Residue behavior and dietary risk assessment of fluopyram in cowpea and determination in nine foodstuffs

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Pesticide residues have been one of the food safety problems that plague consumers. It is necessary to develop validated detection methods to monitor pesticide residues in food. In this study, fluopyram was analyzed in fruits (banana, grape, and citrus) and vegetables (tomato, cucumber, cowpea, pepper, eggplant, and potato) by optimizing the QuEChERS in combination with GC-MS/MS. The recoveries of fluopyram in all food matrices ranged from 87.02% to 101.42% with RSD below 9.25%. The matrix effect of fluopyram ranging from −1.41% to 17.67%. Finally, this market investigation resulted in a total of 19 positive samples out of 128 market samples, all of which fell below the MRL with the exception of one tomato sample, which was above the EU MRL. Field trial of fluopyram on cowpea was conducted, the half-lives of fluopyram was 3.03−3.95 days, terminal residues ranged from .031−.596 mg/kg. Dietary risk assessment was performed on cowpea. The result indicates that the dietary risk of fluopyram in cowpeas is acceptable. The method of detection developed in this study could enable better monitoring of fluopyram residues in foodstuffs.

1 Introduction

Pesticides are frequently used in modern agriculture to protect crops from pests, weeds and pathogenic bacteria. However, the dietary risks and ecological pollution caused by pesticides have been extensively documented (Duan et al., 2016; Deng et al., 2020; Duan et al., 2021). Consuming pesticide-contaminated food is a major food safety hazard, and some pesticides even have carcinogenic, teratogenic and mutagenic risks (Hotchkiss, 1992). Therefore, the analysis and detection techniques of pesticides have gradually become an important research field, especially of the new pesticides developed in recent years, whose hazards are still unclear during long-term exposure and application.

Fluopyram (N-[2-[3-chloro-5-(trifluoromethyl) pyridin-2-yl] ethyl]-2-(trifluoromethyl) benzamide) is a new succinate dehydrogenase-inhibiting fungicide. It is an effective fungicide applied to cucumbers, tomatoes, cowpeas and other crops by spray and drip irrigation. In animal thyroid tumor studies, fluopyram has been reported to produce toxicity, which induces carcinogenesis in the thyroid gland, and leads to an increased risk

of developing tumors (Rouquié et al., 2014). In addition, fluopyram has a significant negative impact on soil microorganisms, especially respiration and biomass, leading to serious changes in the microbial community that are difficult to recover in the short term (Zhang et al., 2014). Maximum residue limits (MRL) for fluopyram have been established in many countries and regions to ensure food safety. For example, China has set MRL for fluopyram in commonly used crops (.01–2.00 mg/kg) (GB 2763–2021). The European Union has set MRL of .01–1.00 mg/kg for most fruits and vegetables (European Commission Pesticides database, 2020). To ensure that agricultural production complies to the MRL, the establishment and development of analytical methods for pesticides is particularly critical. Related studies have already reported the detection of fluopyram. Yogendraiah Matadha et al. (2021) developed the determination of fluopyram in pomegranate for the study of the dissipation process. The analytical method for fluopyram in tomatoes and cucumbers was established by Vargas Pérez et al. (2020) in their study of the residual behavior of fluopyram in greenhouses. Previous analytical method was applicable to fewer foodstuffs and could not complete the monitoring of different fruits and vegetables. According to the properties of fluopyram, it is essential to establish an analytical method that is applicable to a wide range of foodstuff matrix to enable accurate detection and monitoring.

Fluopyram has been widely used for disease and nematode control on tomatoes, grapes and other fruits and vegetables. Proffer et al. (2013) mention fluopyram as one of the most effective methods for controlling leaf spot and powdery mildew on cherries. Fluopyram plays a huge role in the treatment of grapes grey mould and alternating with other pesticides can reduce the development of resistance (Vitale et al., 2016). In addition, Ji et al. (2019) reported that fluopyram was significantly more effective than abamectin in controlling the southern root-knot nematode in tomatoes and could be used for root-knot nematode control in tomatoes. He et al. (2022) found that fluopyram slowed peel browning by inhibiting respiration and increasing glutamate dehydrogenase activity in litchi peel. The current study also indicates that fluopyram is of great potential for application on fruits and vegetables.

