

lowest concentration at which insecticide was identified, which corresponds to a signal-to-noise ratio of 3:1. The LOQ methods were established by identifying the pesticides at various concentrations at which the chromatographic peaks in samples could be identified. A signal-to-noise ratio of 10:1 was chosen as the LOQ (SANTE/12682/2019). Low detection and quantification limits of the proposed approach enable its utilization for the precise assessment of pesticide residues in samples. The matrix-matched calibration showed strong linearity with R^2 determination coefficients for all evaluated pesticides ranging from 0.983 to 0.991.

Volatilization, wash-off, photodegradation, and biotransformation are key mechanisms by which pesticides dissipate on or inside plants. These processes can be impacted by a number of variables such as rainfall, temperature, humidity, plant type, and light, among others (Saber et al. 2016). Correspondingly, the dissipation of pesticides in soil can likewise be influenced by a variety of variables, including soil type, organic matter concentration, pH, and temperature. The primary process for microbial breakdown of flonicamid and spiromesifen in soil may involve breaking of the nitrogen-carbon bond, decarboxylation, and oxidation (Zhang et al. 2018).

Our residue analysis method is effective for monitoring small amounts of flonicamid and spiromesifen in complicated matrices due to its lack of interference, high selectivity and sensitivity, accurate and precise results, and good linearity. The LOD is the smallest concentration at which pesticide can be detected, with a signal-to-noise ratio of 3:1. The LOQ is the concentration at which the pesticides can be accurately measured, with a signal-to-noise ratio of 10:1. The proposed method has low limits of detection and quantification, making it suitable for accurately assessing pesticide residues in samples. The calibration process showed a strong linear relationship between the concentration of pesticides and the measured results. Pesticides can dissipate on or inside plants through volatilization, wash-off, photodegradation, and biotransformation. Various factors such as rainfall, temperature, humidity, plant type, and light can affect these processes (Saber et al. 2016). Similarly, the dissipation of pesticides in soil can be influenced by variables like soil type, organic matter concentration, pH, and temperature. The breakdown of flonicamid and spiromesifen in soil is primarily achieved through microbial processes involving the breaking of the nitrogen-carbon bond, decarboxylation, and oxidation (Zhang et al. 2018).

Our findings are in align with those of Wang et al. (2018) who discovered that flonicamid and its metabolites had half-lives of 1.49–4.59 and 1.97–4.99 d, respectively, in cabbage (*Brassica oleracea* Plenck), while half-lives in soil were 2.12–7.97 and 2.04–7.62 d. It was surprising to observe that flonicamid decomposed rapidly. After spraying 50% flonicamid WG once or twice at the recommended dose or 1.5 times the recommended dose, the highest levels of flonicamid remaining in cabbage and soil after 3, 7, and 14 d were 0.070 and 0.054 mg/kg, respectively.

Under field conditions, Chauhan et al. (2018) found that spiromesifen residue remained on cucumber (*Cucumis sativus* L.) plants after two applications at different doses. The initial deposits of spiromesifen on the cucumber were measured at 0.47 and 0.79 mg/kg. However, these levels decreased and became undetectable after 10 d. The half-lives of spiromesifen in cucumbers were determined to be 5.6 and 4.8 d at regular and double doses, respectively.

Xu et al. (2021) examined the dissipation of flonicamid, dinotefuran, and related metabolites in peaches (*Prunus persica* L. Batsch). Their analysis showed low

variability in the results, with a relative standard deviation between 1.0–8.8%. The detection limit was 0.02 mg/kg, and the average recoveries ranged from 94 to 108%. The dissipation of flonicamid and dinotefuran followed a first-order kinetic model, with half-lives ranging from 6.9–12.4 and 8.1–15.1 d, respectively.

Abdallah et al. (2023) studied spiromesifen and spirodiclofen residues in tomato (*Solanum lycopersicum* L.) fruit using various analytical techniques. The half-lives for spiromesifen and spirodiclofen were found to be 1.49–1.83 and 1.91–2.38 d, respectively, when recommended and doubled recommended doses were administered. After 2 or 3 applications, the final residue concentrations of spiromesifen and spirodiclofen were measured below the European Union maximum residue limits (European Commission 2019).

In conclusion, our results show that flonicamid and spiromesifen can be used as effective agents in a comprehensive aphid (*A. craccivora*) management program and, as such, represent valuable new tools in aphid resistance management. Moreover, the half-lives in faba bean and soil were 1.93–1.96 (flonicamid) and 2.35–2.59 d (spiromesifen) and, based on application of the recommended dosages of the two pesticides on faba bean, the preharvest intervals (PHI) were 7 d (flonicamid) and 10 d (spiromesifen).

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