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Residue behavior and processing factors of thirteen field-applied pesticides during the production of Chinese traditional fermented chopped pepper and chili powder

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ABSTRACT

In this study, the fate, processing factors and relationship with physicochemical properties of thirteen pesticides in field-collected pepper samples during Chinese chopped pepper and chili powder production was systematically studied. The washing, air-drying, chopping and salting and fermentation processes reduced 24.8%–62.8%, 0.9%–26.4%, 25.1%–50.3% and 16.3%–90.0% of thirteen pesticide residues, respectively, while the sun-drying processing increased the residues of eleven pesticides by 1.27–5.19 fold. The PFs of thirteen pesticides were < 1 in chopped pepper production and the PFs of eleven pesticides were more than 1 for chili powder production. The chopped pepper processing efficiency have most negative correlation with octanol–water partition coefficient. In contrast, the chili powder processing efficiency have most positive correlation with vapour pressure. Thus, this study can offer important references for assessment the pesticide residue levels in Chinese traditional fermented chopped pepper and chili powder production from fresh peppers.

Introduction

Pepper is a very popular vegetable in the world because of its unique pungency taste and high nutritional value, and China is the largest producer and consumer of chili pepper (Xu et al., 2021). With high moisture content and perishable texture, fresh chili peppers are difficult to preserve and have short shelf lives, so chili pepper is often processed into capsicum products (Zhang et al., 2019). The primary processing of chili pepper includes drying, pickling, oil processing and so on, and the pickled fermented pepper products include chopped peppers, pickled peppers and pepper sauce (Wang et al., 2019; Xu et al., 2021; Ye et al., 2022). However, various pesticides are applied in pepper fields for disease and pest control, which may pose risks to the environment and food safety (Fenoll et al., 2009; Song et al., 2019). In this study, we selected 13 registered and frequently used pesticides on peppers in China as the research subjects. After pesticide application to crops, a variety more toxic metabolites or degradation products maybe produced in the environment and processing, and then organisms may be exposed to the complicated environments of pesticides and their metabolites (Chen et al., 2019; Bian et al., 2020). In addition, people paid more and more attention to the food safety issues resulting from pesticide residues recently. Monitoring pesticide residues in peppers as well as its processed products is greatly significant (Fig. 1).

The purpose of food processing is to enhance the edibility of food and nutritional quality, increase the value and shelf life of food, while food processing also changes the concentrations of pesticide residues in agricultural products and increases or decreases the content of pesticide residues in the final product (Motarjemi, 2002). And that depends on the different food processing steps, like drying, rinsing, peeling, pickling, juicing, heating and preservation (Alister et al., 2018; Chung, 2018; Li et al., 2021c; Wongmaneepratip et al., 2022). Many factors affect the variation of pesticides during food processing, such as pesticide characteristics (boiling point, solubility, vapor pressure, and octanol–water partition coefficient), plant skin structure, water content and quality characteristics of agricultural products (Han et al., 2016; Chung, 2018; Scholz et al., 2018; Wang et al., 2023). In the current evaluation system for agricultural product quality and safety, pesticide residue risk assessment is usually focuses on primary agricultural products, rarely

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consideration is given to the affection of food processes on pesticide residue variation (Fu et al., 2020; Sun et al., 2020; Paramasivam, 2021; Xiao et al., 2022). This may cause inaccurate assessment of pesticide residue dietary exposure risk in the population. Processing factor (PF), first described by the Environmental Protection Agency (EPA) of United States in 1996 (EPA, 1996), indicates the pesticide residue ratio of processed agricultural products to the raw materials or primary agricultural products (Li et al., 2021). Study regarding pesticide residue fate during food processing and PF introduction into risk assessment meet two purposes: (1) It can monitor the changes in pesticide residues during food processing while laying the theoretical basis for optimizing processing technology. (2) It can make more accurate pesticide residues dietary exposure safety risk assessments and provide references for recommend maximum residue limits (MRLs) of processed products.

In China, chopped pepper has been the representative traditional fermented pepper products, which is directly edible and is also a good cooking condiment. It is prepared through chopping of washed fresh peppers, salt addition, blending as well as sealing fermentation. Its processing product can keep the original pepper spiciness, nutrients and color, and provide the richer taste and fragrance (Wang et al., 2019; Chen et al., 2021). In order to facilitate storage and consumption, fresh peppers are often processed into chili powder too. Researches of the processing of chopped pepper mainly focuses on fermentation technology, fermentation microorganisms and flavor quality (Zhao et al., 2016; Chen et al., 2021; Rathnayaka et al., 2021; Xu et al., 2021; Ye et al., 2022). As we know, changes of multi-pesticide residues during different pepper processing methods (chopped pepper and chili powder production) have not been reported previously. Therefore, carrying out monitoring research concerning pesticide residue changes during processing of Chinese traditional fermented chopped pepper and chili powder are of great importance. Therefore, the current research aimed to: (1) develope a reliable and convenient analysis method to determining 13 pesticides residues within chopped pepper and chili powder by high-performance liquid chromatography tandem mass spectrometry (HPLC-MS/MS); (2) investigate residue changes of the thirteen pesticide residues during the production of chopped peppers and chili powder; (3) calculate the PFs for each step of the chopped pepper and chili powder production; (4) analyze the correlation between processing efficiency and pesticides physicochemical properties in order to elucidate the reasons of the fate of pesticide. The findings of this study will offer references for monitoring pesticide fate during the processing of fermented chopped pepper and dried chili powder from pepper, thereby guiding the appropriate pesticide application for the sake of protecting consumers against possible health hazards induced by corresponding residues.

Materials and methods

Reagents and chemicals

Standard of 13 pesticides (purity ≥ 95.0%) were provided by Dr. Ehrenstorfer GmbH (Germany). The MS grade methanol, acetonitrile and formic acid were provided by Merck (Darmstadt, Germany) and ROE Scientific Inc (Newark, USA), respectively. The Millipore purification system (model Milli-Q Advantage A10, Millipore, USA) was adopted for preparing purified water. HPLC grade acetonitrile, anhydrous magnesium sulfate (MgSO4) and sodium chloride (NaCl) were provided by Sinopharm Chemical Reagent (Beijing, China). Octadecylsilane (C18), primary secondary amine (PSA) along with graphitized carbon (GCB) was provided by Tianjin Bonna-Agela Technologies (Tianjin, China).