In recent years, common methods for the detection and quantification of pesticide residues in fruits and vegetables are indicated GC and LC, and the selection of a corresponding detector for the detection and analysis according to the physicochemical properties of pesticides (Narenderan et al., 2020). Traditional gas and liquid chromatographic methods are inadequate to provide reliable analytical results due to insufficient sensitivity for trace analysis, and sometimes even for MRL of pesticides. Therefore, there is a need to develop new alternative methods in combination with mass spectrometers to improve the sensitivity and accuracy of pesticide residue detection in fruits and vegetables. For example, applying mass detection on the foundation of traditional detection techniques, the method can become more sensitive and accurate. GC-MS/MS with selected ion monitoring mode (SIM) and selected reaction monitoring mode (SRM) greatly reduce matrix interference and occurrence of false positives by detecting ion pairs of target compounds (Ly et al., 2020). A well-defined pre-treatment method is essential when faced with complex foodstuff matrices. Recently, QuEChERS methods have come into play in the field of environmental monitoring, pesticide residue analysis and food analysis due to its simple operation steps, short extraction time and less solvent use (Narenderan et al., 2020; Gabardo et al., 2021; Zhou et al., 2021). For complex matrix, such as those containing large amounts of chlorophyll or sugars, QuEChERS should be adjusted and modified to varying degrees (adsorbent type, adsorbent dosage, etc.).
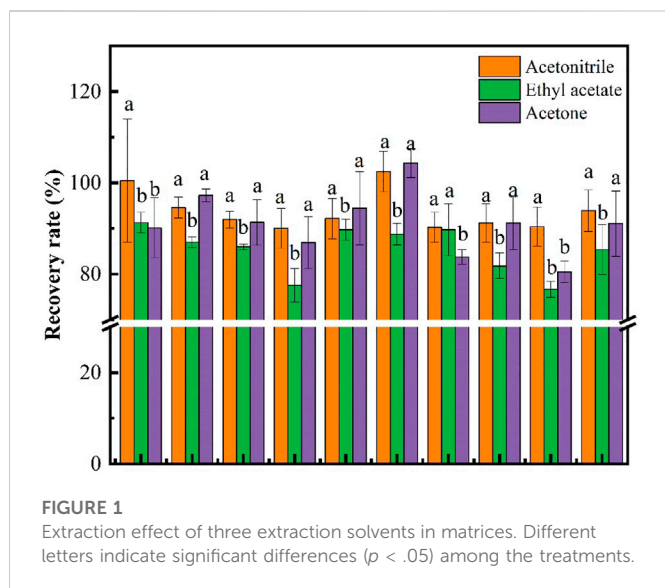
Natural degradation is the main degradation pathway of pesticides in crops, and environmental factors such as light, temperature and moisture are among the most important factors in the dissipation of pesticides in agricultural systems. Mukherjee et al. (2018) studied the ablation of pretilachlor and butachlor at three CO_2 levels and temperatures and found that the half-lives of both herbicides shortened to varying degrees as the CO_2 concentration increased. The half-lives of the two pesticides at 40°C were 9.7 and 19.4 days, respectively, which were nearly half as short as those at 25°C (16.2 and 26.7 days). Kwon and Armbrust (2006) found that chlorothalonil was nearly 90% degraded in water/sediment after 24 h under simulated sunlight conditions. In addition, pesticides are broken down into other substances by plants, microorganisms and animals. Microbial degradation is the more common mode of abatement (de Albuquerque et al., 2018). Microbial degradation is considered to be a more promising method for degrading pesticides (Huang et al., 2018). Yuan et al. (2021) found that *Lactobacillus plantarum* was able to rapidly degrade 81.28% of dimethoate in milk through phosphatase during milk fermentation. In agricultural production, differences in application methods can also slightly influence the process of pesticide dissipation in agricultural systems. Fu et al. (2020) applied acetamiprid and cyromazine at different doses and frequencies to cowpea fields and showed that dissipation of both pesticides slowed down with increasing dose and frequency of application. Similar findings were made by Sakthiselvi et al. (2020) where three concentrations of indoxacarb (60, 90 and 120 g a.i./ha) were applied to tomatoes and the half-life gradually increased with increasing concentration. Plants also play a vital role in the dissipation of pesticides. An example of this is the growth dilution effect caused by plant growth. Not only does plant growth reduce the proportion of pesticide residues in plant material, but vigorous plant growth is accompanied by a faster metabolism, which accelerates the metabolic transformation of pesticides within the plant. Wang et al. (2022) reported that the dissipation rate of emamectin benzoate in tender cowpeas was faster than that in old.

The QuEChERS pretreatment method combined with GC-MS/MS is a convenient and safe detection method. There is still a lack of GC-MS/MS assays for the detection of fluopyram in a variety of fruit and vegetable matrices. In this study, we screened suitable adsorbents by comparing the adsorption effectiveness of seven adsorbents (amino multi-walled carbon nanotubes (MWCNTs-NH$_2$), multi-walled carbon nanotubes (MWCNTS), hydroxylated multi-walled carbon nanotubes (MWCNTs-OH), GCB, C18, PSA and acidic alumina (ALO). The selected adsorbents were used in a modified QuEChERS method combined with GC-MS/MS to detect fluopyram residues in nine foodstuffs (tomato, cucumber, cowpea, pepper, eggplant, potato, banana, grape, and citrus). Among the foodstuffs, field trials were conducted on cowpeas to investigate the dissipation and residue behavior of Fluopyram, which was used to assess the dietary risk of Fluopyram. The aim of this study was to improve the efficiency of monitoring fluopyram in various vegetables and fruits by shortening the analysis time of pesticide residues, which provides theoretical basis and technical support for scientific use of pesticides.

2 Materials and methods

2.1 Reagents and Apparatus

Fluopyram standard was purchased from Shanghai Macklin Biochemical Technology Co. (Shanghai, China). Acetonitrile, ethyl

FIGURE 1
Extraction effect of three extraction solvents in matrices. Different letters indicate significant differences ($p < .05$) among the treatments.

acetate and ethyl acetate were purchased from Xilong Chemical Co. (Shenzhen, China). Acetone was purchased from Guangzhou Chemical Reagent Factory (Guangzhou, China). Sodium chloride was purchased from Beijing Chemical Reagent Company (Beijing, China). PSA and GCB were purchased from Shanghai Ampoule Experimental Technology Co. (Shanghai, China). MWCNTs, MWCNTs-NH$_2$, C18, MWCNTs-OH and ALO was purchased from Shanghai Macklin Biochemical Technology Co. (Shanghai, China). The rotary evaporator was purchased from Shanghai Shensheng Technology Co. (Shanghai, China). Vacuum pump purchased from Wenshi Vacuum Equipment Co. (Linhai, China). The H1850R centrifuge was purchased from Xiang Yi Centrifuge Co. (Hunan, China).

