Environmental Science and Pollution Research (2023) 30:64700–64709
https://doi.org/10.1007/s11356-023-26544-x

RESEARCH ARTICLE

Residual behavior and risk assessment of fluopyram, acetamiprid and chlorantraniliprole used individually or in combination on strawberry

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Received: 13 October 2022 / Accepted: 15 March 2023 / Published online: 18 April 2023

Abstract
In this study, fluopyram (FOR), acetamiprid (ATP), and chlorantraniliprole (CAP) were used individually or in combination at the maximum recommended dose in greenhouse strawberries to research the dissipation dynamics and dietary risks. A multi-residue analytical method for FOR, ATP, and CAP in strawberries using UPLC-MS/MS integrated with the QuEChERS approach was developed with strong linearity ($R^2 \geqq 0.9990$), accuracy (recoveries of 82.62 to 107.79%), and precision (relative standard deviations of 0.58% to 12.73%). The limits of quantification were 0.01 mg kg^{-1}. Field results showed that the half-lives of FOR, ATP and CAP in strawberry fruits were 11.6–12.4 days, 6.1–6.7 days, and 10.9–11.7 days, respectively. The half-lives of the three investigated pesticides showed no significant difference when used individually or in combination. A risk assessment indicated that the dietary intake risks of the three pesticides in grown strawberries were 0.0041 to 7.63% whether applied alone or in combination, which demonstrated that the dietary intake risks of the three pesticides in grown strawberries could be negligible for Chinese male and female consumers, and that even though pesticides were used in combination, there was less cause for concern about the safety. This paper serves as a guide for the safe use of FOR, ATP, and CAP on greenhouse strawberries.

Keywords Fluopyram · Acetamiprid · Chlorantraniliprole · Dissipation behavior · Risk assessment · Strawberry

Introduction

As the "Queen of Fruits" strawberries are renowned for their abundance in dietary fiber, vitamins (vitamin C, vitamin A, etc.), antioxidants (anthocyanin, flavonoids, etc.), and minerals (Ca, Fe, P, etc.), and have enormous economic benefits (Zambon et al. 2022; Malhat et al. 2021). Fresh strawberry production in the world was expected to reach 8.8 million tons in 2020, the output value increased by 5.52% compared with 2019 (FAO 2022). A daily intake of 150 ~ 200 g of fresh strawberries is linked to high nutritional values for the human body, which helps to prevent and lessen the risk of cancer, overweight, type II diabetes, cardiovascular disease, and inflammation (Tulipani et al. 2014; Huang et al. 2022). Considering the winter months, in which there are inadequate sunlight hours for healthy growth, strawberries are cultivated in greenhouses to enhance their competitiveness on the market, appropriate temperature, and humidity make strawberry breeding susceptible to diseases and pests.

Pesticides are unavoidably applied in agricultural production practices to increase product quality and productivity. The indiscriminate, numerous application of pesticides frequently result in pesticide residues exceeding limits, raising the dietary risk to consumers (Balkan and Yılmaz 2022; Khazaal et al. 2022; Nougadère et al. 2012; Tang et al. 2021; Huang et al. 2021; Mehlhorn et al. 2022). Strawberries in greenhouses are particularly vulnerable to pests (*Botrytis cinerea*, *Chaetosiphon fragaefolii*, *Colletotrichum*, and *Frankliniella occidentalis*) and diseases (gray mold and powdery mildew) (Li et al. 2022a; Van Oystaeyen et al. 2022; Wang et al. 2022; Yan et al. 2021). A survey in Beijing concluded that at least one residue was observed in 26.0% of strawberry samples (Li et al. 2022b).

Responsible Editor: Ester Heath

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Fresh strawberries from Shanghai had an acetamiprid maximum concentration of 1.81 mg/kg, with a detection rate of 41.19% (Shao et al. 2021). Pesticides were detected in 39.32% of strawberry samples, and multiple pesticide residues were prevalent in strawberries (Chu et al. 2020). According to statistics by Valera-Tarifa et al., strawberries from Spain contained between 0.02 and 0.07 mg/kg of many residues, including fluopyram and tiophanate-methyl (Valera-Tarifa et al. 2020). Chu et al. found that the concentration levels of acetamiprid (65%), chlorantraniliprole (4%), and procymidone (80%) were 0.01–0.02, 0.01–1.20, and 0.04–3.98 mg/kg in real-world strawberry samples from Anhui (Chu et al. 2020). Pesticide residues in fruits (eaten raw) are relatively persistent due to pesticide fat solubility, particularly eating fruits with skin.