Field trials

The field trial was conducted during March to August 2019 (the spray time was 11July) at experimental base of Hunan Academy of Agricultural Sciences (113°10′ E and 28° 9′ N), Changsha, China). The commonly used pesticides (21% thiamethoxam suspension concentrate, 22.4% spirotetramat suspension concentrate, 2% thiacloprid microcapsule suspension concentrate, 200 g/L imidacloprid soluble concentrate, 15% trifloxystrobin suspension concentrate + 15% tebuconazole suspension concentrate, 200 g/L chlorantraniliprole suspension concentrate, 50% fluazinam suspension concentrate, 10% metalaxyl-M soluble concentrate, 5% emamectin benzoate microemulsion, 250 g/L azoxystrobin suspension concentrate, 40% difenoconazole suspension concentrate, 40% acetamiprid water dispersible granules) in pepper were selected to be target pesticides for this study. The field trials were designed in accordance with the Guideline on Pesticide Residue Trials in China (NY/T 788-2018, 2018). Each treatment was consisted of three replicate plots and one control plot, and the area of each plot was 50 m^2. To avoid cross-contamination, a buffer zone (30 m^2) was utilized to separate the plots. To guarantee sufficient initial precipitates of

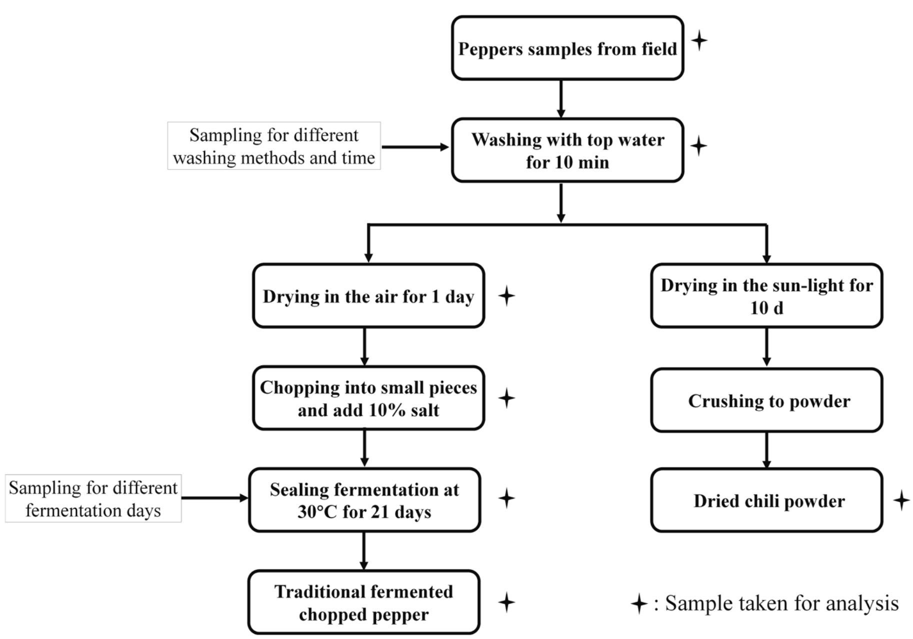

Fig. 1. Scheme for the traditional fermented chopped pepper and dried chili powder production and sample collection points utilized in the present work.

pesticides on chili pepper during the subsequent processing procedures, spraying of target pesticides was carried out on chili pepper under five-fold concentrations of recommended dosage (OECD, 2008). Fifteen kilograms fresh peppers were was collected randomly in each plot after 2 days. All the chili pepper samples were immediately delivered to laboratory for processing.

Preparation and processing of samples

According to traditional process method of chopped pepper and dried chili powder. Chopped pepper processing was performed through four consecutive steps (Wang et al., 2019; Chen et al., 2021), as shown in below:

Process 1. Washing: Fresh pepper samples from field were washed for 10 min under 5.0 L/min water flow rate, and then filtered out the water.

Process 2. Drying in the air: The washed pepper samples were placed in a ventilated place to natural dry the water for 12 h.

Process 3. Chopping: The washed and dried pepper samples were chopped with clean knives and cutting boards to pieces (0.5–1 cm × 0.5–1 cm).

Process 4. Fermentation: Later, 10% (w/w) NaCl was added into the chopped chili samples, discarding pepper juice and putting into 5 L pickle jars, followed by sealing fermentation under 30 °C within the incubator. Samples were collected at 0, 1, 3, 5, 7, 14 and 21 days after fermentation for pesticide residue detection.

The dried chili powder processing was performed through three main steps: washing (method was same as process 1 of chopped pepper), natural drying in sun-light for 10 days and crushing to dried chili powder. The average maximum temperature was 34 °C and humidity was 60 % during natural drying in sun-light.

To analyze the impact of different processing processes on the changes of pesticides residue, fresh peppers, washed peppers, dried peppers, chopped peppers, fermented peppers and dried chili powder samples from different steps were regularly collected for determining pesticide residues.

Sample extraction

Fresh peppers and processed chopped pepper

The proposed extraction and clean-up procedures was based on the quick-easy-cheap-effective-rugged-safe (QuEChERS) method after modification. Homogenized peppers samples (10 g) were accurately weighed and put into a 50 mL polytetrafluoroethylene (PTFE) centrifuge tube. Add 20 mL acetonitrile, then the resultant mixture was vortexed at a relative centrifugal force (RCF) of 2500g for 10 min. Add 2 g NaCl and the tubes were shaken vigorously for 2 min, the tube were centrifuged at 4000g for 5 min. The collect supernatant (1.0 mL) was transferred into the 2 mL micro-centrifuge tube, which contained 50 mg C18, 100 mg anhydrous MgSO4 and 20 mg GCB. The mixture was vortexed at 1500g for 1 min, centrifuged at 10000g for 5 min and filtered through a 0.22-μm nylon syringe filter before LC-MS/MS analysis.