2.2 Analysis method

2.2.1 Solution preparation

Fluopyram standard stock solution (1000 mg/L, ethyl acetate) was configured using a solid standard of fluopyram. The fluopyram standard was weighed 10.0 mg (accurate to .0001 g) and added to 10.0 ml volumetric bottles, fixed with ethyl acetate and stored at −20°C. The standard working solutions (10.0 mg/L and 1.0 mg/L) diluted with ethyl acetate were placed in the refrigerator at 4.0°C until use.

2.2.2 Sample preparation

The sample was weighed 5.00 g and deposited in centrifuge tube (50.0 ml). Added 10.0 ml of acetonitrile and mix the sample for 5 min using a high-speed homogenizer. Afterwards, sodium chloride was accurately weighed 5 g and added to the centrifuge tube and vortexed for 3 min, followed centrifuge the processed tubes for 5 min (5000 r/min). Then supernatant (2 ml) was added to 5.0 ml centrifuge tube containing purifying agent and anhydrous MgSO$_4$ and vortexed for 5 min and centrifuged at 5,000 r/min for 10 min. Removed 1 ml of supernatant from centrifuge tube and rotary evaporated at 40°C, then was re-dissolved with ethyl acetate and subsequently injected into the GC-MS/MS system. Sample preparation flow chart in Supplementary Figure S1.

2.2.3 GC-MS/MS

The analysis of fluopyram was carried out on a Thermo Fisher gas chromatograph equipped with a TRACE 1300 gas chromatograph and a TSQ 9000 triple quadrupole mass spectrometer. The column was a Thermo Fisher TG-5SilMS weakly polarised capillary column (30 m × .25 mm×.25 μm). The programmed ramp-up was started at 120°C and held for 2 min, then increased to 300°C at a rate of 30°C min^{-1} and held for 2 min, for a total run time of 10 min. The transmission line temperature and ion source temperature were both 280°C. The mass spectrometer sampled electron ionization (EI) for the quantitative analysis of fluopyram in SRM. Two transitions were used for quantification and qualification, with 144.9 > 95 (14 eV) and 144.9 > 75 (20 eV) for fluopyram.

2.3 Method validation

2.3.1 Linearity and recovery of the method

The established method for the determination of fluopyram in fruits and vegetables was evaluated in terms of linearity, accuracy and precision according to the document SANTE/11312/2021 (European Commission, 2021). Linearity was evaluated by linear fitting of fluopyram measurements for all foodstuffs matrix at seven concentration levels. The analysis was considered accurate when $R^2 > .99$ (Li et al., 2021).

Accuracy was verified by spiking experiments at three concentration levels. Fluopyram was added to blank matrix of nine fruits and vegetables for spiked recovery at levels of .01, .2, and 2 mg/kg in grapes, tomatoes, and peppers; and .01, .1, and 1 mg/kg in the remaining fruits and vegetables. The treatments were performed according to the extraction method in Section 2.2.2. The spiking experiment was repeated three times for each level and the relative standard deviation (RSD) was calculated to verify the precision.

2.3.5 Matrix effect

Matrix effects (ME) can affect the reliability and sensitivity of analytical methods. The ME of fluopyram in each matrix was calculated using the following formula (Zaidon et al., 2019):

$$ME = \frac{B - A}{A} \times 100\%$$

A and B represent the slope of the standard curve under ethyl acetate solution and blank matrix solution, respectively.

2.4 Actual sample analysis

2.4.1 Market sample collection

Market samples are collected and analysed in order to verify the reliability of the detection method in the application process. The samples are randomly selected and are representative. 128 samples were collected from the market in Sanya, Hainan Province, during June and July 2022. The market samples were analysed for residues according to the established detection method to count the residues of fluopyram in fruits and vegetables.

2.4.7 Field trial

In addition to market samples, residue analysis was performed on field samples as an example of cowpea samples. The field trial was
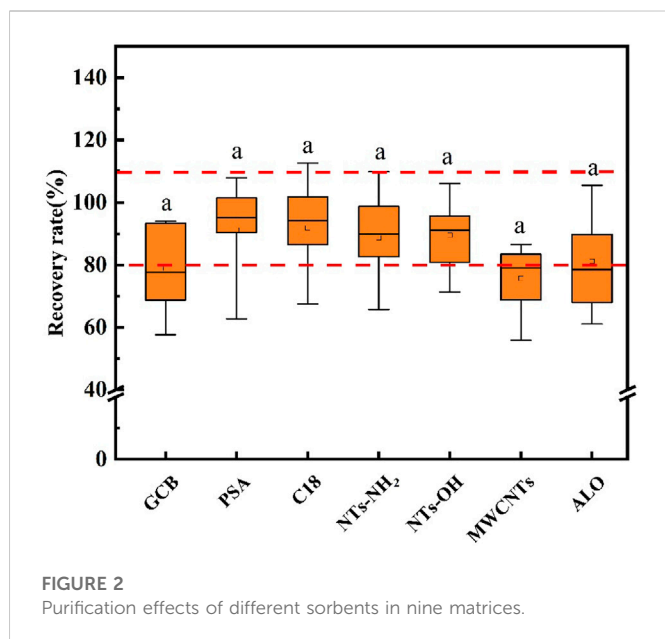
FIGURE 2
Purification effects of different sorbents in nine matrices.

TABLE 1 Composition of the two pre-treatment methods.