Fluopyram (pyridine ethyl benzamide fungicide) has been widely used in strawberry production in recent years to manage gray mold, powdery mildew, and downy mildew caused by pathogenic fungi (Panda et al. 2018). A broad-spectrum insecticide for touch and stomach poisoning is acetamiprid (belongs to the nitro methylene heterocyclic compounds). Aminopyralid supervision of strawberry aphids is an effective factor in strawberry planting in many zones, which has an excellent control effect (Dara 2016). A broad-spectrum insecticide of the anthranilic diamides class called chlorantraniliprole can effectively and specifically stimulate ryanodine receptors to control pests, particularly lepidopteran pests of various crops (Lahm et al. 2007). Spraying several pesticides is now the most effective method of preventing and controlling illnesses and pests in greenhouse strawberries (Sánchez et al. 2019). The phenomenon of mixed contamination with several pesticide residues in strawberries results from the combined contamination of multiple pesticides in practical application. Studies on the kinetics of residue dissipation caused by mixed contamination in strawberries with fluopyram, acetamiprid, and chlorantraniliprole have not yet been reported. In addition, acetamiprid and chlorantraniliprole are not currently approved for usage in China on strawberries. Therefore, study on the combined contamination of fluopyram, acetamiprid, and chlorantraniliprole in strawberries is essential for development of strawberry industry.

In the present study, owing to the top spot in the Full List of EWG's 2022 Shopper's Guide to Pesticides in Produce™ (https://www.ewg.org/foodnews/full-list.php), strawberry was chosen as a representative fruit to explore the residue dissipation and half-life of mixed pesticides under a greenhouse environment. Moreover, the chronic and acute dietary intake risks of fluopyram, acetamiprid, and chlorantraniliprole in strawberries were evaluated for various groups of Chinese male and female customers.

Materials and methods

Chemicals and reagents

Reference standards of fluopyram (FOR: purity 99.8%), acetamiprid (ATP: purity 99.75%), and chlorantraniliprole (CAP: purity 97.28%) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). The commercial formulations of fluopyram (41.7% suspension concentrate, SC; registration No.: PD20121664), chlorantraniliprole (20% SC; registration No.: PD20190180), and acetamiprid (20% soluble powder, SP; registration No.: PD20101762) were purchased from Bayer AG (Leverkusen, Germany), FMC Corporation (Philadelphia, USA) and Nuopuxin Group Co., Ltd. (Shenzhen, China), respectively.

Acetonitrile (ACN) and formic acid of chromatographic grade were purchased from Merck KGaA (Darmstadt, Germany); analytical-grade sodium chloride (NaCl) was purchased from Yida Chemical Reagent Co., Ltd. (Zhejiang, China).

Three types of QuEChERS d-SPE clean-up kits and m-PFC columns with different proportions of anhydrous magnesium sulfate ($MgSO_4$), primary secondary amine (PSA), octadecylsilane (C_{18}), and pesticarb (PC) were purchased from Bonna-Agela Technologies (Tianjin, China). QuEChERS d-SPE clean-up kit A: PSA 50 mg + C_{18} 50 mg + $MgSO_4$ 150 mg; QuEChERS d-SPE clean-up kit B: PSA 50 mg + PC 8 mg + C_{18} 50 mg + $MgSO_4$ 150 mg; QuEChERS d-SPE clean-up kit C: PSA 50 mg + PC 50 mg + C_{18} 50 mg + $MgSO_4$ 150 mg. And the m-PFC with MWCNTs (5 mg + PSA 15 mg + $MgSO_4$ 150 mg) was used to test the clean-up of pesticides in strawberry samples.

Field trials design and sample collection

The strawberry field trials were carried out in April 2020 and guided by the criteria of NY/T 788–2018 (MARA 2018). This experiment was conducted in Hangzhou, Zhejiang province (latitude 30.30°N, longitude 119.91°E). The experimental block was set up as four test plots (T_1, T_2, T_3, and T_4) and a blank control plot (T_0). Each treatment (setting three repetitions) was conducted in a plot of 30 m^2, and the blank control plots were employed without pesticide application. The scheme designs of the experimental trials are listed in Table 1. Samples were taken from control treatments or tested treatments at intervals of 2 h, 1, 3, 5, 7, and 10 days after spraying pesticides to explore the dissipation of residual FOR, ATP, and CAP. Strawberry samples were, at random, gathered at 2 h, 3, 5, 7, and 10 days after the last spraying to monitor the final residues of FOR, ATP, and CAP. Strawberry samples collected in the field were removed from the stalks and sepals, mixed and reduced according to the quadratic

Table 1 Field experiment design scheme

Treatments	Pesticides	Dosage (g a.i./ha)	Application times	Application interval (day)
T_1	FOR	97	2	7
T_2	ATP	45		
T_3	CAP	39		
T_4	FOR + ATP + CAP	97 + 45 + 39		

FOR Fluopyram, *ATP* acetamiprid, *CAP* chlorantraniliprole. *a.i.* active ingredient

method. After homogenization, all samples were stored frozen at − 18 °C in a freezer pending determination.

Analytical techniques

Extraction and purification

Five grams of each treated strawberry sample (which consisted of triple replicates) were weighed into a 50-mL centrifuge tube with 10-mL of 1% formic acid acetonitrile by shaking for 10 min. Then 3 g of sodium chloride was added to the centrifuge tube, shaken for 5 min and centrifuged at 5000 rpm for 5 min. For the cleanup of the strawberry supernatant, 1.6-mL of 1% formic acid acetonitrile extract was transferred to a purification tube (2 mL, PSA 50 mg, C_{18} 50 mg, $MgSO_4$ 150 mg), then vortexed for 1 min, centrifuged at 10,000 rpm for 5 min, and the supernatant was filtered through a 0.22 µm organic membrane for LC–MS/MS analysis.

