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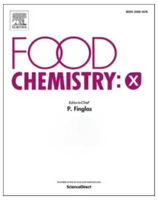

# Dissipation, accumulation, distribution and risk assessment of fungicides in greenhouse and open-field cowpeas

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ABSTRACT

Pesticide residues in cowpeas have raised worldwide concern. However, only a few studies have focused on pesticide accumulation and distribution in greenhouse and open-field cowpeas. Field trial results suggest that difenoconazole, dimethomorph, thifluzamide and pyraclostrobin dissipated faster in open fields (mean half-lives, 1.72–1.99 days) than in greenhouses (2.09–3.55 days); moreover, fungicide residues in greenhouse cowpeas were 0.84–8.19 times higher than those in the open-field cowpeas. All fungicides accumulated in the greenhouse and open-field cowpeas after repeated spraying. Fungicide residues in old cowpeas were higher than those in tender cowpeas, and residues in the upper halves of cowpea pods were higher than those in the lower halves. In addition, cowpeas distributed in the lower halves of the plants had higher fungicide residues. Our findings suggest that greenhouse cultivation contributed to the pesticide residues in cowpeas after repeated spraying, although the levels of dietary health risks remained acceptable under both cultivation scenarios.

## 1. Introduction

Cowpea (*Vigna unguiculata* L. Walp.) is one of the most commonly consumed vegetables in China and has considerable economic and nutritional value (Wang et al., 2021a). In China, large-scale areas of cowpeas have been planted in greenhouses and open fields to meet consumers' demand and increase farmers' income (Huan et al., 2016). Cowpea favours high temperatures and humid climates and therefore easily infested and damaged by various plant diseases (Mahesha et al., 2022); as a result, fungicides are often overused by farmers to guarantee cowpea yield and quality, potentially producing dietary exposure risks (Duan et al., 2016; Zhang et al., 2022). Although a series of strict measures have been taken to reduce the use of pesticides in cowpeas, it is still a vegetable with serious issues regarding pesticide residues (Cui et al., 2023a). Given the potential health hazards of fungicides to humans, it is crucial to understand residue fate and distribution in cowpeas after application.

Several studies have found that pesticides are widespread in cowpeas based on market monitoring samples (Cui et al., 2021; Duan et al., 2016; Luo et al., 2023; Zhang et al., 2022). Some studies have reported the residue behaviour and dietary risk assessment of pesticides in cowpeas using field experiments (Fu et al., 2020; Li et al., 2022a,b; Wang et al., 2021a). However, only a few studies have compared the residue differences in cowpeas under greenhouse and open-field conditions. Many factors, such as rainfall, temperature, humidity, solar radiation and wind speed, may be different between these two cultivation scenes and result in different degradation rates of pesticides in cowpeas, finally generating different dietary exposure risks (Bojacá et al., 2013; Liu et al., 2022). Besides, existing literature has mainly studied the pesticide dissipation and terminal residues in cowpeas at the final spraying; only a few have paid attention to the residue patterns of pesticide accumulation after repeated spraying. Single and repeated applications have been proven to generate different pesticide dissipation and accumulation patterns in crops (Wang et al., 2021b). Therefore, residue characteristics

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and accumulation effects of fungicides in both greenhouse and open-field cowpeas after repeated spraying should be fully studied to ensure food safety and the well-being of consumers.

Factors that influence pesticide distribution in cowpeas include pesticide traits, application doses, plant morphology and other environmental factors. For instance, Wang et al. (2021a) found that the micro-emulsion formulations aggravated emamectin benzoate residues in cowpeas than the emulsifiable concentrate with the same application amounts of active ingredients, and the pesticide dissipated faster in tender cowpeas than in old cowpeas. Hydroponic experiments suggested that residues of acetamiprid and cyromazine in cowpeas presented a distribution trend of leaves > stems > roots, and that the transport modes of both pesticides in cowpea tissues were passive (Zhang et al., 2023). Fu et al. (2020) reported that the single and mixed-use of pesticides in cowpeas could result in different half-lives of pesticides in cowpeas. However, fewer studies have focused on pesticide distribution, which is affected by cowpeas themselves. Cowpea is a sub-erect, trailing or climbing and annual herbaceous plant. How pesticide residues are distributed in the upper and lower cowpeas is largely unknown. Moreover, whether pesticides are evenly distributed in long cowpea pods needs further research. Understanding the residue distribution of pesticides in different cowpea parts and types is all-important to reduce the dietary exposure risk and improve food safety.