Number	A	B	C	Method
1	PSA	C18	MWCNTs-OH	50 mg A+50 mg B+50 mg C
2	PSA	C18	MWCNTs-NH$_2$	50 mg A+50 mg B+50 mg C

conducted in Sanya, Hainan Province, China (18°23′N, 109°9′E). Cowpeas were selected for the dissipation and terminal residue tests, with an area of 100 m² (20 m × 5 m). A buffer zone of 2 m width was divided between adjacent test areas. The field trials referred to **NY/T 788-2018** (Guidelines for pesticide residue trials in crops) issued by China.

Dissipation: 41.7% fluopyram suspension was applied at 62.55 g a.i./ha (the maximum recommended dose). The dissipation experiment was applied when the cowpea fruits were halfway through growth to mature fruit. Cowpeas were collected in the upper, middle and lower layers of the cowpea plants, respectively. Cowpea samples were collected randomly for analysis at 0 (2 h), 1, 3, 5, 7, 10, and 14 days after application. All samples were labelled and stored at −20°C for further analysis. The dissipation of fluopyram in cowpea samples from field was delineated by a first-order kinetics model.

Terminal residues: The applied doses included a low dose of 62.55 g a.i./ha and a high dose of 93.825 g a.i./ha. Fluopyram was applied three or four times. The spraying interval of fluopyram was 7 days. Cowpea samples were collected at 5, 7, and 10 days after the last application. The picked cowpea were briefly processed and stored in a −20°C refrigerator.

2.5 Risk assessment

The long-term dietary risk and short-term dietary risk of fluopyram were assessed using national estimated daily intakes (NEDI) and risk quotients (RQ) based on data published by WHO GEMS/FOOD (Global Environment Monitoring System/Food

Contamination Monitoring and Assessment Programme) in combination with the median residue values for fluopyram, the MRLs and the acute reference dose (ARfD). The calculation formula is as follows (Institute of Quality Standards and Testing Technology for Agro-products and Chinese Academy of Agricultural, 2007):

$$NEDI = \sum Fi \times STMR$$

$$RQ = \frac{NEDI}{ADI \times bw1} \times 100\%$$

The above formula is used for long-term risk assessment, where STMR represents the median pesticide residue; Fi represents the dietary reference intake of a food for Chinese residents; bw1 represents the average body weight of Chinese residents (63 kg) (Wang et al., 2022); and ADI is the allowable daily intake of fluopyram, ADI = .012 mg/(kgbw).

$$NESTI = \frac{U \times HR \times v + (LP - U) \times HR}{bw2}$$

$$\%ARfD = \frac{NESTI}{ARfD} \times 100$$

The above formula is used for short-term dietary risk assessment. HR represents the maximum residue level; LP represents the large meal consumption of food (.3882 kg); U represents the quality of individual products in terms of edible portions (.0194 kg); v is the coefficient of variation, usually taken as three; bw2 represents the average body weight of our population of different sexes at all ages (Wu and Li, 2015). ARfD stands for acute reference dose, and fluopyram has an ARfD of .5 mg/(kgbw). Typically, %ARfD >100 indicates an unacceptable short-term exposure risk; conversely, it indicates an acceptable short-term dietary risk.

2.6 Statistical analysis

All the analysis was performed in triplicate. The results are expressed as mean and RSD. All analyses were performed using Microsoft Excel 2016 and IBM SPSS Statistics 23. Significant difference procedures were reported at $p < .05$ level. The graphics were drawn using Origin 2018.

3 Results and discussion

3.1 Optimization of QuEChERS method

3.1.1 Extraction solvent selection

In the analysis of pesticide residues, the selection of a suitable extraction solvent can be effective extraction of pesticides from the foodstuff matrix, the commonly used organic solvent extractants include acetonitrile, acetone and ethyl acetate (Dušek et al., 2020; Maragou et al., 2020; Tong et al., 2021). Three different extraction solvents were added to the nine foodstuff samples, and spiked recovery tests (.1 mg/kg) were conducted to screen the suitable extraction solvents. The results in Figure 1 showed that the highest average recovery among the nine fruits and vegetables was obtained from acetonitrile (93.91%), followed by acetone (91.12%), while

TABLE 2 Spiked recoveries and relative standard deviations (RSD) for fluopyram (*n* = 3).

Matrix	Spike level (mg/kg)	Method 1[a]		Method 2[b]	
		Average recovery (%)	RSD (%)	Average recovery (%)	RSD (%)
Cowpea	1	108.31	4.60	101.42	1.17
	0.1	97.38	3.36	97.70	2.59
	.01	88.81	7.96	95.67	8.37
Cucumber	2	95.30	1.54	95.05	1.78
	0.2	96.53	6.63	98.08	3.96
	.02	96.40	4.91	93.96	6.85
Eggplant	1	90.19	8.25	92.74	2.50
	0.1	93.98	1.17	96.80	.81
	.01	102.45	3.55	97.00	2.39
Pepper	2	89.24	3.32	92.50	6.19
	0.2	93.61	7.46	98.94	6.26
	.01	99.07	5.15	95.69	3.88
Potato	1	91.46	3.67	96.14	2.57
	0.1	91.02	2.63	95.79	1.44
	.01	101.34	3.89	94.15	1.83
Tomato	1	91.80	1.60	97.77	1.92
	0.1	94.43	3.26	93.26	1.21
	.01	98.64	1.52	94.01	1.52
Banana	2	94.56	3.97	88.12	1.37
	0.2	91.00	1.29	95.96	6.99
	.02	78.46	1.32	94.24	3.08
Orange	1	101.96	4.15	94.45	3.19
	0.1	96.67	2.17	93.36	2.14
	.01	89.15	7.55	87.78	4.52
Grape	1	93.43	3.04	101.32	8.81
	0.1	78.19	2.05	94.60	1.59
	.01	70.38	1.75	87.02	9.25