Instrumental parameters

Strawberry samples were analyzed on a Waters UPLC/XEVO TQ-MS triple quadrupole liquid chromatograph mass spectrometer (Waters, USA). 2.0 µL of sample was injected onto a Waters Acquity UPLC® BEH C_{18} column (2.1 mm * 100 mm, 1.7 µm) kept at 40 °C. The mobile phase consisted of acetonitrile (100%) (phase A) and formic acid aqueous solution (0.1%) (phase B) with a gradient elution program: 0–1.2 min, 10% A, and 90% B; 1.2–3.5 min, 90% A, and 10% B; 3.5–4.0 min, 10% A, and 90% B. The mobile phase flow rate was 0.25 ml/min. ESI (electrospray ionization) with a positive ion mode was performed at a capillary voltage of 3.0 kV. The desolvent temperature was set at 800 °C and the desolvent gas flow was at 400 L Hr^{-1}. The MS analyses of FOR, ATP and CAP were conducted in the multiple reaction monitoring (MRM) mode, the detailed mass spectrometric parameters of pesticides (FOR, ATP, and CAP) are listed in Table S1.

Method validation

Following China Guideline NY/T 788–2018, the analytical method was verified (MARA 2018). Analytical parameters include limit of quantification (LOQ), linearity, accuracy, and precision, as well as matrix effect (ME) (Tesoro et al. 2022). The coefficient of determination (R^2) of the matrix-matched standard calibration curves in the concentration range of 0.002 to 0.1 mg/L with six concentration levels (0.002, 0.005, 0.01, 0.02, 0.05, and 0.1 mg/L) was used to determine the linearity. By conducting recovery tests at three different fortification levels (10, 100, and 1000 µg kg^{-1}), the method's accuracy and precision were evaluated. The lowest fortifying level tested was the LOQ of the approach.

Pesticide analysis

Calculation of matrix effects, dissipation kinetics, and half-life

The values of MEs were calculated by the following Eq. (1):

$$ME = \left(S_m - S_s\right)/S_s \times 100 \quad (1)$$

S_s and S_m are the slopes of the calibration curves of the solvent and the matrix, respectively. If the value calculated by Eq. (1) is positive, which indicates a strong matrix effect, and if it is negative, which means a weak matrix effect.

The dissipation kinetics and half-life ($T_{1/2}$) for targeted pesticides (FOR, ATP, and CAP) in strawberries were calculated using Eqs. (2) and (3) (Li et al. 2021):

$$C_t = C_0 e^{-kt} \quad (2)$$

$$T_{1/2} = ln2/k \quad (3)$$

C_t and C_0 are the concentrations of pesticide residue (mg kg^{-1}) at time t and 0 (day) after spraying, respectively. The k in Eq. (3) is the degradation rate constant of the corresponding pesticide.

Exposure assessment and risk characterization

The RQ_c (chronic risk quotient) and RQ_a (acute risk quotient), which are considered reliable indicators of the dietary risk assessment in fruits, were determined by Eqs. (5) and (7) (FAO/WHO JMPR, 2021) based on the dietary consumption data of Chinese residents of various ages:

$$NEDI = C \times F \quad (4)$$

$$RQ_c(\%) = \frac{NEDI}{bw \times ADI} \times 100 \quad (5)$$

C (mg kg^{-1}) is the average residual value of the actual monitoring strawberry sample, F (g day^{-1}) represents fruit intake, bw (kg) is the average weight of the population, NEDI (mg kg^{-1} day^{-1}) is the national estimated daily intake, ADI is the acceptable daily intake (mg kg^{-1} day^{-1}) and the value refers to the national standard (MARA 2021), $RQ_{chronic} > 100\%$ means the risk is unacceptable.

$$NESTI = \frac{HC \times LP}{bw} \quad (6)$$

$$RQ_a(\%) = \frac{HC \times LP}{bw \times ARfD} \times 100 \quad (7)$$

HC (mg kg^{-1}) is the highest residue, LP is the maximum consumption of fruits, NESTI (mg kg^{-1} day^{-1}) is the national estimated short-term intake, ARfD is the acute reference dose (mg kg^{-1} day^{-1}), and the value refers to the national standard (MARA 2021). $RQ_{acute} < 100\%$ means the risk is acceptable.

Statistical analysis

The residual experimental data were analyzed by OriginPro 2016 (OriginLab, USA). All the data were the mean that calculated by triplicate samples. Statistical significance was set at $p < 0.05$.

Results and discussion

Method optimization and validation

After a series of method optimization procedures, 1% formic acid acidified acetonitrile was selected as the best extraction solvent owing to its highest recoveries (94.37–100.29%) and the relative standard deviation (RSD) being between 1.62 and 4.84% (Fig. 1A). The extraction solvent volume of 10-mL was opted as the best extraction amount since it exhibited a better extraction performance than the other extraction amount (5-mL) with recoveries of 99.28–101.01% by purification material npc (Fig. 1B). Npc was chosen as the purification material for pesticides FOR, ATP, and CAP from strawberries due to its lower absorption capacity and stronger ability to remove impurities than the other three purification materials (Fig. 1C).

