Residue behavior and risk assessment of pyraclostrobin and tebuconazole in peppers under different growing conditions

Ercheng Zhao
Beijing Academy of Agriculture and Forestry Sciences
Anqi Xie
Beijing Academy of Agriculture and Forestry Sciences
Dong Wang
Beijing Academy of Agriculture and Forestry Sciences
Xiaoying Du
Beijing Academy of Agriculture and Forestry Sciences
Bingjie Liu
Beijing Academy of Agriculture and Forestry Sciences
Li Chen
Beijing Academy of Agriculture and Forestry Sciences
Min He
Beijing Academy of Agriculture and Forestry Sciences
Pingzhong Yu
Beijing Academy of Agriculture and Forestry Sciences
Junjie Jing (jingjunjie@ipepbaafs.cn)
Beijing Academy of Agriculture and Forestry Sciences https://orcid.org/0000-0002-9046-599X

Research Article

Keywords: pyraclostrobin, tebuconazole, residue, peppers, risk assessment

Posted Date: April 11th, 2022

DOI: https://doi.org/10.21203/rs.3.rs-1441045/v1

Abstract

To evaluate the residue behavior and risk of pyraclostrobin and tebuconazole in peppers, an analytical method for the determination of these two fungicides in peppers was developed using Ultra-high Performance Liquid Chromatography-triple quadrupole mass spectrometry (UPLC-MS/MS). Pepper samples were extracted with acetonitrile, and cleaned up with primary secondary amine (PSA) and graphitized carbon black (GCB). The average recoveries for three fortification levels of pyraclostrobin and tebuconazole in peppers were 86.7-101.4% and 81.7-104.4% with relative standard deviations (RSDs) of 4.0-7.2% and 3.8–10.9%, respectively. The limit of quantifications (LOQs) for the two fungicides in peppers were 0.01 mg/kg. Terminal residue trial of 30% pyraclostrobin and tebuconazole suspension concentrate (SC) on peppers was investigated under open fields and greenhouses conditions. The results showed that the terminal residues of pyraclostrobin and tebuconazole in peppers were lower than the maximum residue limits (MRLs) of peppers established by GB 2763－2021 (0.5 mg/kg for pyraclostrobin and 2 mg/kg for tebuconazole). A statistical t-test was used to study the significant difference between open fields and greenhouses, and the results indicated that there is no significant difference between different planting conditions of greenhouses and open fields. Using international estimate of short-term intake (IESTI) calculation model of Joint FAO/WHO Meeting on Pesticide Residues (JMPR), the acute dietary exposure risk of two fungicides in peppers was acceptable for general population with the IESTIs varied from 0–3% of ARfD for pyraclostrobin and 0–5% for tebuconazole.

1. Introduction

As we all know, pesticides were widely used as a chemical prevention and control measure for plants to be away from diseases, pests and weed damage. However, because of extensive usage of pesticides, the residue and environmental pollution problem, such as water, soil and air, presents public concerns more and more (Deng et al. 2019). Human health carries certain risks on pesticide residue for the reason of food chain concentration, passive/active exposure and chronic/acute toxicity for users and consumers (Voltz et al. 2022). In order to evaluate the residue level of pesticides, the maximum residue limits (MRLs) were established to supervise the quality of agricultural products and had important influence on international trade between different countries.

Vegetables, which take 30% proportion of human diet intake, are the main pathway of pesticide residue dietary risk to human (Claeys et al. 2011). Pepper (*Capsicum annuum*), which is a very common kind of vegetables, has different pharmacological functions, such as gastric protection, anti-inflammation, and obesity treatment (Wu et al. 2020). China is the largest production and consumption country of peppers (Wang et al. 2009). As a popular kind of vegetables, peppers have higher output value and economic benefits than cabbages in China (Dai et al. 2005). But, during the growing process, peppers always suffer from different diseases including anthrax. Many chemicals have been marketed to prevent pepper' diseases as fungicides, such as pyraclostrobin and tebuconazole.