[a]50 mg PSA, 50 mg C18, 50 mg MWCNTs-OH, and 200 mg $MgSO_4$.
[b]50 mg PSA, 50 mg C18, 50 mg MWCNTs-NH_2, and 200 mg $MgSO_4$.

ethyl acetate was the least effective extraction (85.39%). However, the more polar acetone may extract more impurities that would interfere with the analysis of the target compound (Zhou et al., 2021), and that ethyl acetate did not perform satisfactorily in grape (77.56%) and eggplant (76.66%), acetone and ethyl acetate were not suitable as extraction solvents for fluopyram. The extraction of acetonitrile was satisfactory. Therefore, the extraction study of acidic acetonitrile was not performed in this study. In several previous studies, acetonitrile was also used for the extraction of fipronil from meat products and acetamiprid from cowpea (Fu et al., 2020; Han et al., 2021). Therefore, acetonitrile was chosen as the extraction solvent for fluopyram for the further study.

3.1.2 Screening the adsorbent

The choice of sorbent for QuEChERS could vary depending on the analyte being used. Fruit and vegetable matrices are rich in pigments, water, polysaccharides and acids, a comparison of seven purification agents, including MWCNTs, MWCNTs-NH₂, MWCNTs-OH, PSA, GCB, C18, and ALO, was used to select suitable purification agents for the next step in the study. These adsorbents have been used extensively for the pretreatment of pesticide residues in foodstuffs (Gonzalez-Curbelo et al., 2013; Chen et al., 2014; Chen et al., 2019; Chen H. et al., 2021).

The sorbents were compared at the .1 mg/kg level of fluopyram additive, the results are shown in the Supplementary Table S1,

TABLE 3 Linear equation, ME, and LOQ of fluopyram in nine foodstuff matrices by GC-MS/MS.

Matrix	Range (μg/kg)	Linear equation	R^2	ME (%)	LOQ (mg/kg)
Cowpea	10–1000	Y = 551164x + 174.73	.9998	14.72	.01
Cucumber	10–2000	Y = 552241x+142.79	.9998	14.99	.01
Eggplant	10–1000	Y = 514946x + 293.29	.9997	7.18	.01
Pepper	10–2000	Y = 515037x + 287.95	.9997	7.20	.01
Potato	10–1000	Y = 473653x + 318.04	.9993	−1.41	.01
Tomato	10–1000	Y = 563626x + 381.75	.9997	17.31	.01
Banana	10–2000	Y = 545982x + 115.38	.9998	13.64	.01
Orange	10–1000	Y = 512304x + 183.18	.9999	6.63	.01
Grape	10–1000	Y = 544522x + 293.45	.9998	13.34	.01

FIGURE 3
GC-MS/MS chromatograms of foodstuff samples spiked with 2 mg/kg fluopyram [(A) eggplant; (B) citrus; (C) banana; (D) cowpea; (E) tomato; (F) cucumber; (G) chili; (H) grape; (I) potato].
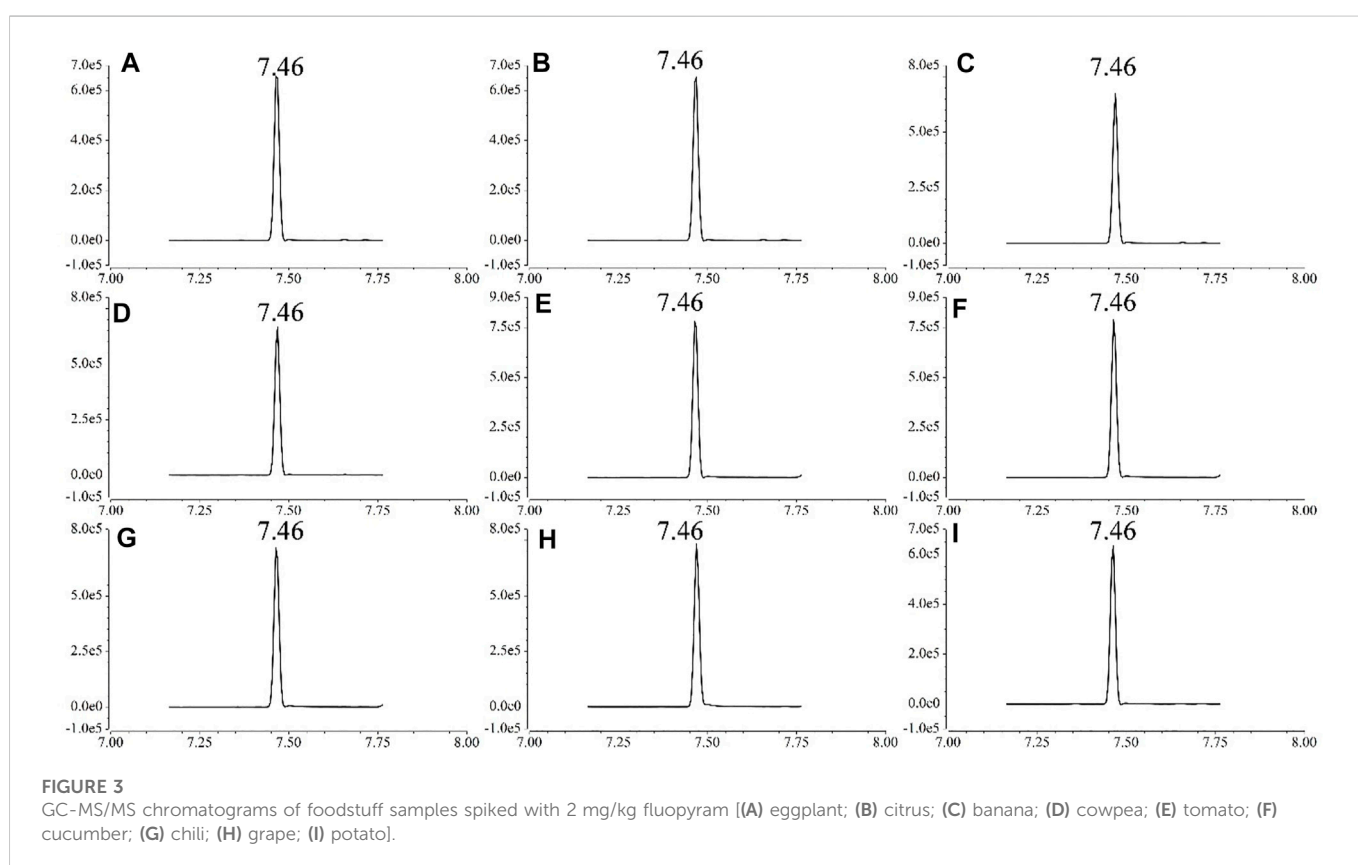
where the extraction of the seven sorbents in different fruit and vegetable matrices varied considerably. The recovery was unsatisfactory in different food matrices when any adsorbent was used alone. For example, the highest recovery in banana was only 71.35%, and in grapes the highest recovery was only 80.90% except for C18 and MWCNTs-NH$_2$. However, in cucumber, which was a relatively simple matrix, the lowest recovery of all adsorbents was 85.20%, and all were in the range of 80%–110%.