The linearity examination between the concentrations of tested pesticides and their peak areas revealed that FOR, ATP, and CAP had good linear relations with determination coefficients (R^2) ≧ 0.999 in ACN solvent solution and matrix-matched standard solutions (Table S2). The strawberry matrix weakened the signals of the three examined pesticides since the ME values were less than 1 (Table S2). As a result, matrix-matched standard solutions were chosen for the quantitative assessment of three examined pesticides in strawberry samples. The LODs and LOQs of FOR, ATP, and CAP in strawberries were 2 μg kg^{-1} and 10 μg kg^{-1}, respectively. The LOD of CAP in strawberry is slightly lower than the value reported by Balkan and Karaağaçlı (2.82 μg kg^{-1}) (Balkan and Karaağaçlı 2023). Similarly, the same result appears in Kasperkiewicz's study (2.5 μg kg^{-1}) (Kasperkiewicz and Pawliszyn 2021). To validate and evaluate the method's accuracy, recoveries of the pesticides FOR, ATP and CAP were done at spiked levels of 10, 100 and 1000 mg kg^{-1}, with five duplicates examined for each level (Table 2). The average recoveries of tested pesticides in strawberries varied from 82.62% (CAP) to 107.79% (FOR), with RSDs ranging from 0.58 to 12.73%, the accuracy of FOR in this study (108%) is significantly higher than the 32% of Valera-Tarifa's method (Valera-Tarifa et al. 2020). The addition recovery test revealed that the analytical method was linear and accurate, and that it could identify and analyze the tested pesticide levels in strawberries.

Dissipation and terminal residue levels of pesticides fluopyram, acetamiprid and chlorantraniliprole in strawberries

Dissipation of fluopyram in strawberries

The dissipation curves of fluopyram alone or in a joint are shown in Fig. 2A, the dissipation equation and correlation coefficient (R^2), as well as the $T_{1/2}$ are listed in Table 3. After carefully examining the R^2 values for the fitting curve of fluopyram, the results showed that the first-order kinetics is the best match model for capturing the kinetics of pesticide dissipation. The R^2 value for fluopyram dissipation in a alone application (0.9407) is significantly higher than that in a combination application (0.7775). Fluopyram's dissipation half-life in strawberries was 11.6 (alone) and 12.4 (joint), with no significant differences related to application mode. The initial concentrations of fluopyram were 0.245 ± 0.066 mg kg^{-1} (alone) and 0.175 ± 0.028 mg kg^{-1} (joint) at 2 h after twice spraying. Within 1 to 3 days of alone application and 3 to 5 days of joint application, the residual concentration of pesticides in strawberries increased slightly, indicating that pesticide absorption by strawberries was greater than their own degradation. The residue in strawberries continued to decrease after that, with ultimate residue amounts of 0.108 ± 0.002 mg kg^{-1} (alone) and 0.097 ± 0.030 mg kg^{-1} (joint), respectively, which were far