Our study was the first to systematically investigate the dissipation, accumulation, distribution and risk assessment of four fungicides, i.e. difenoconazole (DIF), dimethomorph (DIM), pyraclostrobin (PYR) and thifluzamide (THI) (Fig. 1), in cowpeas under open-field and greenhouse conditions. These fungicides are the most frequently used on cowpeas for multiple times to control various plant diseases, such as anthracnose, brown spots, rusts and epidemic diseases (https://www.chinapesticide.org.cn/zwb/dataCenter). Worryingly, these four fungicides were frequently detected in market cowpea samples, and some residues even exceeded the maximum residue limits (Cui et al., 2021; Gong et al., 2022; Luo et al., 2023; Zhang et al., 2022). The main objectives of this study were to (1) compare the difference in fungicide dissipation and accumulation in greenhouse and open-field conditions; (2) determine the difference in the distribution of fungicide residues in different cowpea parts and types; (3) study the dietary exposure risk of fungicides in children and adults from greenhouse and open-field cowpeas. This study aimed to understand and compare the residue fate of fungicides in greenhouse and open-field cowpeas and provide a scientific basis for the rational use of these fungicides.

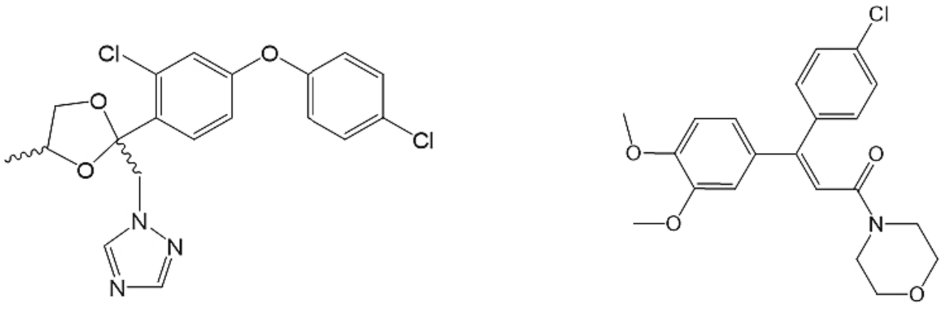
## 2. Materials and methods

### 2.1. Materials and reagents

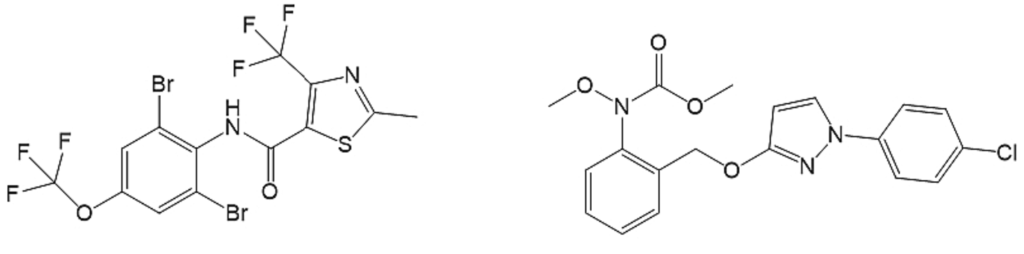
Certified reference standards of DIF, DIM, PYR and THI (all 1000 mg/L) were purchased from the Alta Scientific Co., Ltd. (Tianjin, China). Methanol, acetonitrile and formic acid were of high-performance liquid chromatography (HPLC) grade and were purchased from Macklin Biochemical Co., Ltd. (Shanghai, China). Ammonium acetate (HPLC grade) was purchased from Sigma–Aldrich Chemical Co., Ltd. (Darmstadt, Germany). Sodium chloride (NaCl) and anhydrous magnesium sulfate ($MgSO_4$) (analytical grade) were purchased from Sinopharm Chemical Reagent (Shanghai, China). Graphitised carbon black (GCB) and primary secondary amine (PSA) were purchased from Agela Technologies (Beijing, China). Mixed stock solutions (100 mg/L) were stored at −20 °C in the dark.