As can be seen from Figure 2, the adsorption of GCB, MWCNTs and ALO was not satisfactory and the average recovery was below 80%, especially for banana, which were only 57.60%, 55.86% and

61.10% (Supplementary Table S1). The average recovery of PSA, C18, MWCNTs-NH$_2$ and MWCNTs-OH were all in the range of 80%–110%. PSA contains amino functional groups and is effective in adsorbing acids from fruit and vegetable matrices. C18 can produce relatively high adsorption of non-polar compounds through van der Waals forces (Wang et al., 2019; Liu et al., 2021). MWCNTs-NH$_2$ and MWCNTs-OH has a strong adsorption effect on interfering substances due to their large specific surface area (Pallavi et al., 2021). After a comprehensive evaluation, PSA, C18, MWCNTs-NH$_2$ and MWCNTs-OH were selected for combined adsorption in this study to determine the optimum adsorbent formulation.

TABLE 4 Residue of fluopyram in fruits and vegetables in Sanya.

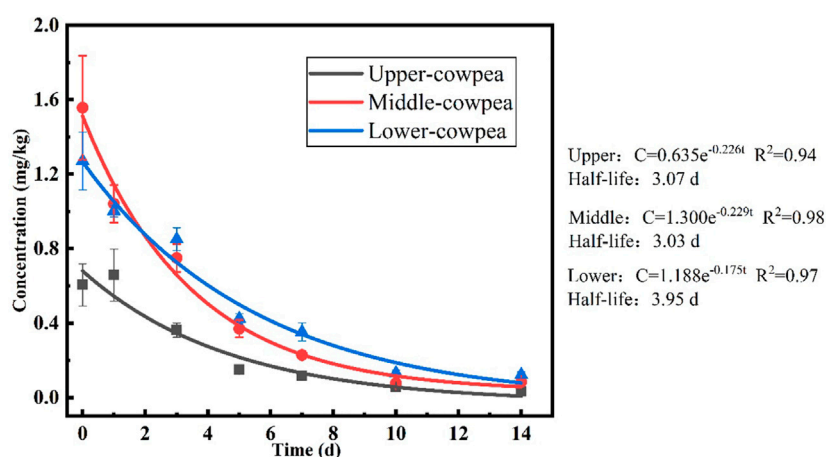| Food	Sample number	Number of positives	MAX residue (mg/kg)	MRL (China)	MRL (EU)
Cowpea	20	6	.18	1	3
Cucumber	20	10	.34	0.5	0.6
Eggplant	10	0		—	0.4
Pepper	12	0		2	-
Potato	16	0		.03	.08
Tomato	20	3	.84	1	0.5
Banana	10	0		0.3	0.8
Orange	10	0		1	0.5
Grape	10	0		2	2
Total	128	19	.84		

FIGURE 4
Dissipation and half-life of fluopyram residues in cowpea.

3.1.3 Optimizing the adsorbent

PSA, C18, MWCNTs-OH, and MWCNTs-NH$_2$ were identified as adsorbents for optimization. Considering the similar functions of MWCNTs-NH$_2$ and MWCNTs-OH, both of which have good pigment removal, two combination formulations were designed, as shown in the Table 1. In previous studies, QuEChERS has mostly used 50 mg of sorbent (Fu et al., 2020; Zhou et al., 2021; Wang et al., 2022), so this study has added 50 mg of each sorbent.