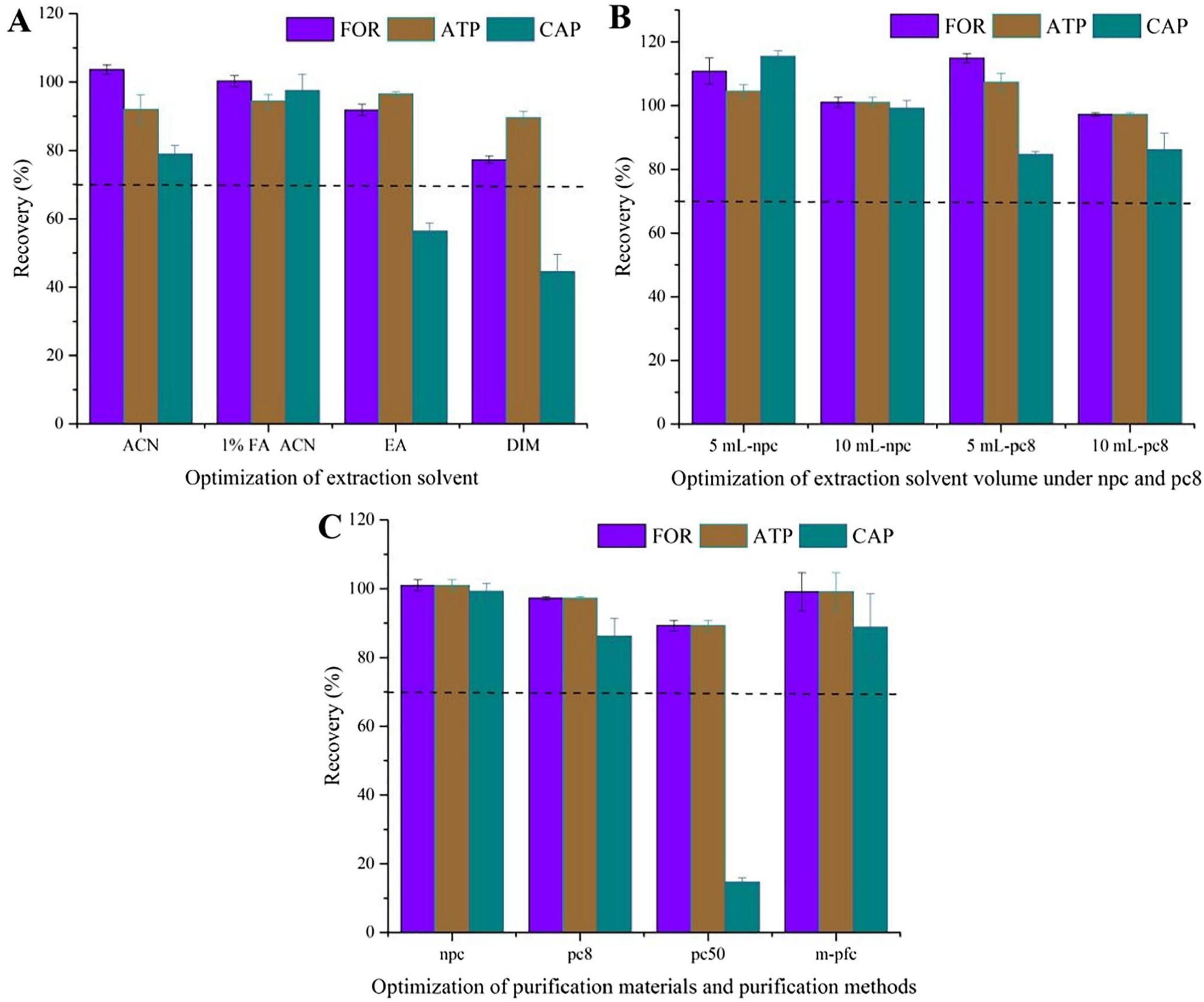


Fig. 1 Optimization of extraction solvent (**A**), extraction solvent volume under npc and pc8 (**B**) and purification materials and purification methods (**C**) in pesticides fluopyram (FOR), acetamiprid (ATP) and chlorantraniliprole (CAP) determination

Table 2 Recoveries and relative standard deviations (RSDs) of pesticides fluopyram, acetamiprid and chlorantraniliprole in strawberry samples

Analyte	Spiked level (μg kg^{-1})	Mean recoveries (%)	RSDs (%) $n=5$
Fluopyram	10	107.79	0.58
	100	101.31	2.18
	1000	103.41	2.13
Acetamiprid	10	99.72	4.61
	100	97.91	1.00
	1000	93.56	2.79
Chlorantraniliprole	10	94.60	12.73
	100	82.62	3.20
	1000	90.84	1.28

lower than the MRLs (minimum residue limits) of China (0.4 mg kg^{-1}), the European Union (0.1 mg kg^{-1}), and Australia (1.5 mg kg^{-1}).

Dissipation of acetamiprid in strawberries

The dissipation of ATP in alone and joint applications in strawberries followed by first order kinetics were illustrated in Fig. 2B, their half-lives were alike (6.1 days for alone and 6.7 days for joint) (Table 3). The R^2 values showed there was no marked variation whether they were applied alone or joint (Table 3). The initial concentrations of ATP were 0.089 ± 0.009 mg kg^{-1} (alone) and 0.089 ± 0.005 mg kg^{-1} (joint) at 2 h after twice spraying. And the dissipation of ATP in strawberries at 1 day was 18.06% by joint, which was remarkable higher than that under alone. The residual