Dried chili powder

Homogenized powder samples (2 g) were accurately weighed and put into a 50 mL polytetrafluoroethylene (PTFE) centrifuge tube, add 5 mL ultra-pure water in the tube, followed by 1-min shaking of the mixture. Add 10 mL acetonitrile, then the resultant mixture was vortexed at a relative centrifugal force (RCF) of 2500g for 10 min. Add 2 g NaCl and the tubes were shaken vigorously for 2 min, the tube were centrifuged at 4000g for 5 min. The collect supernatant (1.0 mL) was transferred into the 2 mL micro-centrifuge tube, which contained 50 mg C18, 50 mg of PSA, 100 mg anhydrous MgSO4, and 30 mg of GCB. The mixture was vortexed at 1500g for 1 min, centrifuged at 10000g for 5 min and filtered through a 0.22-μm nylon syringe filter before LC-MS/MS analysis.

LC-MS/MS analysis

Pesticides in samples were separated with the Agilent ZORBAX RRHD Eclipse plus C18 column (3.0 mm × 150 mm, 5 μm, Agilent Technologies, Santa Clara, CA, USA) on the high-performance liquid chromatography system (Agilent 1290 Series, USA). The column temperature during the detection was 35 °C. Mobile phase included acetonitrile (A) together with 0.1% (v/v) formic acid aqueous solution (B). The injection volume and flow rate were set to 2.0 μL and 0.4 min/L. Additionally, elution conditions were shown below, 10% A (0–1.0 min), 10–90% A (1.0–12.0 min), 90% A (12.0–13.0 min), 90–10% A (13.0–14.0 min), and 10% A (14.0–15.0 min), at the overall analysis time of 15.0 min.

Mass spectrometry is carried out using the AB Sciex QTRAP® 4500 system (AB SCIEX, Foster City, CA, USA) that contained the electrospray ionization source (ESI) in the positive ion mode. All compounds were determined in the multiple reactions monitoring (MRM) mode. The following conditions were set: ion spray voltage 5500 V, ion source temperature 550 °C, curtain gas 45 psi, along with ion source gas 1 and gas 2 at 40 psi. The optimized parameters for MS/MS of all the pesticides and metabolites were displayed in Table 1.

Method verification

The method performance was validated based on following items: linearity, matrix effect (ME), sensitivity, precision and accuracy (Rutkowska et al., 2018). Our method linear range was 0.0005–1.0 mg L^{-1}, as evaluated through standard solvent solutions as well as standard matrix-matched solutions. The matrix affect was examined depending on solvent slope ratio and matched calibration. Method sensitivity can be demonstrated by limit of quantification (LOQ) together with limit of detection (LOD). The LODs were calculated as minimum concentration levels where signal-to-noise (S/N) ratio was 3 and LOQs was estimated to be minimum spiked level of the analysis method (NY/T 788-2018, 2018). The precision and accuracy were obtained with recovery studies by spiking pesticides-free matrix at 0.002, 0.01, 0.1 and 1.0 mg kg^{-1}.

Calculation formula and statistical analysis

PF was calculated using Eq. (1) (FAO and WHO, 2016):

$$PF = \frac{\text{residue concentration (mg/kg) in processed product}}{\text{residue concentration (mg/kg) in RAC}} \tag{1}$$

Matrix effect (ME) was calculated using equation (2) (Liu et al., 2022):

$$ME\,(\%) = \left(\frac{\text{slope of calibration curve in matrix}}{\text{slope of calivration curve in solvent}} - 1\right) \times 100 \tag{2}$$

Where the negative ME value indicates matrix-induced signal curbing, whereas the positive value stands for signal enhancing. RAC is raw agricultural commodity.

Every assay was carried out thrice. Data were represented by mean ± standard deviation. One-way ANOVA plus Tukey's test was applied in statistical analysis ($p < 0.05$) performed with SPSS Version 19.0 (SPSS Inc. Chicago, IL, USA).

Results and discussion

Sample extraction optimization as well as analytical method purification and validation

During sample purification procedure, average recoveries of all pesticides were above 75% with different purification agent combinations (50 mg PSA + 10/20/30 mg GCB, 50 mg C18 + 10/20/30 mg GCB)

Table 1
Optimal parameters of MS/MS on thirteen pesticides and six metabolites.

Serial number	Analyte	Quantitative ion pair (*m/z*)	Qualitative ionpair (*m/z*)	CE (eV)	DP (V)	Retention time (Min)
1	Imidacloprid	256.1/209.0	256.1/175.0	19/25	66	5.64
2	Thiacloprid	253.0/125.9	253.0/89.9	27/53	71	6.65
3	Spirotetramat	374.1/302.1	374.1/330.1	21/21	91	9.69
4	Thiamethoxam	291.9/211.0	291.9/181.0	17/29	56	4.75
5	Azoxystrobin	404.0/372.1	404.0/329.1	19/39	76	10.01
6	Acetamiprid	223.1/125.9	223.1/90.0	27/43	61	5.94
7	Difenoconazole	406.0/251.0	406.0/188.1	31/57	111	11.28
8	Metalaxyl	280.2/220.1	280.2/192.1	17/23	66	8.49
9	Emamectin	886.4/158.1	886.4/82.1	39/129	126	9.18
10	Chlorantraniliprole	483.9/452.8	483.9/285.8	21/21	81	9.25
11	Tebuconazole	308.1/70.0	308.0/124.9	53/51	6	10.31
12	Trifloxystrobin	409.1/186.0	409.1/145.0	25/61	56	12.23
13	Fluazinam	465.0/372.8	465.0/135.1	41/15	41	12.62
14	B-mono	304.1/254.1	304.1/91.0	23/67	96	6.77
15	B-enol	302.1/216.0	302.1/207.0	35/29	121	7.26
16	B-glu	464.1/302.1	464.1/215.9	17/57	31	4.18
17	B-keto	318.1/300.0	318.1/214.1	15/39	66	7.79
18	Trifloxystrobin acid	395.1/186.2	395.1/145.0	14/38	35	10.77
19	Clothianidin	249.9/169.0	249.9/131.9	19/19	46	5.32

Note: CE = collision energy (eV), DP = declustering potential (V).

for fresh peppers and dried chili powder matrices. While the adsorption capacity of purification agent was weak without GCB, and the color of the extract was darkest (Fig. S2). Therefore, we used the combinations of purification agent (50 mg C18 + 20 mg GCB) to purify fresh peppers. Nonetheless, the purification agent combination (50 mg PSA + 50 mg C18 + 30 mg GCB) achieved favorable performance in the purification of dried chili powder extracts.