Pyraclostrobin, which is one kind of strobilurin group fungicides developed by BASF company, acts through inhibition of mitochondrial respiration by blocking electron transfer within the respiratory chain, which in turn causes important cellular biochemical processes to be severely disrupted, and results in cessation of fungal growth (JMPR 2003). Pyraclostrobin has already been registered on 57 categories of crops including peppers in China. GB 2763－2021 has established pyraclostrobin's MRL (0.5 mg/kg) on peppers. Pyraclostrobin is generally used for preventing different diseases including mildew, powdery mildew, etc. (C. MacBean 2015). For example, pyraclostrobin could be applied to prevent four Colletotrichum species on peppers in greenhouse trials collocated with difenoconazole (Shi et al. 2021), prevent Fusarium asiaticum and Fusarium graminearum on wheat without cross-resistance (Zhao et al. 2021), prevent bacterial and fungal diseases in grape combined with dimethomorph (Wang et al. 2018), et al. However, pyraclostrobin could also make negative influence on bees that it would lead to significant deleterious effects in stingless bees at a colonial level (da Costa Domingues et al. 2020). Furthermore, the residue of pyraclostrobin on fruits and vegetables could cause food safety problem easily for the reason of hard removal (Yang et al. 2020). It is necessary to clarify the residue on fruits and vegetables. The analysis methods for pyraclostrobin included GC-MS/MS (Park et al. 2021), HPLC (de Melo Abreu et al. 2006) and LC-MS/MS (Li et al. 2020), et al.

Tebuconazole is a broad-spectrum triazole fungicide developed by Bayer. As a seed dressing tebuconazole is effective against various smut and bunt diseases of cereals. As a foliar spray it controls numerous pathogens such as rust species, powdery mildew and scale in various crops (JMPR 1994). Tebuconazole has been registered on peppers in China and GB 2763－2021 has established tebuconazole's MRL (2 mg/kg) on peppers. Although, tebuconazole had significant effects on fungal diseases of fruits, vegetables, beans and food crops as both pre-harvest and post-harvest applications (Shuang et al. 2021), it may cause negative effects of reproductive success for farmland birds through the ingestion of seeds (Lopez-Antia et al. 2021). Furthermore, there are many determination methods on tebuconazole for its high sensitivity, such as LC-UV (Miyauchi et al. 2005), LC-MS/MS (Pallavi et al. 2021), et al.

Based on the researches above, there's no studies paid attention to the residue behavior of peppers applied with preparations mixed by pyraclostrobin and tebuconazole, the acute dietary exposure of two fungicides on peppers, and the significant difference of residue for different planting conditions: greenhouse and open field. So it is necessary to study these aspects to improve the food safety data of two pesticides on peppers.

The purpose of this study were: (1) to develop a method to simultaneously determine pyraclostrobin and tebuconazole in peppers using UPLC-MS/MS combine with an optimized quick, easy, cheap, effective, rugged, and safe (QuEChERS) sample preparation, and (2) to study the residue behavior of pyraclostrobin and tebuconazole applied on peppers, then (3) to evaluate if the significant difference exist between different planting conditions of greenhouse and open field by t-result test, finally (4) to evaluate the acute dietary exposure risk of two fungicides on peppers

2. Material And Methods

2.1 Chemicals and reagents

The standards of pyraclostrobin (100 mg/L) and tebuconazole (100 mg/L) were obtained from Agro-Environmental Protection Institute Ministry of Agriculture. (AEPI, Beijing, China). 30% Suspension concentrate (SC) containing of 10% pyraclostrobin and 20% tebuconazole was from by Bissell, Henan Agricultural Science And Technology Co. Ltd. (Henan, China). HPLC grade methanol and acetonitrile, were purchased from Dikma Technologies Inc. Analytical grade sodium chloride (NaCl) and anhydrous magnesium sulfate ($MgSO_4$) were purchased from Beijing Chemical Reagent Company (Beijing, China). Formic acid (88%), were purchased from Thermo Fisher Scientific. Primary secondary amine (PSA) and graphitized carbon black (GCB), were purchased from Agela Technologies (Tianjin, China). Ultrapure water was obtained by Master-S30UV pure water system(Hitech Instruments Co. Ltd. Shanghai, China).

Mixed standard stock solutions (10 mg/L) of pyraclostrobin and tebuconazole were prepared in pure acetonitrile. All solutions were stored in the refrigerator under 4 ºC.