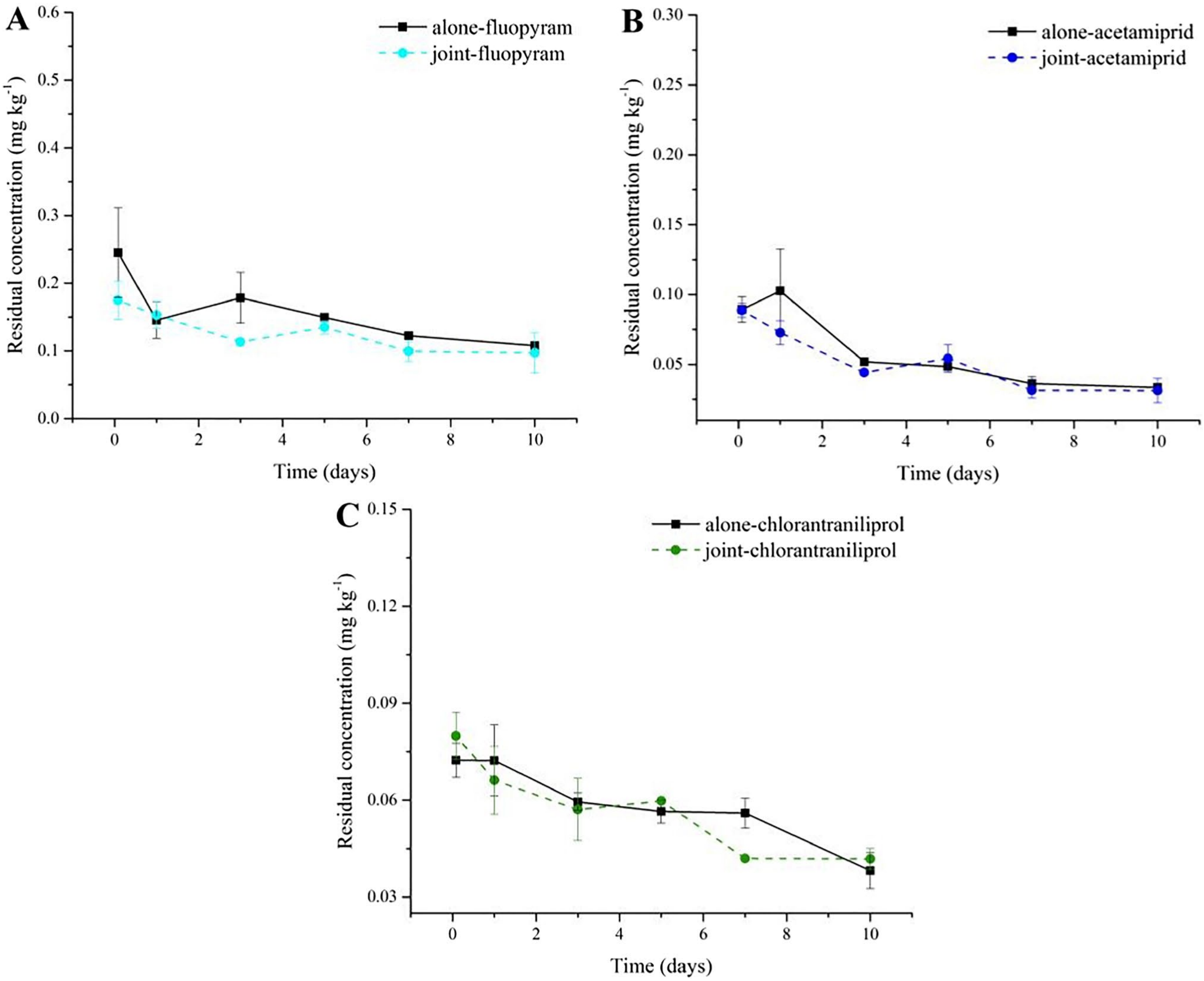


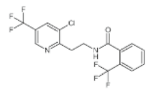
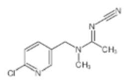
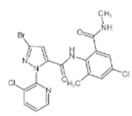
Fig. 2 Dissipation curves of pesticides fluopyram (**A**), acetamiprid (**B**), and chlorantraniliprole (**C**) in strawberry samples after alone and joint applications

concentration of ATP in strawberries increased somewhat after 2 h to 1 day of single application and 3 to 5 days of combined application. The residue in strawberries continued to decrease after that, with ultimate residue amounts of 0.034 ± 0.003 mg kg^{-1} (alone) and 0.031 ± 0.009 mg kg^{-1} (joint), respectively, which were well below the MRLs of China (1 mg kg^{-1}), Korea (1 mg kg^{-1}) and the USA (1 mg kg^{-1}), and slightly higher than the MRLs of the European Union (0.02 mg kg^{-1}). The final digestion rates of ATP in strawberries were 62.47% (alone) and 64.75% (joint).

Dissipation of chlorantraniliprole in strawberries

The concentration curves of CAP were depicted in Fig. 2C, and the dissipation behaviors were estimated using the first-order kinetics equation, with the kinetics parameters provided in Table 3. The dissipation curves of CAP in strawberries alone and in the combination of FOR, CAP, and ATP matched well, with R^2 values of 0.8666 ~ 0.9041. The residues of CAP were 0.072 ± 0.005 mg kg^{-1} (alone) and 0.080 ± 0.007 mg kg^{-1} (joint), respectively, with the sampling interval at 2 h after twice spraying. The dissipation of CAP in strawberries were 0.05% (alone) and 17.22% (joint) after 2 h. The residues, on the other hand, can be swiftly eliminated in the first 3 days, while a portion of the residues is incorporated into cellular components and slowly degrades over time. The final remains of CAP in strawberries were 0.038 ± 0.006 mg kg^{-1} (alone) and 0.042 ± 0.003 mg kg^{-1} (joint), respectively, which were much lower than the MRLs of CAC (0.5 mg kg^{-1}), China (2 mg kg^{-1}), and the USA (0.6 mg kg^{-1}), and

Table 3 Physicochemical properties, residual kinetics, determination coefficients (R^2) and half-life ($T_{1/2}$) of fluopyram (FOR), acetamiprid (ATP), and chlorantraniliprole (CAP) in strawberries under alone and mixed applications

Pesticides	Molecular weight	Chemical structure	Log Kow	Application patterns	Residual kinetics	(R^2)	$T_{1/2}$ (days)
FOR	396.7		5.136	alone	$C = 0.2260e^{-0.0596t}$	0.9407	11.6
				mixed	$C = 0.1603e^{-0.0561t}$	0.7775	12.4
ATP	222.7		2.066	alone	$C = 0.0905e^{-0.114t}$	0.8676	6.1
				mixed	$C = 0.0783e^{-0.104t}$	0.8286	6.7
CAP	483.2		4.721	alone	$C = 0.0749e^{-0.0594t}$	0.9041	11.7
				mixed	$C = 0.0741e^{-0.0634t}$	0.8666	10.9

Note: Log K_{ow}: logarithm of octanol – water partition coefficient

slightly lower than the MRLs of the European Union (0.05 mg kg^{-1}). After 10 days, the digestion rates of CAP in strawberries were 47.26% (alone) and 47.70% (joint).