The calibration curve exhibited well linearity ($R^2 > 0.99$) at 0.0005–1.0 mg L^{-1} within matrix-matched standard solution for thirteen pesticides (Table 2). The fresh chopped peppers and chili powder matrices impacted the curbing or enhancing of analytical signal, and ME values were −58.8% to 44.5% and −77.5% to 71.6%, respectively. The matrix effect of fresh chopped peppers and chili powder were medium and strong, respectively. The high MEs in chopped peppers and chili powder could be due to the presence of undesired compounds (including residual volatiles, oils, pigments and other substances co-eluting with the pesticides) (Liu et al., 2022). Consequently, for ensuring method accuracy, we adopted matrix-matched calibration standards in quantification due to the complexity of sample matrix. As observed from Table 2, LOQs and LODs of thirteen target compounds within fresh chopped peppers and dried chili powder were 0.002–0.01 mg kg^{-1} and 0.0005 mg kg^{-1}, respectively. Mean recoveries with five replications for each matrix were 72.8%-105.1% under four spiked levels (0.002, 0.01, 0.1, 1.0 mg kg^{-1}), with standard deviations (RSDs) were < 10.3% in each pesticide (Table 3). The results demonstrated that our method could satisfy the accuracy, precision and sensitivity in monitoring the thirteen target compounds in fresh chopped peppers and dried chili powder. The LC–MS/MS total ion chromatogram (TIC) of thirteen pesticides and six metabolites in standard solution, peppers and chili powder were showed in Fig. S1.

Residue dynamic of thirteen pesticides during production of Chinese traditional fermented chopped pepper

The initial depositions of the thirteen pesticides in unwashed fresh peppers were range from 0.0081 to 0.873 mg kg^{-1}. Table 4 displayed the residual dynamics of the thirteen pesticides during the processing of Chinese traditional fermented chopped pepper and dried chili powder. As a result, thirteen pesticide contents gradually decreased during the production of chopped pepper.

Table 2
Calibration Curve Coefficients (R2), LOQs (mg/kg), LODs (mg/L) and ME (%) of thirteen pesticides in fresh chopped peppers and dried chili powder.

Analyte	Fresh chopped peppers				Dried chili powder			
	R^2	LOQ	LOD	ME	R^2	LOQ	LOD	ME
Imidacloprid	0.9984	0.002	0.0005	0.3	0.9995	0.01	0.0005	−41.5
Thiacloprid	0.9997	0.002	0.0005	−53.7	0.9990	0.002	0.0005	−39.1
Spirotetramat	0.9978	0.002	0.0005	−52.4	0.9935	0.002	0.0005	−42.7
Thiamethoxam	1.0000	0.002	0.0005	−28.6	0.9999	0.01	0.0005	−52.2
Azoxystrobin	0.9960	0.002	0.0005	−4.1	0.9977	0.002	0.0005	71.6
Acetamiprid	0.9997	0.002	0.0005	−52.6	0.9988	0.002	0.0005	−47.0
Difenoconazole	0.9997	0.01	0.0005	−23.1	0.9953	0.002	0.0005	−11.5
Metalaxyl	0.9949	0.01	0.0005	36.1	0.9961	0.002	0.0005	33.3
Emamectin benzoate	0.9923	0.002	0.0005	44.5	0.9964	0.01	0.0005	45.7
Chlorantraniliprole	0.9950	0.002	0.0005	−35.0	0.9983	0.002	0.0005	1.2
Tebuconazole	0.9998	0.002	0.0005	−51.4	0.9985	0.002	0.0005	−51.6
Trifloxystrobin	0.9983	0.002	0.0005	40.1	0.9915	0.002	0.0005	32.0
Fluazinam	0.9991	0.002	0.0005	−53.3	0.9976	0.002	0.0005	−77.5
B-mono	0.9999	0.01	0.0005	−57.5	1.0000	0.01	0.0005	−56.7
B-enol	0.9994	0.01	0.0005	−57.4	0.9932	0.002	0.0005	−54.9
B-glu	0.9999	0.002	0.0005	13.6	0.9997	0.01	0.0005	−9.9
B-keto	0.9998	0.01	0.0005	−58.8	0.9986	0.01	0.0005	−53.8
Trifloxystrobin acid	0.9991	0.01	0.001	−38.0	0.9944	0.002	0.0005	−20.7
Clothianidin	0.9990	0.002	0.0005	−38.3	0.9996	0.002	0.0005	−27.4

Table 3
Mean recoveries and Relative Standard Deviations (RSDs) for thirteen pesticides in fresh peppers and dried chili powder (n = 5).