### 2.2. Field trials

The field trials were conducted from June to July 2023 in Jiyang District, Shandong Province, China (116°98′E and 36°98′N). The experiment plots were divisible into two distinct plots, i.e. a control plot (50 $m^2$) and a test plot (100 $m^2$) in both the greenhouse and open field. DIF suspension concentrate, DIM water dispersible granule, THI suspension concentrate and PYR suspension concentrate were sprayed at their highest recommended dosages of 112.5 g a.i $ha^{-1}$, 300 g a.i $ha^{-1}$, 75 g a.i $ha^{-1}$ and 75 g a.i $ha^{-1}$, respectively. The fungicides were sprayed once every seven days and were sprayed three times during the experiment. The first pesticide spray was applied to mature greenhouse



**Difenoconazole** **Dimethomorph**



**Thifluzamide** **Pyraclostrobin**

**Fig. 1.** Chemical structures of DIF, DIM, PYR and THI.

and open-field cowpeas. To compare the residue dissipation and accumulation of fungicides in the greenhouse and open-field cowpeas, three representative cowpea samples (≥1.0 kg) were randomly collected from each of the experiment plots at 2 h, 1, 3, 5 and 7 days after each spraying. To compare the residue distribution of fungicides in different cowpea parts and types, tender (10–20 cm in length) and old (≥50 cm in length) cowpeas, the upper (near the stems) and lower half parts of the same pods and cowpeas distributed in the upper and lower half of the plants (schematic diagrams are shown in Figure S1), were collected on the third day after the final spraying. All samples were chopped, homogenised and maintained in a refrigerator at −18 °C until analysis.

### 2.3. Analytical procedure

The Quick, Easy, Cheap, Effective, Rugged and Safe (QuEChERS) method (Anastassiades et al., 2003) was used to extract four fungicides from cowpea samples with a minor modification. In brief, 10.00 g cowpea homogenate was placed into a 50-mL centrifuge tube, and this was followed by an addition of 10 mL acetonitrile. All tubes were then vortically extracted for 5 min, followed by an addition of 1.5 g of NaCl and 4.0 g of anhydrous $MgSO_4$. After shaking for another 1 min, each tube was centrifuged for 5 min at 5000 rpm, and 1.5 mL of the supernatant solution was placed into a 2-mL micro-centrifuge tube that contained purification agents: 50 mg of PSA, 20 mg of GCB and 150 mg of anhydrous $MgSO_4$. Next, the tube was vortexed for 3 min and centrifuged for 5 min at 5000 rpm. After that, the supernatant solution was filtered through a 0.22-μm nylon syringe filter for instrumental analysis.

The four fungicides were detected using a 1290 Infinity II HPLC system possessing a 6495 triple quadrupole mass spectrometer (MS/MS) system (Agilent, USA). A Poroshell 120 EC-C18 column (2.1 mm × 50 mm, i.d., 2.7 μm, Agilent, USA) was utilised for the analysis at a temperature of 40 °C, and the injection volume was 2 μL. The mobile phases consisted of acetonitrile (A) and aqueous solution containing 0.1 % acetic acid and 5 mmol/L of ammonium acetate (B) at a flow rate of 0.3 mL/min. Gradient elutions were performed as follows: 0–1 min, 5 % A; 1–2 min, 95 % A; 2–4 min, 95 % A; 4–4.1 min, 5 % A; 4.1–5.5 min, 5 % A. Typical MS parameters were set as follows: capillary voltage, 4000 V (positive) and 3000 V (negative); nozzle voltage, 1500 V (positive) and 1500 V (negative); gas temperature of 250 °C and a flow rate of 14 L/min; sheath gas temperature of 325 °C and a flow rate of 11 L/min; nebuliser, 35 psi. The analysis was conducted in multiple reaction monitoring (MRM) mode in the positive and negative ion modes. The MRM parameters of the four analytes are shown in Table S1.