2.2 Apparatus

UPLC-MSMS system consisted of a Waters Acquity UPLC connected with a Xevo TQD triple quadrupole mass spectrometer was used for instrumental analysis. Other instruments used in these experiments were as follows: JY 2002 electronic balance (Shanghai Shunyuhengping Scientific Instrument Co. Ltd.), ME155DU electronic balance (Mettler Toledo Co. Ltd.), UMV-2 Multi-Tube Vortex Mixer (Beijing Yousheng United Technology Co. Ltd.), TDZ5-WS, H 1650-W centrifuge (Changsha Xiangyi Technology Co. Ltd.), and Foss 2094 homogenizer (Foss, Denmark).

2.2 Field experiments

According to the factor of planting scale, cultivation mode, climatic conditions etc, for peppers, supervised field experiments were performed in 12 different sites including Beijing(BJ), Inner Mongolia(IM), Shanxi(SX), Henan(HeN), Hunan(HuN), Sichuan(SC), Gansu(GS), Shandong(SD), Shanghai(SH), Guangdong(GD), Jiangxi(JX) and Guangxi(GX) in 2020, which were followed by the Guideline for the testing of pesticide residue in crops (NY/T 788 2018). Under the premise of sufficient sample quantity, the field experiment plot consists of check experiment plot and treatment experiment plot, each of which was not less than 50 m^2.

To evaluate the terminal residues of pyraclostrobin and tebuconazole in peppers, the 30% fungicide suspension concentrate (SC) was sprayed on the surface of peppers at the initial stage of anthracnose. The SC formulation was dissolved in water and sprayed on the treatment plot with an electric sprayer at the dosage of 315 g a.i/ha which is the highest recommended dosage. And the fresh water was used for the check plot area correspondingly which was isolated 3 m from the treatment plot area. The total application times were 3 with a 7-days application interval, and the pre-harvest interval (PHI) was 5 days. More than 2 kg representative pepper fruits (not less than 24 pepper fruits) were randomly collected from 12 pre-selected sampling points at 5 and 7 days after spraying, and 2 relatively independent samples were collected in each field trial plot.

As the process of laboratory samples pretreatment, all the peppers of each independent field were cut into 1-cm-length segments and mixed, then parted with quartation method, finally reserved into 2 samples (laboratory sample A and B), each of which was not less than 200 g. All samples were stored in deep freezer at -20°C.

2.3 Analytical methods

The field pepper samples were homogenized with appropriate dry ice by homogenizer before sample preparation.

2.3.1 Extraction and cleanup

Extraction

10.0 g of homogenized pepper sample was accurately weighed into a 50 mL polytetrafluoroethylene centrifuge tube. Afterwards, 20 mL acetonitrile was added and vortex mixed by a UMV-2 Multi-tube vortex mixer for 5 minutes, 3 g sodium chloride and 3 g anhydrous sodium chloride was added and vortex mixed for 1 minute. Then the tube was centrifuged for 5 min at 4000 rpm, waiting for cleanup.

Cleanup

1.5 mL supernatant in the above-mentioned tube was transferred into a 2 mL centrifuge tube which was filled with 50 mg PSA, 10 mg GCB and 150 mg anhydrous sodium chloride. After that, the 2 mL centrifuge tube was vortex mixed for 1 minute and centrifuged for 3 minutes at 12000 rpm. Then the supernatant was transferred into a 2 mL precut injection vial after filtered with 0.22 μm polypropylene filter, and finally analyzed by UPLC-MS/MS.

2.3.2 Instrumental conditions

A Waters UPLC system, consisted of a sample manager (SM), an ACQUITY UPLC binary solvent manager (BSM), and a column heater assemblied with a Waters ACQUITY BEH C_{18} column (2.1 mm×100 mm, 1.7 μm particle size) was used for the separation of analytes. The mobile phase consisting of solvent A (methanol) and solvent B (0.1% (v/v) formic acid in ultra-pure water) was pumped at a flow rate of 0.3 mL/min, with an injection volume of 1 μL. A gradient elution was performed (time 0 min, 5% A; 2 min, 95% A; 4.2 min, 5% A; 6 min, 5%A). The retention time of two fungicides were not later than 3.5 min. The temperatures of column heater and sample manager were maintained at 40 ºC and 5 ºC, respectively.