Analyte	Mean recoveries (%) (RSD, %)							
	Fresh peppers (mg/kg)				Dried chili powder (mg/kg)			
	0.002	0.01	0.1	1.0	0.002	0.01	0.1	1.0
Imidacloprid	96.7(6.4)	90.5(9.7)	87.9(10.3)	88.4(5.7)	–	81.0(9.6)	87.5(5.6)	91.1(6.1)
Thiacloprid	77.4(3.8)	84.5(5.6)	82.4(7.0)	88.1(3.4)	81.8(2.1)	88.6(3.9)	89.2(3.3)	90.0(3.7)
Spirotetramat	92.7(2.8)	93.2(4.0)	95.7(7.4)	89.6(6.1)	72.8(2.8)	86.4(6.5)	88.2(6.2)	88.3(2.8)
Thiamethoxam	98.0(3.4)	92.9(9.1)	88.4(6.2)	88.6(2.5)	–	83.8(6.6)	89.1(4.8)	88.8(4.9)
Azoxystrobin	105.1(3.1)	94.9(7.5)	88.0(2.8)	87.7(1.8)	85.0(4.8)	87.8(5.1)	86.6(5.3)	–
Acetamiprid	103.7(3.5)	86.0(3.9)	88.4(6.5)	90.9(5.4)	84.4(3.4)	79.6(3.1)	76.1(2.4)	80.2(7.1)
Difenoconazole	–	78.2(1.1)	98.1(5.7)	98.0(0.6)	75.6(3.0)	91.0(9.0)	82.6(3.3)	75.4(2.8)
Metalaxyl	–	87.1(7.8)	102.4(1.7)	92.4(1.9)	86.7(2.1)	77.3(6.3)	79.1(1.3)	80.4(1.7)
Emamectin benzoate	90.7(3.2)	79.4(7.5)	84.7(2.8)	85.9(1.5)	–	85.0(3.8)	89.9(1.3)	102.6(3.6)
Chlorantraniliprole	100.3(6.1)	98.1(5.2)	97.1(2.6)	98.1(2.3)	84.1(6.2)	83.0(8.9)	98.2(6.5)	86.4(7.0)
Tebuconazole	80.6(3.9)	86.4(2.5)	90.2(3.4)	96.6(6.1)	82.1(1.9)	81.0(0.9)	90.2(5.3)	91.1(9.7)
Trifloxystrobin	103.6(5.0)	100.5(4.8)	98.1(5.9)	98.3(4.5)	83.6(6.1)	90.7(10.0)	92.1(2.0)	89.7(5.7)
Fluazinam	87.7(4.0)	86.4(2.5)	81.9(3.7)	88.4(3.4)	74.0(4.6)	78.2(3.9)	97.6(5.1)	94.4(5.7)
B-mono	76.0(6.5)	94.9(9.5)	87.8(4.3)	86.7(3.9)	–	85.1(2.7)	86.8(3.9)	93.4(1.9)
B-enol	–	96.2(9.5)	95.2(3.1)	88.8(4.7)	90.8(3.6)	91.0(9.4)	84.3(4.9)	88.0(1.2)
B-glu	91.5(9.8)	84.5(8.8)	95.4(4.7)	93.3(7.1)	–	82.6(5.8)	80.8(4.6)	89.9(8.9)
B-keto	–	98.2(9.6)	101.6(2.4)	103.2(9.2)	–	92.3(2.0)	95.1(4.2)	86.0(9.4)
Trifloxystrobin acid	95.6(4.8)	92.8(7.8)	94.8(2.0)	95.9(7.2)	93.5(8.5)	80.2(8.8)	81.1(2.8)	82.5(2.5)
Clothianidin	98.8(7.1)	91.1(2.7)	90.7(1.2)	98.2(3.4)	85.1(9.7)	91.9(2.2)	90.7(1.9)	92.1(3.2)

Note: "-" represents the recovery rate does not meet the requirements.

Table 4
Thirteen pesticides residues (mean ± SD, mg/kg) in intermediate and final products of fermented chopped peppers and dried chili powder (n = 3).

Analyte	Unwashed primary peppers	Washed peppers	Air-dried peppers	Chopped peppers	Fermented chopped peppers(21d)	Sun-dried chili powder
Imidacloprid	$0.374^{a} \pm 0.053$	$0.235^{b} \pm 0.027$	$0.173^{c} \pm 0.012$	$0.127^{d} \pm 0.014$	$0.093^{e} \pm 0.011$	$0.206^{b} \pm 0.005$
Thiacloprid	$0.670^{b} \pm 0.008$	$0.293^{c} \pm 0.018$	$0.240^{c} \pm 0.049$	$0.178^{d} \pm 0.011$	$0.149^{e} \pm 0.002$	$3.474^{a} \pm 0.154$
Spirotetramat	$0.816^{b} \pm 0.073$	$0.569^{c} \pm 0.026$	$0.526^{c} \pm 0.009$	$0.335^{d} \pm 0.018$	$0.262^{d} \pm 0.007$	$1.917^{a} \pm 0.067$
Thiamethoxam	$0.873^{b} \pm 0.046$	$0.521^{c} \pm 0.026$	$0.487^{c} \pm 0.014$	$0.321^{d} \pm 0.003$	$0.260^{d} \pm 0.015$	$1.321^{a} \pm 0.011$
Azoxystrobin	$0.848^{b} \pm 0.028$	$0.426^{c} \pm 0.008$	$0.410^{c} \pm 0.021$	$0.205^{d} \pm 0.014$	$0.142^{e} \pm 0.002$	$1.510^{a} \pm 0.035$
Acetamiprid	$0.330^{b} \pm 0.014$	$0.223^{c} \pm 0.006$	$0.221^{c} \pm 0.035$	$0.130^{d} \pm 0.014$	$0.070^{e} \pm 0.004$	$1.220^{a} \pm 0.007$
Difenoconazole	$0.816^{b} \pm 0.043$	$0.352^{c} \pm 0.020$	$0.306^{d} \pm 0.048$	$0.152^{e} \pm 0.007$	$0.091^{f} \pm 0.001$	$1.755^{a} \pm 0.037$
Metalaxyl	$0.462^{b} \pm 0.013$	$0.172^{c} \pm 0.012$	$0.150^{c} \pm 0.005$	$0.093^{d} \pm 0.005$	$0.035^{f} \pm 0.016$	$2.335^{a} \pm 0.031$
Emamectin benzoate	0.0081 ± 0.001	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Chlorantraniliprole	$0.323^{b} \pm 0.008$	$0.243^{c} \pm 0.013$	$0.215^{c} \pm 0.026$	$0.161^{d} \pm 0.001$	$0.125^{e} \pm 0.004$	$1.037^{a} \pm 0.029$
Tebuconazole	$0.594^{b} \pm 0.003$	$0.259^{c} \pm 0.038$	$0.239^{c} \pm 0.066$	$0.150^{d} \pm 0.022$	$0.086^{e} \pm 0.003$	$1.070^{a} \pm 0.043$
Trifloxystrobin	$0.389^{b} \pm 0.028$	$0.240^{c} \pm 0.012$	$0.233^{c} \pm 0.007$	$0.123^{d} \pm 0.017$	$0.051^{e} \pm 0.008$	$1.067^{a} \pm 0.034$
Fluazinam	$0.154^{b} \pm 0.008$	$0.084^{c} \pm 0.002$	$0.081^{c} \pm 0.008$	$0.050^{d} \pm 0.005$	$0.005^{e} \pm 0.0002$	$0.195^{a} \pm 0.004$
Metabolite						
B-mono	N.D.	N.D.	N.D.	N.D.	N.D.	0.002 ± 0.0001
B-enol	$0.254^{b} \pm 0.005$	$0.071^{c} \pm 0.006$	$0.045^{d} \pm 0.005$	$0.028^{e} \pm 0.003$	< LOQ	$1.273^{a} \pm 0.0450$
B-glu	$0.003^{b} \pm 0.0004$	$0.002^{c} \pm 0.0007$	$0.002^{c} \pm 0.0002$	< LOQ	< LOQ	$0.009^{a} \pm 0.0004$
B-keto	$0.018^{b} \pm 0.001$	$0.009^{c} \pm 0.002$	$0.008^{c} \pm 0.0004$	$0.006^{c} \pm 0.0002$	$0.002^{d} \pm 0.0004$	$0.189^{a} \pm 0.003$
Trifloxystrobin acid	$0.014^{b} \pm 0.0002$	$0.007^{c} \pm 0.0001$	$0.007^{c} \pm 0.0002$	< LOQ	$0.005^{c} \pm 0.0003$	$0.037^{a} \pm 0.0050$
Clothianidin	$0.008^{b} \pm 0.0002$	$0.007^{c} \pm 0.0003$	$0.006^{d} \pm 0.0001$	$0.004^{e} \pm 0.0001$	$0.002^{d} \pm 0.0001$	$0.063^{a} \pm 0.0006$