To verify the reliability of two methods, three levels of spiked recovery tests were designed in nine food matrices, with the spiked levels containing MRL. The results of the comparison of the recoveries at the three fluopyram levels are shown in Table 2. Method 1 showed a range of 70.38%–108.31% with RSD of 1.17%–8.25% at the three spiked levels; Method 1 showed a range of 87.02%–101.42% with RSD of .81%–8.81%. The recoveries and RSD of both methods were in accordance with the SANTE guidelines to analyse the pesticides residues. However, Method 1 is not as satisfactory as Method 2 in grapes and bananas. The recoveries of Method 1 were 70.38%

(.01 mg/kg) and 78.19% (.1 mg/kg) in grapes and 78.46% (.1 mg/kg) in bananas. Method 2 had the lowest recovery of 87.02% across all foodstuffs. What is clear is that Method 2 is a better method. This may be because MWCNTs-NH$_2$ contains more amino groups than MWCNTs-OH (Chen S. et al., 2021), which can additionally adsorb more acidic substances and ensure a more stable pretreatment method. It has been reported that the higher number of nitrogen atoms in MWCNT-NH$_2$ can form hydrogen bonds with the hydrogen atoms in other interfering substances and thus adsorb more interfering substances (Yu et al., 2020). Therefore, Method 2 was chosen as the final pre-treatment method in this study.

3.2 Method validation

Each blank matrix was treated by selected pre-treatment methods and the resulting blank matrix solutions were diluted into a series of matrix standard solutions at concentrations of .01, .02, .05, .1, .2, .5,

TABLE 5 The terminal residue levels of fluopyram in cowpea (*n* = 3).

Sampling time d)	Sampling part	62.55 g a.i./ha		93.825 g a.i./ha	
		3 times	4 times	3 times	4 times
5	Upper[a]	.137 ± .019	.152 ± .016	.198 ± .009	.216 ± .015
	Middle[b]	.356 ± .055	.431 ± .032	.495 ± .015	.518 ± .033
	Lower[c]	.456 ± .079	.494 ± .049	.567 ± .029	.596 ± .033
7	Upper	.077 ± .011	.084 ± .011	.120 ± .008	.136 ± .038
	Middle	.175 ± .026	.182 ± .041	.240 ± .017	.260 ± .016
	Lower	.288 ± .051	.295 ± .057	.394 ± .135	.439 ± .105
10	Upper	.031 ± .006	.041 ± .011	.060 ± .016	.076 ± .030
	Middle	.052 ± .005	.050 ± .008	.088 ± .017	.126 ± .031
	Lower	.096 ± .034	.113 ± .032	.151 ± .075	.171 ± .067

[a]Cowpeas collected from the upper layers of the plant.
[b]Cowpeas collected from the middle layers of the plant.
[c]Cowpeas collected from the lower layers of the plant.

TABLE 6 The long-term dietary exposure risk assessment of fluopyram.

Food classification	Fi (kg)	References residue limits (mg/kg)	Sources	NEDI (mg)	ADI (mg)	RQ (%)
Rice and its products	.2399	.02	EU	.004798	.012 × 63	
Flour and its products	.1385	—				
Other cereals	.0233	.07	China	.001631		
Tubers	.0495	.03	China	.001485		
Dried beans and their products	.016	—				
Dark vegetables	.0915	.463	STMR	.0423645		
Light vegetables	.1837	.09	China	.016533		
Fruits	.0457	1	China	.0457		
Livestock and poultry	.0795	1.5	China	.11925		
Milk and its products	.0263	0.8	China	.02104		
Egg and its products	.0263	2	China	.0526		
Fish and shrimp	.0301	—				
Vegetable oil	.0327	—				
Soy sauce	.009	—				
Sugar, starch	.0044	.04	China	.000176		
Salt	.012	—				
Total	.8462			.418	.756	55.33

and 1.0/2.0 mg/L. Linear regression of the measured data for fluopyram concentrations was performed using Excel, fluopyram has a satisfactory linearity in every matrix and the R^2 was >.999 (Table 3).

Three parallel recovery experiments were carried out on blank matrix samples at three spiked levels to validate the reliability of the method, and the recovery of fluopyram ranged from 87.02% to 101.42% and RSD between .81% and 9.25% (Table 3), in accordance with the requirement of SANTE guideline, indicating that the method can meet the requirements for routine analysis of the target compounds. The lowest concentration of the recovery experiment was taken as LOQ (for all matrices this is .01 mg/kg). As shown in Figure 3, fluopyram was detected in each matrix without interference from other compounds.

The standard curves were established using pure solvents cannot be used for residue analysis and detection in actual samples, because

TABLE 7 The short-term dietary exposure risk assessment of fluopyram in cowpea.

Age	Gender	Body weight (kg)	ARfD (mg/kg·bw)	NESTI (mg/kg·bw)	%ARfD
2–7	—	19.7	0.5	.0142	2.84
8–12	—	33.1	0.5	.0077	1.54
13–19	Male	56.4	0.5	.0045	.90
	Female	50.0	0.5	.0051	1.02
20–50	Male	63.0	0.5	.0040	.81
	Female	56.0	0.5	.0045	.91
51–65	Male	65.0	0.5	.0039	.78
	Female	58.0	0.5	.0044	.88
>65	Male	59.5	0.5	.0043	.86
	Female	52.0	0.5	.0049	.98

the matrix effects could enhance or diminish the response of the instrument to the target (Han et al., 2021). The matrix standard curve and matrix effect were listed in Table 3. It was found that the matrix effect of fluopyram was acceptable in all matrices, with all resulted ranging from −20% to +20% (−1.41% to −17.67%), which could be considered as a better QuEChERS method (Walorczyk, 2014). Yogendraiah Matadha et al. (2021) and Vargas Pérez et al. (2020) have both developed methods for the detection of fluopyram, but only for one or two food matrices. There are limitations in the practical application. In contrast, the method developed in this study is applicable to nine food matrices and can be better applied to the monitoring of pesticide residues. In summary, the method is reliable and can fulfill the demands of pesticide monitoring and analysis. The MRL of fluopyram in foodstuffs registered by countries and organizations are shown in Supplementary Table S2.