The qualitative and quantitative analysis of two fungicides was conducted by a triple quadrupole mass spectrometer equipped with an electrospray ionization (ESI^+) source. A multiple reactions monitoring (MRM) detection was performed in the positive ionization mode with a capillary voltage at 3.0 kV, a source temperature at 150 ºC, and a desolvation temperature at 450 ºC. The 99.95% nitrogen was used as source gas at 50 L/h flow rate for the cone and 600 L/h flow rate for the desolvation. The 99.99% Argon with a pressure of 2 – 3 mbar was used as collision gas. The MS parameters of two fungicides including cone voltage and collision energy were optimized individually to get perfect sensitivity and resolution (Table 1). A Masslynx v.4.1 (Waters, USA) software with targetlynx was used to acquire and analyze data.

Table 1
The MS parameters of pyraclostrobin and tebuconazole.

Compound	Retention time	Qualitative ions (m/z)	Quantitative ions (m/z)	Cone voltage(V)	Collision energy (V)
Pyraclostrobin	3.08	388.0/163.2	388.0/194.0	12	22
				12	12
Tebuconazole	3.07	308.0/151.0	308.0/124.9	20	34
				20	24

Table 2
Average recovery and RSD of pyraclostrobin and tebuconazole in pepper samples spiked at different levels (n = 5)

Compound	Matrix	Fortification levels (mg/kg)	Average recovery(%)	RSD (%)
Pyraclostrobin	Pepper	0.01	89.7	7.0
		0.5	101.4	8.7
		2	86.7	4.0
Tebuconazole	Pepper	0.01	81.7	10.9
		0.5	104.4	5.0
		2	97.3	3.4

2.4 Determination of significant difference between greenhouses and open fields

T-test is a common statistic method to test whether there is significant difference between two groups of data. In this study, the situation for the residues of different plant conditions fit the 2-tails t-test mode. The significant difference exists between the two groups data if the calculated probability of t-test was lower than 0.05, and does not exist on the contrary. By comparison, the extremely significant difference was existed with the probability lower than 0.01.

2.5 Acute dietary exposure risk assessment

As the guide of the JMPR, for each food commodity, the highest expected residue (highest residue in the edible portion of a commodity [*HR*] or highest residue in a processed commodity [*HR-P*]) and the highest large portion (*LP*) data for the general population (all ages) and children (6 years and under) were used for the calculation of the international estimate of short-term intake (*IESTI*). The *LP* data were derived from national dietary survey data by WHO. The *IESTIs* calculation of peppers fit the case **1** for children (Formula 1), that the concentration of residue in a composite sample (raw or processed) reflects that in the large portion size of the commodity, and fit the case **2a** for general population (Formula 2), that the unit weight of the edible portion (U_e) is lower than that of the large portion. (JMPR 2019)

$$IESTI = \frac{LP \times HR}{bw} \quad 1$$

$$IESTI = \frac{[U_e \times HR \times v + (LP - U_e) \times HR]}{bw} \quad 2$$

The different definitions applied in the formula was as followed:

LP

highest large portion provided (97.5th percentile of eaters), kg/d;

HR

highest residue in composite sample of edible portion found in data from supervised trials data, mg/kg;

bw

average body weight for a population age group, kg;

U_e

edible portion of the unit weight, kg;

v = variability factor represents the ratio of the 97.5th percentile residue to the mean residue in single units.

3. Results And Discussion

3.1 Method validation

A serial standard calibration curves were used to evaluate the sensitivity of the method. To improve the accuracy of the method, the matrix standard calibration curves were applied to the quantitative calculation instead of solvent standard calibration curves. The calibration curves were constructed with standard concentrations against responses of quantitative ion chromatographic peak. As the result showed, the linearity turned out excellent with the correlation coefficient (*r*) of the two fungicides was higher than 0.999. The limit of detection (LOD) and limit of quantification (LOQ) were 0.001mg/kg and 0.01 mg/kg, respectively. To evaluate the accuracy and precision of the method, recovery experiments of pyraclostrobin and tebuconazole were performed in pepper samples. As the fortified levels of 0.01, 0.5 and 2 mg/kg, the average fortified recoveries of pyraclostrobin were ranged from 86.7-101.4% with the relative standard deviation (RSD) of 4.0-7.2%, and the recoveries of tebuconazole were ranged from 81.7-104.4% with the relative standard deviation (RSD) of 3.4–10.9% on the other hand, which meant the accuracy and precision of present method met the Guideline (NY/T 788–2018). Typical chromatograms were shown in Fig. 1.