Note: a-f = Values marked by diverse letters stand for significant difference ($P < 0.05$); N.D. = not detected; B-mono, B-enol, B-glu and B-keto stand for abbreviation of spirotetramat-mono-hydroxy, spirotetramat-enol, spirotetramat-enol-glucoside and spirotetramat-keto-hydroxy, respectively.

Washing

Washing represents the initial processing step of chopped pepper production. Many studies have reported that washing reduces pesticide residues (Kaushik et al., 2009; Chung, 2018; Zhang et al., 2020). In this work, two washing method (rinsing and soaking) were investigated the pesticides removal effects. The results showed that the pesticide residue of peppers after rinsing is reduced by 0%-56.2%, 1.6%-52.5% and 2.2%-41.6% compared to that after soaking at 5 min, 10 min and 15 min, respectively (Fig. S3). Overall, rinsing reduced more residues of all thirteen pesticides than soaking, and the pesticides residues decreased as washing time extended, but the decrease slowed down after 10 min. Considering efficiency and cost factors, this study adopted 10 min as the washing treatment time. Our results showed that rinsing reduced all pesticides residues ranging from 24.8% to 62.8% (Table 4). The removal rate of metalaxyl in the washing process was the highest (62.8%), which might be related to its greater water-solubility (S_w = 26000 mg/L) along with lower octanol–water partition coefficient values (log Kow = 1.71). The removal rate of chlorantraniliprole was the lowest (24.8%), which might be related to its low water-solubility (S_w = 0.88 mg/L) together with high octanol–water partition coefficient values (log Kow = 2.86). The residue remove effectiveness is affected by diverse factors, including not only pesticides physicochemical properties, but also application concentration, washing environment, plant surface properties and so on (Yigit and Velioglu, 2020). Acetamiprid is highly soluble in water (Sw = 2950 mg/L), but it was only reduced by 32.4%, which may be due to its systematic properties. Systemic pesticides are more likely settled in internal tissues and are more difficult to be washed and removed. Overall, pesticides with high water solubility are easier to remove than pesticides with low water solubility. However, the extent of reducing pesticide levels through washing is determined by many factors and is not always related to water solubility and octanol–water partition coefficient (He et al., 2020). Table S1 provides the physiochemical characters of thirteen pesticide.

Air-drying, chopping and salting

Next, the washed pepper samples were placed in a ventilated place to natural dry the water for 12 h. Air-drying can remove water from pepper surface to prevent affecting the subsequent fermentation (Wang et al., 2019). Thirteen pesticide residues were further reduced by 0.9 to 26.4% on the process of air-drying (Table 4). Following, the washed and dried pepper samples were chopped into small pieces peppers, where chopped peppers should be prepared with addition of salt before natural fermentation. Because salt is essential and have an important impact on flavor and texture of fermented chopped peppers (Chen et al., 2021). The residues of the thirteen pesticides were decreased by 25.1–50.3% after chopping and salting process (Table 4). This may be associated with the physical degradation resulting from pepper cell fragmentation and chemical degradation caused by the enzymes and plant acids (Hou et al., 2020).

Fermentation

After chopping and salting, fermentation is an important process during chopped pepper production. The fermentation microorganisms were come from fresh pepper surface as well as processing conditions (Xu et al., 2021). The results showed that thirteen pesticides residues were decreased by 16.3–90.0% during fermentation process (Table 4). Significantly, the removal rate of fluazinam in the fermentation process was the highest (90.0%) and following by metalaxyl (62.4%), the removal rate of thiacloprid was the lowest (16.3%). Meanwhile, the concentrations of all thirteen pesticides were continuously decreased during the 21 days of fermentation, and metalaxyl, emamectin benzoate and fluazinam decreased more sharply (Fig. S4). Pesticide reduction during fermentation is mostly associated with biological/chemical degradation caused by microbial (Regueiro et al., 2015; Saeedi Saravi and Shokrzadeh, 2016; Quan et al., 2020). Such microorganisms can utilize pesticides to be the sources of energy and carbon. Several previous studies showed that fermentation affected pesticide residue dissipation from diverse plant-derived fermented foodstuffs (Han et al., 2016; Saeedi Saravi and Shokrzadeh, 2016; Alister et al., 2018; Hou et al., 2020; Quan et al., 2020; Wongmaneepratip et al., 2022). On the other hand, pesticides might also affect the microbial growth and population multiplication in the fermentation step (Cus & Raspor, 2008; Francesca & Maurizio, 2008). Emamectin benzoate, a biological pesticide that is derived from the natural fermentation products of *Streptomyces bacteria* and easy to be degraded. Emamectin benzoate was only detected in the unwashed primary pepper samples during the whole process (Table 4).