3.3 Actual sample analysis

3.3.1 Residue of fluopyram in the market sample

Based on the analytical method developed in this study, a total of 128 fruit and vegetable samples were tested for fluopyram residues in June and July 2022 in Sanya City, Hainan Province (Table 4), with a total of 19 positive samples. There were 10 cases of cucumber, 6 cases of cowpea and 3 cases of tomato. All samples did not exceed the limit according to GB 2763-2021, but one sample of tomato exceeded the EU MRL (.5 mg/kg).

3.3.2 Residue behavior of fluopyram in field cowpea

The samples from the field trials were analysed using the established method and the dissipation of fluopyram on cowpea was in accordance with the first order kinetic model. As shown in Figure 4, the half-life of fluopyram in cowpea plants ranged from 3.07 to 3.95 days. The half-life values reported in this study were similar to those of mango under similar treatments. On mango fruit, the half-life of fluopyram was 4.3–5.4 days (Mohapatra et al., 2018). This indicated that the persistence of fluopyram was weak in cowpea. The half-life of fluopyram in watermelon was 6.48–6.60 days (Dong and Hu, 2014). The dissipation in cowpea is faster than that in watermelon. The main reasons for this may be caused by differences in climatic conditions and crop types.

Apart from this, the half-life of fluopyram in cowpea was 3.07 days in the upper layer and 3.03 and 3.95 days in the middle and lower layers, respectively (Figure 4). The dissipation rate of cowpea in the upper and middle layers was higher than that in the lower. Cowpeas in the upper and middle layers have a stronger tendency to grow and a faster metabolism. Thus, there was a higher growth dilution effect than the lower cowpeas. Pesticides are generally degraded gradually as plants grow, which is one of the significant pathways for pesticide dissipation. Similar results have been reported in previous studies that significant differences in pesticide dissipation rate between tender and old cowpeas (Wang et al., 2022). In addition, environmental factors such as sunlight, temperature and humidity also play a fundamental role in the dissipation (Farha et al., 2016). For example, pesticides on greenhouse crops commonly dissipate more slowly than in the open due to lack of light and confined space (Chen H. et al., 2021). Upper and middle cowpeas have more exposure to sunlight, which promoted faster dissipation of fluopyram.

As shown in Table 5, the terminal residues of fluopyram in cowpea ranged from .031–.596 mg/kg. The terminal residues of fluopyram in cowpea increased with the frequency of spraying and application rate. In terms of spatial distribution, fluopyram residues were higher in the lower cowpea than in the middle and upper layers, with the least residues in the upper layer. This was similar to the findings following the application of boscalid and pyraclostrobine in grape fields (Chen et al., 2019). In China and EU, the MRL for fluopyram in cowpea (with pods) are 1 mg/kg and 3 mg/kg. Residue levels at 5, 7, and 10 days after fluopyram application were below the MRLs (China and EU). This indicates that cowpea is relatively safe to consume for 5 days after the application of fluopyram at the recommended dose.

3.4 Dietary risk assessment

Humans can gradually enrich pesticides through the living environment and food chain, leading to different hazards and diseases (Yang et al., 2020). Although most of the pesticides can be removed during food processing and cooking, the safety risk of pesticides is still not negligible (Liu et al., 2016). In this study, a risk assessment of cowpea fruit was carried out based on residue data from field trials.

The terminal residues of fluopyram in cowpea ranged from .031 to .596 mg/kg, with a STMP of .463 mg/kg and HR of .596 mg/kg. Based on the information reviewed, the ADI and ARfD were set at .012 and .5 mg/kg bw (PPDB: Pesticide Properties DataBase, 2022), respectively. The calculated NEDI, RQ and NESTI are recorded in Tables 6, 7.

In the long-term dietary risk assessment, the RQ value for fluopyram was 55.33%, which is less than 100%, indicating that the long-term dietary risk of this pesticide is acceptable (Fan et al., 2019). As shown in Table 7. The short-term dietary risk of fluopyram in cowpea was calculated using NESTI and ranged from .78% to 2.84%, with %ARfD less than 100% for all age groups, with the highest risk for children aged 2–7 years (2.84%), but well below 100%, indicating that the short-term dietary risk of fluopyram in cowpea is extremely low.

4 Conclusion

In this study, an analytical method was developed for the analysis of fluopyram in nine different plant matrices. The method was further optimised based on the QuEChERS method, and the clean-up effects of seven purification agents were compared. Four purification agents were selected, among which the combination of PSA, C18 and MWCNTs-NH$_2$ could meet the purification requirements well. The recoveries of the nine foodstuffs from 87.02% to 101.42% with relative standard deviations below 9.25%. Finally, a total of 19 positive samples out of 128 market samples were analyzed based on the method used in this study, all samples were below the MRL but one case of tomato was above the EU MRL. Field trial of fluopyram on cowpea was conducted, and the half-lives of fluopyram was 3.03–3.95 days and terminal residues ranged from .031–.596 mg/kg. Dietary risk assessment was performed on cowpea. This result indicated that the dietary risk of fluopyram in cowpeas was acceptable. The establishment of a method for the determination of fluopyram in different crops is beneficial to better monitor the residue levels of fluopyram, to protect the dietary safety of consumers and to provide technical means for subsequent study.

Data availability statement

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding authors.

Author contributions

SR: Data curation and Writing—Original draft preparation. YZ: Data Curation. SZ: Validation and Writing-review and editing. HL: Validation and Investigation. XL: Methodology. LW: Writing-review and editing. MW: Supervision. CZ: Supervision and Funding acquisition.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Supplementary material

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fenvs.2023.1105524/full#supplementary-material

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