3.2. Terminal residues

The terminal residues of pyraclostrobin and tebuconazole of 12 different field experiment sites in peppers were shown in Table 3 and Table 4. The residues of pyraclostrobin varied from 0.032–0.48 mg/kg for the interval of 5 days, and 0.018–0.47 mg/kg for the interval of 7 days. The residues of tebuconazole varied from 0.048-1.2 mg/kg for the interval of 5 days, and 0.025-1.0 mg/kg for the interval of 7 days. The highest residue value of pyraclostrobin (0.48 mg/kg) and tebuconazole (1.2 mg/kg) in peppers was lower than the MRLs established by GB 2763 – 2021 (0.5 mg/kg and 2mg/kg, respectively).

Table 3
The terminal residues of pyraclostrobin in peppers.

Compound	Planting conditions	Location	PHI(days)	Residue (mg/kg)		
				1	2	Average
Pyraclostrobin	Greenhouse	IM	5	0.032	0.058	0.045
			7	0.018	0.031	0.025
		SX	5	0.11	0.084	0.097
			7	0.070	0.11	0.090
		GS	5	0.11	0.067	0.088
			7	0.15	0.088	0.12
		BJ	5	0.30	0.25	0.28
			7	0.17	0.27	0.22
		SD	5	0.20	0.21	0.21
			7	0.18	0.19	0.19
		SH	5	0.47	0.48	0.48
			7	0.34	0.47	0.40
	Open field	HeN	5	0.14	0.18	0.16
			7	0.17	0.11	0.14
		JX	5	0.12	0.12	0.12
			7	0.084	0.087	0.086
		HuN	5	0.26	0.18	0.22
			7	0.25	0.174	0.21
		GX	5	0.14	0.19	0.17
			7	0.21	0.21	0.21
		SC	5	0.052	0.060	0.056
			7	0.060	0.055	0.058
		GD	5	0.17	0.22	0.20
			7	0.15	0.17	0.16

Table 4
The terminal residues of tebuconazole in peppers.

Compound	Planting conditions	Location	PHI(days)	Residue (mg/kg)		
				1	2	Average
Tebuconazole	Greenhouse	IM	5	0.048	0.088	0.068
			7	0.025	0.048	0.037
		SX	5	0.18	0.14	0.16
			7	0.096	0.15	0.12
		GS	5	0.23	0.13	0.18
			7	0.22	0.17	0.19
		BJ	5	0.42	0.34	0.38
			7	0.32	0.48	0.4
		SD	5	0.34	0.38	0.36
			7	0.47	0.49	0.48
		SH	5	1.2	1.1	1.1
			7	0.82	1.0	0.91
	Open field	HeN	5	0.10	0.14	0.12
			7	0.10	0.08	0.09
		JX	5	0.12	0.13	0.13
			7	0.084	0.090	0.087
		HuN	5	0.63	0.43	0.53
			7	0.6	0.41	0.5
		GX	5	0.22	0.15	0.19
			7	0.25	0.23	0.24
		SC	5	0.085	0.099	0.092
			7	0.097	0.081	0.089
		GD	5	0.55	0.60	0.58
			7	0.51	0.63	0.57

On the other hand, 12 different field experiment sites consist of 6 greenhouses and 6 open fields, and the residue results of different sites turned out to be diverse. Using t-test function, the probability of t-test between different plant conditions was calculated. The t-test results of two fungicides residue in peppers for two plant conditions were shown in Table 5. The t-test result indicated that, as the condition of 2 tails and bi sample quadratic mean deviation assumption, the calculated t-test probabilities of two fungicides in peppers for 5, 7 days intervals between greenhouse and open field were varied from 0.532–0.622, which meant the significant difference did not exist between different planting conditions of greenhouse and open field.

Table 5
T-test results of pyraclostrobin and tebuconazole residue in peppers.