### 2.4. Dietary intake risk assessment

Dietary intake risk was conducted for both chronic and acute assessments according to the method recommended by the Food and Agriculture Organization / World Health Organization (FAO/WHO, 2023). To assess the dietary intake risk of chronic exposure to fungicides from cowpeas, the national estimated daily intake (NEDI, μg/kg bw/d) and chronic risk quotient (RQc) were calculated with the using Equations (1) and (2):

$$\mathrm{NEDI} = \mathrm{STMR} \times \mathrm{F} / \mathrm{bw} / 1000 \tag{1}$$

$$\mathrm{RQc} = \mathrm{NEDI} / \mathrm{ADI} \tag{2}$$

To assess the dietary intake risk of acute exposure to fungicides from cowpeas, the international estimation of short-term intake (IESTI, μg/kg bw/d) and acute risk quotient (RQa) were calculated with the using Equations (3) and (4):

$$\mathrm{IESTI} = \mathrm{LP} \times \mathrm{HR} / \mathrm{bw} / 1000 \tag{3}$$

$$\mathrm{RQa} = \mathrm{IESTI} / \mathrm{ARfD} \tag{4}$$

Here, STMR and HR are respectively the median and highest residue concentrations in the cowpeas (μg/kg). F is the average consumption of cowpeas (g/d), and LP is the large portion of cowpeas (g/d). bw is the body weight for the different age group populations (kg). ADI is the acceptable daily intake of a given fungicide (μg/kg bw/d), and ARfD is the acute reference dose of a given fungicide (μg/kg bw/d). RQ is the risk quotient; the larger the RQ values, the higher the health risk; if RQ > 1, it poses an unacceptable risk. Detailed parameters/exposure factors used for health risk assessment are listed in Table S2.

### 2.5. Data analysis

To assess the residue dissipation of fungicides in cowpeas, residual data were fitted with the first-order kinetic equation using Equation (5), and the half-life ($t_{1/2}$) was calculated using Equation (6).

$$C_t = C_0 \times e^{-kt} \tag{5}$$

$$t_{1/2} = (\ln 2)/k \tag{6}$$

Here, $C_0$ and $C_t$ are the residue concentrations of fungicides at the initial time 0 and a given time t, respectively.

To assess the residue accumulation of fungicides in cowpeas after repeated spraying, residue accumulation (RA) values were calculated using Equation (7) as described by Wang et al. (2021b).

$$\mathrm{RA} = 1{:}\ (C2/\mathrm{C1}){:}\ (\mathrm{C3}/C2) \tag{7}$$

Here, C1, $C2$ and C3 are the residue concentrations of fungicides at the same time plot after the first, second and third spraying, respectively.

The statistical analysis between old and tender cowpeas, upper and lower half parts of cowpea pods and cowpeas distributed in the upper and lower half parts of plants was performed using Student's *t*-test with SPSS 25.0 software (IBM Corporation, USA). A one-way analysis of variance with Duncan's test was used to determine the statistical significance of the differences between fungicide residues at different sampling time points after each spray. The differences were considered statistically significant when the P value was < 0.05.

## 3. Results

### 3.1. Method validation

The detection method was validated in linearity, the limit of quantification (LOQ), matrix effect (ME), precision and accuracy following the standards described in the SANTE/11312/2021 (https://food.ec.europa.eu/system/files/2023–11/pesticides_mrl_guidelines_wrkdoc_2021-11312.pdf), and the results are shown in Table 1. The calibration curves of the four fungicides in different matrices indicated a good linearity with the correlation coefficients ($R^2$) from 0.9918 to 1 in the range of 1–2000 μg/kg. The LOQ of the four fungicides was 1 μg/kg, which was the lowest spiked recovery concentration in this study. Considering the potential signal suppression or enhancement induced by the cowpea matrices, the ME values were calculated using the following formula, ME = [slope (matrix) / slope (solvent) − 1] × 100 %. DIF, DIM and PYR showed strong signal suppression with ME values from −68.24 % to −20.74 %, whereas THI showed strong signal enhancement with a ME value of 54.28 %. Thus, all fungicides were quantified in cowpeas using matrix-matched calibration curves by external standard methods to avoid the ME. Recovery experiments were performed at spiked levels of 1, 10, 100 and 2000 μg/kg for all fungicides to assess the accuracy and precision of this method, and five replicates were done at each spiked level. Satisfactory average recoveries were 83.38 %–106.84 % for different analytes in cowpeas with relative standard deviations of 1.12 %–9.21 %. All data were considered to be acceptable, and our method was reliable for the determination of the selected four fungicides in the cowpea samples.