Comparison of pesticide dissipation in strawberries

The initial deposits of FOR, ATP, and CAP in strawberries were similar when used alone and joint. The concentrations of ATP and CAP under alone application were slightly higher than those of joint application. The FOR, ATP and CAP residues in strawberries decreased to 0.149 ± 0.0001 mg kg^{-1}, 0.048 ± 0.002 mg kg^{-1}, and 0.056 ± 0.004 mg kg^{-1} for alone application after 5th day, but increased to 0.135 ± 0.009 mg kg^{-1}, 0.054 ± 0.010 mg kg^{-1}, and 0.060 ± 0.0001 mg kg^{-1} for joint application. The dissipations of FOR, ATP, and CAP in strawberry residues at the beginning were slower than those at the end. The terminal concentrations (after the 10th day) of FOR, ATP, and CAP in strawberries showed no significant difference whether used in combination or alone. Besides, the dissipation half-life values in strawberries were 11.6 and 12.4 days for FOR, 6.1 and 6.7 days for ATP, and 11.7 and 10.9 days for CAP at alone and joint application, respectively. The dissipation half-life of combination application increased by 0.07 (FOR) and 0.10 (ATP) times and decreased by 0.07 (CAP) times when compared to alone application. The results showed that the differences in half-life caused by alone and joint applications were not statistically significant. The results of this investigation on FOR in pomegranate (Matadha et al. 2021) were consistent with its half-life of 7.3 ~ 15.0 days. Xiao et al. reported the $t_{1/2}$ of ATP in honeysuckle was 5.37 days (Xiao et al. 2022), Moreover, the $t_{1/2}$ of 5.78 days in pigeon pea (Kansara et al. 2021), 6.50 days in celery (Zhang et al. 2022), and 10.0 days in cabbage (Lee et al. 2019) was stated for CAP.

Residues on greenhouse plants peaked in the hours following spraying, then gradually decreased over the next few days, resulting from pesticide degradation (Matadha et al. 2021). Pesticide degradation in plants is primarily influenced by the pesticide's nature, plant metabolic transformation, and microbial degradation (Li et al. 2020). After application, the three pesticides' residues are in the following order: FOR (0.108 ± 0.002 ~ 0.097 ± 0.030 mg kg^{-1}) > CAP (0.038 ± 0.006 ~ 0.042 ± 0.003 mg kg^{-1}) > ATP (0.034 ± 0.003 ~ 0.031 ± 0.009 mg kg^{-1}), respectively. Pesticide dissipation can also be affected by differences in enzymes and microorganisms (Diez et al. 2017; Muñoz-Leoz et al. 2013). The $T_{1/2}$ of the tested pesticides also followed the sequence: FOR (11.6 ~ 12.4) > CAP (10.9 ~ 11.7) > ATP (6.1 ~ 6.7), respectively. The $T_{1/2}$ orders of the three pesticides in this greenhouse trial were consistent with K_{ow} (Table 3). In contrast, FOR has the highest residual and persistent properties that can lead to potential groundwater contamination, and ATP has a lower risk of dissipation than FOR and CAP. For joint application, there are no statistically pronounced variations in the $T_{1/2}$ and final residue levels of the three pesticides, which suggests that there is no substantial interaction between the three pesticides, and that the aggregate effect of the three pesticide mixes is solely dependent on individual effects (Chu et al. 2008).

Dietary risk assessment

Chronic dietary exposure assessment

In addition to comparing ultimate residue concentrations and MRL values, dietary intake risk assessment could be used to evaluate the safety of FOR, CAP, and ATP in strawberries. The ADI values of FOR, ATP, and CAP were 0.01, 0.07, and 2 mg (kg b.w.)$^{-1}$, respectively. For distinct groups of male and female consumers in China (this chapter selects 10 typical groups), body weights and daily intakes were 17.9–65.0 kg and 75.5–229.1 g day^{-1}, respectively (Wang et al. 2021). Tables S4–S6 (Supplementary information) illustrate the RQ_c caused by three pesticide residues found on strawberries in distinct age and gender groups. The values of RQ_c ranged from 2.06 to 7.63% after spraying FOR at 1, 3, 5, 7, and 10 days (Table S4). And the RQ_c values of ATP were between 0.096 and 0.63% (Table S5), the RQ_c of CAP ranged between 0.0041 and 0.016% (Table S6). For three pesticides, the risk of chronic dietary exposure to strawberry residues was highest in the 8- to 12-year-old group. The chronic risks of three pesticides' intake were ranked in the order of FOR > ATP > CAP. The chronic risks (low to high) of the different groups were in an order of over 65-year-old males < 20–50-year-old males < over 65-year-old females < 51–65-year-old females < 51–65-year-old males < 20–50-year-old females < 13–19-year-old females < 13–19-year-old males < 4.5% < 2–7-year-old group < 8–12-year-old group (FOR used alone after 3 days).