Compound	**Application interval**	**Planting conditions**	**Average residue**						**T-test result (*P*)**
pyraclostrobin	5 days	Greenhouse	0.045	0.097	0.088	0.28	0.21	0.48	0.532
		Open field	0.16	0.12	0.22	0.17	0.056	0.2	
	7 days	Greenhouse	0.025	0.09	0.12	0.22	0.19	0.4	0.622
		Open field	0.14	0.086	0.21	0.21	0.058	0.16	
tebuconazole	5 days	Greenhouse	0.068	0.16	0.18	0.38	0.36	1.1	0.582
		Open field	0.12	0.13	0.53	0.19	0.092	0.58	
	7 days	Greenhouse	0.037	0.12	0.19	0.4	0.48	0.91	0.568
		Open field	0.09	0.087	0.5	0.24	0.089	0.57	

3.3. Dietary exposure risk assessment

Considering the individual residue values closing to the MRLs and the data variability, it is quite necessary to evaluate the international estimate of short-term intake (*IESTI*) for the dietary exposure risk assessment.

Using the formula 1 and formula 2, the calculated IESTI results of pyraclostrobin and tebuconazole in peppers were shown in Table 6. As the results showed that, for pyraclostrobin, the ARfD was 0.7 mg/kg bw (JMPR 2003), and the calculated IESTIs was 3.45 μg/kg for general population (> 1 years) and not consumption (NC) for the children (2–6 yeas), respectively. The IESTIs was 0.5% of the ARfD for general population and 0% for children. For tebuconazole, the ARfD was 0.3 mg bw (JMPR 1994), and the calculated IESTIs was 8.61 μg/kg for general population (> 1 years) and not consumption (NC) for the children (2–6 yeas), respectively. The IESTIs was 3% of the ARfD for general population and 0% for children. Therefore, the acute dietary exposure to residues of pyraclostrobin and tebuconazole in peppers was unlikely to present a public health concern.

Table 6
The calculated IESTI results of pyraclostrobin and tebuconazole residue in peppers.

Compound	ARfD, mg/kg bw	Codex code	Commodity	Processing Code	*STMR* mg/kg	*HR* mg/kg	Country	Population group	*n*	Body weight(*bw*), kg	Large portion (*LP*), g/person	Uni edi por g
pyraclostrobin	0.7	VO 0444	Peppers	raw with skin	0.155	0.48	China	Gen pop, > 1 years	1743	53.2	295.71	43.
		VO 0444	Peppers	raw with skin	0.155	0.48	Netherlands	Child, 2–6 years	0	18.4	NC	9.6
tebuconazole	0.3	VO 0444	Peppers	raw with skin	0.2	1.2	China	Gen pop, > 1 years	1743	53.2	295.71	43.
		VO 0444	Peppers	raw with skin	0.2	1.2	Netherlands	Child, 2–6 years	0	18.4	NC	9.6

n: Total number of consumption values within the distribution where the 97.5 percentile is taken from

NC: No consumption

NR: Not relevant

Case 1: The concentration of residue in a composite sample (raw or processed) reflects that in the large portion size of the commodity.

Case 2a: The unit weight of the edible portion (U_e) is lower than that of the large portion.

4. Conclusions

Terminal residue field trials of 30% pyraclostrobin and tebuconazole SC on peppers were carried out under different planting conditions in 12 field experiment sites. A simultaneous determination method of pyraclostrobin and tebuconazole in peppers by UPLC-MS/MS was developed, and the recoveries of pyraclostrobin and tebuconazole in pepper matric were 86.7-101.4% with the RSDs of 4.0-7.2% and 81.7-104.4% with the RSDs of 3.4–10.9%, respectively. The LODs and LOQs of the two fungicides were 0.001 mg/kg and 0.01 mg/kg, respectively. The accuracy and precision of the method met the Guideline (NY/T 788–2018). As the results of terminal residue trials, the residue level of pyraclostrobin and tebuconazole in peppers were lower than the MRLs (0.5 mg/kg and 2 mg/kg) established in GB 2763 – 2021. On the basis of terminal residue results, the proposal for rational application of 30% pyraclostrobin and tebuconazole SC for preventing pepper anthracnose was as followed: the application times was maximum 3 times at the dosage of 315 g a.i/ha during the initial stage of disease. The application interval was 7 days and the PHI was 5 days.