In this study, the residue changes of metabolites of spirotetramat (spirotetramat-enol, spirotetramat-mono-hydroxy, spirotetramat-keto-hydroxy, and spirotetramat-enol-glucoside), thiamethoxam (clothianidin) and trifloxystrobin (trifloxystrobin acid) were investigated. The residues of all the metabolites were gradually decreased during chopped pepper production, and spirotetramat-mono-hydroxy was never detected (Table 4).

Residue change of thirteen pesticides during production of dried chili powder

Dry processing represents an old method of food preservation (Hou et al., 2020; Li et al., 2021), which is also be applied to product the chili powder. It can improve the preservation of the peppers by removing water in the food. The main change of pesticide residues during drying are related to the water loss-induced residual enrichment, along with the thermal degradation- and photolysis-induced residual degradation (Li et al., 2021). The residue level of imidacloprid and emamectin benzoate were decreased during the sun drying. While the residue level of other eleven pesticides in dried chili powder were 1.27–5.19 fold higher than those in fresh peppers. (Table 4). The residue level of the metabolites of spirotetramat and thiamethoxam were also increased during chili powder production (Table 4).

PFs

In general, different processing methods will lead to different pesticide residues within the eventual products, sometimes the opposite. PFs can be calculated for determining how processing affects pesticide residues in a product. Table 5 showed that the PFs of washing, air-drying, chopping and salting, fermentation and sun-drying for the thirteen compounds were 0.37–0.75, 0.74–0.99, 0.50–0.75 and 0.10–0.84, respectively. The PFs of thirteen pesticides during all processing process of chopped pepper were < 1, indicating that chopped pepper processing steps promoted pesticide dilution thus decreasing the exposure risk. In washing step, the PFs of 13 pesticides were 0.37–0.75 and the PFs of most pesticides were less than other process, which were owing to removal of pesticide residue on the surface of peppers by washing. During fermentation, the PFs of the thirteen pesticides ranged from 0.10 to 0.84, demonstrating that this step led to an obvious reduction of the thirteen pesticides. Notably, fluazinam and metalaxyl were removed 90% and 62.4% during the fermentation process. In addition, the whole process of chopped peppers production entirely eliminated the residue of emamectin benzoate, with PFs of < 0.39 for the other pesticides in the entire procedure. Overall, these results presented chopped peppers processing contributed to pesticide dilution and decrease human exposure risk to pesticide threats.

PFs for thirteen pesticides in drying were calculated, which were 0.88–13.58 in sun-drying and 0.55–5.19 in the overall procedure (Table 5). There were only the PFs of imidacloprid and emamectin benzoate were < 1, that of other eleven pesticides were greater than 1. These results suggested that sun-drying caused residual degradation of imidacloprid and emamectin benzoate and residual accumulation of other eleven pesticides. The PFs of thiacloprid and metalaxyl were highest (5.19 and 5.05) (Table 5), indicating that the residual enrichment of thiacloprid and methamphetamine during the drying process is relatively high. Meanwhile, the findings in this study also validated that food processing methods such as drying and other concentration methods easily caused residue enrichment and increased pesticides exposure risk.

Relationship between processing efficiency and pesticides physicochemical properties

Jankowska and Łozowicka (2022) reported that the pesticides physicochemical properties, such as, octanol–water partition coefficient (log Kow), solubility in water (Sw), vapour pressure, degradation point and molecular weight (MW), play an important role in food processing. On the other hand, Zhao et al. (2018) reported that the Pearson's correlation coefficients analysis can be used to analyze the correlation between the degradation rate and pesticides physicochemical properties. In this study, the relationships between the key processing efficiency of fermented chopped pepper and dried chili powder and pesticides physicochemical properties were analyzed by Pearson's correlation coefficients, as shown in the heatmap (Fig. 2). The results showed that the correlation analysis yielded a strong negative correlation between PF of washing and physicochemical properties like vapour pressure ($r = -0.49$), solubility in water ($r = -0.41$ whole). This indicated that pesticides with high water solubility and high vapour pressure are easily carried away by flow water during the washing process. The correlation analysis showed a strong negative correlation between PF of fermentation and pesticides physicochemical properties like octanol–water partition coefficient ($r = -0.56$), which means that pesticides with high octanol–water partition coefficient are easily degradation caused by fermentation microbial. Interestingly, it is a positive correlation between PF of sun-drying and pesticides physicochemical properties like solubility in water ($r = 0.68$), vapour pressure ($r = 0.70$). This indicated that pesticides with high water solubility and high vapor pressure become more difficult to degrade as water content decreases during the drying process.

Table 5
Processing factors (PFs) of thirteen pesticides following diverse processing processes.

Analyte	Washing	Air-drying	Chopping and salting	Fermentation	Whole procedure of chopped peppers	Sun-drying	Whole procedure of chili powder
Imidacloprid	0.63	0.74	0.73	0.73	0.25	0.88	0.55
Thiacloprid	0.44	0.82	0.74	0.84	0.22	11.86	5.19
Spirotetramat	0.70	0.92	0.64	0.78	0.32	3.37	2.35
Thiamethoxam	0.60	0.93	0.66	0.81	0.30	2.54	1.51
Azoxystrobin	0.50	0.96	0.50	0.69	0.17	3.54	1.78
Acetamiprid	0.68	0.99	0.59	0.54	0.21	5.47	3.70
Difenoconazole	0.43	0.87	0.50	0.60	0.11	4.99	2.15
Metalaxyl	0.37	0.87	0.62	0.38	0.07	13.58	5.05
Emamectin benzoate	–	–	–	–	–	–	–
Chlorantraniliprole	0.75	0.88	0.75	0.78	0.39	4.27	3.21
Tebuconazole	0.44	0.92	0.63	0.57	0.14	4.13	1.80
Trifloxystrobin	0.62	0.97	0.53	0.41	0.13	4.45	2.74
Fluazinam	0.55	0.96	0.62	0.10	0.03	2.32	1.27

Note: "-" represents Not detected or < LOQ and the PF is not determined.