FOR had the highest chronic intake risk of the three pesticides, which was primarily attributed to the initial application dose. In the case of ATP and CAP, the lower chronic intake risk for CAP (2 mg (kg bw)$^{-1}$) was mainly due to its much higher ADI than ATP (0.07 mg (kg bw)$^{-1}$). The residual data proved that the greenhouse-cultured strawberries were safe for consumption after being sprayed with three pesticides (FOR, ATP, and CAP). Furthermore, no difference was observed between the RQ_c of pesticides alone and joint application in strawberries gathered from a greenhouse trial. The results revealed that the dietary intake risk of three pesticides in strawberries grown in the greenhouse could be ignored, and the strawberries were safe for Chinese customers even though the tested pesticides were applied in combination and sprayed in accordance with the suggested method.

Whole diet risk assessment

According to the existing results of FOR with the highest chronic risk, the whole diet risk of FOR was further assessed. Table S7 illustrates the MRLs of three pesticides in strawberries approved by various countries. The reference MRLs for this paper were chosen based on the following sequence: China comes first, followed by the CAC, the EU, Japan, Korea, and America. Table S3 shows the Fi and the Chinese dietary model (Li et al. 2021). The food classifications of FOR registered in China contain tubers, dried beans and their products, dark vegetables, light vegetables, fruits, nuts, vegetable oil, sugar, starch, and soy sauce. Strawberries are categorized as fruits. The assessment results showed that the risk of dietary intake FOR (alone and mixed application) was less than 100% (Table S3 and Table S8). Furthermore, the population meal statistics was shown in this dietary risk evaluation date from 2002. However, the public's daily dietary intake may have altered significantly over the years, and the consequences might be undervalued as a matter of fact.

Acute diet exposure assessment

The WHO (World Health Organization) has ascertained that ARfDs (acute reference doses) for some pesticides, which include CAP, are unnecessary. The ARfDs values of the remaining pesticides, FOR and ATP, were 0.5 and 0.1 mg kg^{-1}, respectively. Table S9 exhibits the RQ_a of the pesticides FOR and ATP in six consumption groups with body weights of 13.4–61.3 kg and daily intakes of 339.4–510.2 g day^{-1}, respectively (Chu et al. 2020). The values of RQ_a ranged from 0.32 to 1.48% after spraying FOR in different groups. And the RQ_a of ATP ranged from 0.77 to 3.14% in 60–70-year-old males and 2–4-year-old females, respectively. The acute risks (low to high) of the six groups were in the sequence of 60–70-year-old males < 18–30-year-old males < 60–70-year-old females < 18–30-year-old females < 2–4-year-old males < 3.0% < 2–4 year-old females (ATP used alone). Females were at a slightly higher risk of pesticide exposure from consumed strawberries than males. The RQ_a of FOR and ATP were far less than 100%, which is within the scope of safe consumption.

Conclusion

In this paper, a multi-residue analytical method for fluopyram, acetamiprid, and chlorantraniliprole in strawberries was established using UPLC-MS/MS combined with the QuEChERS approach by optimizing the extraction solvent, the volume of the extraction solvent, the purification technique and the purifying material. The method had average recoveries ranging from 82.62 to 107.79%, relative standard deviations varying from 0.58 to 12.73%, and the limits of quantification and detection were 0.01 and 0.002 mg kg^{-1}, respectively. To gain an understanding of the residue dissipation trends in various application ways of three pesticides on strawberries, the residue dissipation and ultimate residue trials of fluopyram, acetamiprid, and chlorantraniliprole by alone and joint applications on strawberries were performed in a greenhouse. The half-live of fluopyram was 11.6–12.4 days, acetamiprid was 6.1–6.7 days, and chlorantraniliprole was 10.9–11.7 days. The residue dissipation trials revealed no noticeable difference in the residue dissipation traits and half-lives of fluopyram, acetamiprid, and chlorantraniliprole when applied alone or in combination. The residue concentrations on days 1, 3, 5, and 7 will not exceed the Chinese MRLs when the recommended maximum dose is used. The residue trials demonstrated that the greenhouse-grown strawberries were safe for consumers after spraying with three pesticides, even though pesticides were applied in combination.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s11356-023-26544-x.

Acknowledgements The authors appreciate the contributions of all participants in this research.

Author contribution Yanjie Li: conceptualization, data analysis, programming, writing-original draft preparation, writing-reviewing, and editing. Yuqin Luo: writing- original draft preparation, and data analysis. Jinhua Jiang: investigation, writing-reviewing, and editing. Hongmei He: sample analysis. Changpeng Zhang: methodology, writing-reviewing and editing, supervision, and project administration. Xueping Zhao: funding acquisition.

Funding This work was supported by the National Key Research and Development Program of China (No. 2019YFC1605605) and the Basic Public Welfare Project of Zhejiang Province of China (No. LGN21C140006).

Data availability The authors confirm that the data supporting the findings of the current study are available within the article. Further supplementary data is available from the corresponding author upon reasonable request.

Code availability Not applicable.

Declarations

Ethics approval and consent to participate. Not applicable.

Consent for publication Not applicable.

Competing interests The authors declare no competing interests.

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