The t-test results of the terminal residue for two different planting conditions showed that there was no significant difference between greenhouses and open fields for the residues of two fungicides. The dietary risk assessment results indicated that the acute dietary exposure to residues of pyraclostrobin and tebuconazole was unlikely to present a public health concern.

Declarations

Funding

This study was supported by the National Key Research and Development Program (2016YFD0200208), National Natural Science Foundation of China (031701822), and Innovation Capability Construction Program Of Beijing Academy Of Agriculture And Forestry Sciences (KJCX20200302-06).

Author Contributions

All authors contributed to the study conception and design. the whole study design was performed by Ercheng Zhao. The optimization of the analysis method was performed by Dong Wang and Min He. The pretreatment of all the field samples performed by Xiaoying Du and Bingjie Liu. the sample preparation procedure for all the samples was performed by Anqi Xie. The UPLC-MS/MS analysis was performed by Li Chen and Pingzhong Yu. Data collection and analysis were performed by Junjie Jing. The first draft of the manuscript was written by Junjie Jing, and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

Data availability

Not applicable.

Ethics approval and consent to participate

Not applicable.

Competing Interests

The authors have no relevant financial or non-financial interests to disclose.

Consent for publication

Not applicable.

References

1. MacBean C (2015) The Pesticide Manual. Chemical Industry Press, Beijing
2. Claeys WL, Schmit JF, Bragard C, Maghuin-Rogister G, Pussemier L, Schiffers B (2011) Exposure of several belgian consumer groups to pesticide residues through fresh fruit and vegetable consumption. Food Control 22(3):508–516. https://doi.org/10.1016/j.foodcont.2010.09.037
3. Da Costa Domingues CE, Bello Inoue LV, da Silva-Zacarin ECM, Malaspina O (2020) Fungicide pyraclostrobin affects midgut morphophysiology and reduces survival of Brazilian native stingless bee Melipona scutellaris. Ecotox Environ Safe 206:111395. https://doi.org/10.1016/j.ecoenv.2020.111395
4. Dai XZ, Liu ZM (2005) On current situation and its development trends of the pepper industry in china. J Chin Caps 4:1–6 in Chinese
5. De Melo Abreu S, Caboni P, Cabras P, Garau VL, Alves A (2006) Validation and global uncertainty of a liquid chromatographic with diode array detection method for the screening of azoxystrobin, kresoxim-methyl, trifloxystrobin, famoxadone, pyraclostrobin and fenamidone in grapes and wine. Anal Chim Acta 573–574:291–297. https://doi.org/10.1016/j.aca.2006.01.090
6. Deng YY, Dai HM, Zeng M, Gguan L, Luo XW, Zhang C, Tian J, Zhang J, Li Y, Xi Q, Zhao MW, Jiang M, Zhao LL (2019) Knowledge and behavior regarding pesticide use: a survey among caregivers of children aged 1–6 years from rural China. Environ Sci Pollut R 26:23037–23043. https://doi.org/10.1007/s11356-019-05560-w
7. GB/T 2763 (2021) National food safety standard- maximum residue limits for pestic-ides in food, China
8. JMPR (1994) http://www.fao.org/agriculture/crops/thematicsitemap/theme/pests/lp-e/lpet/en/. Accessed 28 Apr 2021
9. JMPR (2003) http://www.fao.org/agriculture/crops/thematicsitemap/theme/pests/lp-e/lpet/en/. Accessed 28 Apr 2021
10. JMPR (2019) http://www.fao.org/agriculture/crops/thematicsitemap/theme/pests/lp-e/lpet/en/. Accessed 28 Apr 2021
11. Li H, Yang S, Li TB, Li XH, Huang XP, Gao YY, Li BX, Lin J, Mu W (2020) Determination of pyraclostrobin dynamic residual distribution in tilapia tissues by UPLC-MS/MS under acute toxicity conditions. Ecotox Environ Safe 206:11182. https://doi.org/10.1016/j.ecoenv.2020.111182