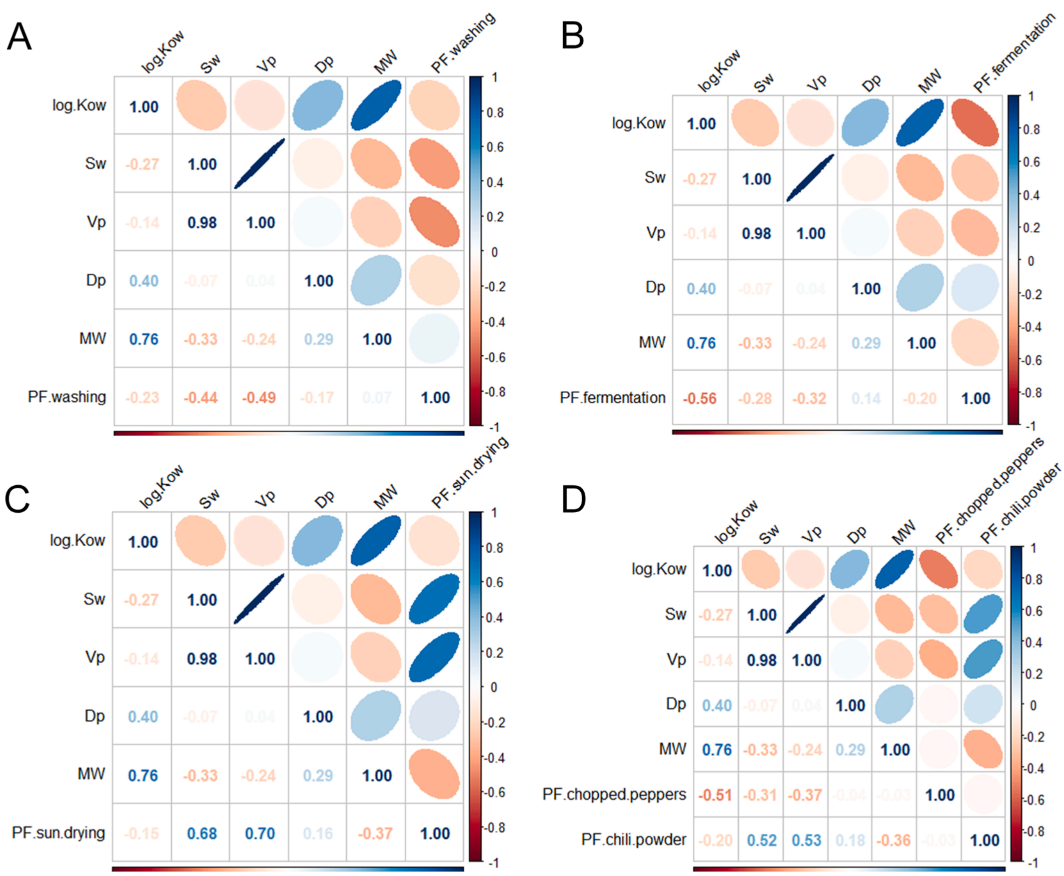

Fig. 2. Heatmap based on Person's correlation coefficients showing relation between processing effectiveness and physicochemical of the thirteen pesticides. Note: Molecular weight (MW), solubility in water (Sw), octanol–water partition coefficient (log Kow), degradation point (Dp) and vapour pressure (Vp) were the chosed pesticides physicochemical properties. PF. washing were the PFs of thirteen pesticides during washing processing. PF. fermentation were the PFs of thirteen pesticides during fermentation processing. PF. sun-drying were the PFs of thirteen pesticides during sun-drying processing. PF.chopped peppers were the PFs of thirteen pesticides during production of fermented chopped pepper. PF. chili powder were the PFs of thirteen pesticides during production of chili powder.

Throughout the entire process, the correlation analysis showed a negative correlation between PF of fermented chopped pepper and pesticides physicochemical properties like octanol–water partition coefficient (r = -0.51), solubility in water (r = -0.31) and vapour pressure (r = -0.37), which means that PF value is lower for higher log Kow pesticides. In contrast, it is a positive correlation between PF of dried chili powder and pesticides physicochemical properties like solubility in water (r = 0.52), vapour pressure (r = 0.53) and degradation point (r = 0.18). While the log Kow and MW were observed for negative correlations with PF of dried chili powder (r = -0.20, r = -0.36), indicating that when pesticides become more polar, a lower processing efficiency was obtained.

Conclusion

The current research proposed a sensitive and creditable QuEChERS-HPLC–MS/MS method to determine multiple pesticides in Chinese traditional fermented chopped pepper and dried chili powder. Subsequently, the residue dynamic and processing factors of thirteen pesticides during chopped pepper and chili powder processing were analyzed. Specific processing steps (washing, air-drying, chopping, salting, fermentation, sun-drying and crushing) impacted pesticides degradation or enrichment during chopped pepper and chili powder production. The washing, air-drying, chopping and salting and fermentation decreased the residues of thirteen pesticides by 24.8%–62.8%, 0.9–26.4%, 25.1–50.3% and 16.3–90.0%, respectively. While the sun-drying and crushing increased the residues of eleven pesticides by 1.27–5.19 fold. The PFs were<1 for all chopped pepper process steps, but the PFs were more than 1 (except imidacloprid and emamectin benzoate) for chili powder. Therefore, chopped peppers processing eliminated pesticides residues but chili powder processing concentrated them. The processing efficiency of fermented chopped pepper have a negative correlation with log Kow, solubility in water and vapour pressure. In contrast, the processing efficiency of chili powder has a positive correlation with solubility in water, vapour pressure and degradation point and a negative correlation with log Kow and MW. Consequently, these new findings should be considered in future production to ensure the safety of processed food. This study not only contributes to investigate the residue changes of pesticides in the processing of Chinese traditional fermented chopped pepper and chili powder from fresh peppers, but also offers reliable references for the risk assessment of pesticides in chopped pepper and chili powder made from pepper.

CRediT authorship contribution statement

Kailong Li: Conceptualization, Writing – original draft, Methodology, Writing – review & editing. **Tongqiang Chen:** Formal analysis, Investigation, Validation. **Xiaobin Shi:** Formal analysis, Investigation, Validation. **Wuying Chen:** Formal analysis, Validation. **Xiangwen Luo:** Resources. **Hao Xiong:** Resources. **Xinqiu Tan:** Formal analysis, Validation. **Yong Liu:** Project administration. **Deyong Zhang:** Funding acquisition, Writing – review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data that has been used is confidential.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fochx.2023.100854.

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