12. Lopez-Antia A, Ortiz-Santaliestra ME, Mougeot F, Camarero PR, Mateo R (2021) Birds feeding on tebuconazole treated seeds have reduced breeding output. Environ Pollut 271:116292. https://doi.org/10.1016/j.envpol.2020.116292
13. Miyauchi T, Mori M, Ito K (2005) Application of solid-phase extraction to quantitatively determine cyproconazole and tebuconazole in treated wood using liquid chromatography with UV detection. J chromatogr A 1063:137–141. https://doi.org/10.1016/j.chroma.2004.11.086
14. Pallavi MS, Harischandra Naik R, Ratnamma, Nidoni U, Bheemanna M, Pramesh D (2021) Simultaneous determination, dissipation and decontamination of fungicides applied on cabbage using LC-MS/MS. Food Chem 355:129523. https://doi.org/10.1016/j.foodchem.2021.129523
15. Park E, Lee J, Lee J, Lee J, Lee HS, Shin Y, Kim JH (2021) Method for the simultaneous analysis of 300 pesticide residues in hair by LC-MS/MS and GC-MS/MS, and its application to biomonitoring of agricultural workers. Chemosphere 277:130215. https://doi.org/10.1016/j.chemosphere.2021.130215
16. Shi NN, Ruan HC, Jie YL, Chen FR, Du Y-X (2021) Characterization, fungicide sensitivity and efficacy of Colletotrichum spp. from chili in Fujian, China. Crop Prot 143:105572
17. Shuang Y, Zhang T, Zhong H, Li L (2021) Simultaneous enantiomeric determination of multiple triazole fungicides in fruits and vegetables by chiral liquid chromatography/tandem mass spectrometry on a bridged bis(beta-cyclodextrin)-bonded chiral stationary phase. Food Chem 345:128842. https://doi.org/10.1016/j.foodchem.2020.128842
18. Voltz M, Guibaud G, Dagès C, Douzals JP, Guibal R, Grimbuhler S, Grünberger O, Lissalde S, Mazella N, Samouëlian1 A, Simon S (2022) Pesticide and agro–ecological transition: assessing the environmental and human impacts of pesticides and limiting their use. Environ Sci Pollut R 29:1–5. https://doi.org/10.1007/s11356-021-17416-3
19. Wang S, Zhang Q, Yu Y, Chen Y, Zeng S, Lu P, Hu D (2018) Residues, dissipation kinetics, and dietary intake risk assessment of two fungicides in grape and soil. Regul toxicol pharm 100:72–79. https://doi.org/10.1016/j.yrtph.2018.10.015
20. Wang YP, Zhang SG, He J, Zhang J (2009) Current situation and developing trend of hot pepper industry in china and abroad. Mod Agric Sci 16(6):267–270 in Chinese
21. Wu QY, Bai PZ, Xia YT, Xia YJ, Xu BW, Dai K, Zheng ZY, Guo MSS, Fung, Kelly WC, Dong TTX, Tsim KWK (2020) Capsaicin Inhibits the Expression of Melanogenic Proteins in Melanocyte via Activation of TRPV1 Channel: Identifying an Inhibitor of Skin Melanogenesis. J Agric Food Chem 68:14863–

14873. https://doi.org/10.1021/acs.jafc.0c06321

22. Yang XH, Liu HJ, Mu R, Zhao NN, Jia MH (2018) Removal effects of six kinds of cleaning methods on strobilurin pesticide residues in fruits and vegetables. Sci Technol Food Ind 39(4):197–201 in Chinese
23. Zhao Z, Sun R, Su Y, Hu J, Liu X (2021) Fate, residues and dietary risk assessment of the fungicides epoxiconazole and pyraclostrobin in wheat in twelve different regions, China. Ecotoxicol Environ Safe 207:111236. https://doi.org/ 10.1016/j.ecoenv.2020.111236

Figures

Figure 1

Typical chromatograms of UPLC-MS/MS. Typical chromatograms of UPLC-MS/MS: (a) Typical chromatogram of pyraclostrobin standard (0.1 mg/L) (b) Typical chromatogram of tebuconazole standard (0.1 mg/L) (c) Typical chromatogram of blank peppers for pyraclostrobin (d) Typical chromatogram of blank peppers for tebuconazole (e) Typical chromatogram of pepper spiked with pyraclostrobin (0.5 mg/kg) (f) Typical chromatogram of pepper spiked with tebuconazole (0.5 mg/kg)