**Table 1**
Regression equations, correlation coefficients ($R^2$), matrix effects (MEs), average recoveries (%) and relative standard deviations (RSDs, %) for DIF, DIM, PYR and THI.

| Fungicide | Matrix | Regression equation | $R^2$ | ME (%) | Average recovery, % (RSD, %) | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | 1 μg/kg | 10 μg/kg | 100 μg/kg | 2000 μg/kg |
| DIF | acetonitrile | $y = 52563x + 660737$ | 0.9918 | – | | | | |
| | cowpea | $y = 41663x + 61249$ | 1 | −20.74 | 91.18 (9.21) | 88.89 (8.53) | 94.07 (1.16) | 95.45 (1.41) |
| DIM | acetonitrile | $y = 67894x + 217378$ | 0.9989 | – | | | | |
| | cowpea | $y = 50959x - 156{,}560$ | 0.9991 | −24.94 | 88.32 (4.42) | 87.63 (4.66) | 88.07 (2.17) | 89.15 (1.12) |
| PYR | acetonitrile | $y = 146447x - 108{,}068$ | 0.9977 | – | | | | |
| | cowpea | $y = 46507x - 6815$ | 1 | −68.24 | 87.54 (3.65) | 83.38 (4.77) | 89.73 (2.83) | 91.51 (3.63) |
| THI | acetonitrile | $y = 783x + 2666$ | 0.9992 | – | | | | |
| | cowpea | $y = 1208x + 9871$ | 0.9979 | 54.28 | 106.84 (4.31) | 96.50 (6.97) | 104.73 (3.90) | 103.33 (2.23) |

### *3.2. Dissipation behavior and residue accumulation of fungicides in greenhouse and open-field cowpeas*

The dissipation dynamics of the four selected fungicides in cowpeas after each spraying are listed in Table 2. On the whole, all fungicides exhibited a stepped downwards trend in residue amounts after spraying, and pesticide residues increased with an increase in spraying times (Fig. 2). The dissipation half-lives of fungicides in cowpeas in the open field were 1.79–2.09 d for DIF, 1.72–2.41 d for DIM, 1.67–1.81 d for PYR and 1.49–2.54 d for THI, whereas those in the greenhouse were 1.72–3.54 d for DIF, 2.35–5.25 d for DIM, 1.67–2.30 d for PYR and 2.03–3.35 d for THI (Table 2). The average half-lives of DIF, DIM, PYR and THI of the three successive sprays in the greenhouse were 1.36, 1.78, 1.21 and 1.39 times higher than those in the open field. The results indicated that the selected fungicides dissipated faster in the open field than in the greenhouse.

The residue accumulation of fungicides in cowpeas after repeated spraying was assessed based on the RA values and the calculated results are shown in Table 2. The average RA values of DIF, DIM, PYR and THI in the field were 1: 1.30: 1.28, 1: 1.29: 0.98, 1: 1.24: 1.15 and 1: 1.34: 1.14, and those in the greenhouse were 1: 1.63: 1.49, 1: 1.27: 1.18, 1: 1.11: 2.17, and 1: 1.39: 1.63, respectively. The results suggested that repeated spraying could result in the residue accumulation of the selected fungicides in both the greenhouse and open-field cowpeas. A $C_{GH}$ / $C_{OF}$ value that was expressed by dividing the fungicide residues in the greenhouse cowpeas by the residues in the open-field cowpeas at each same time plot was used to assess the residue differences between the greenhouse and open-field cowpeas. As shown in Table 2, the $C_{GH}$ / $C_{OF}$ values range for DIF is 0.92–4.81, 0.84–7.48 for DIM, 0.98–4.00 for PYR and 0.86–8.19 for THI. Almost all $C_{GH}$ / $C_{OF}$ values were higher than 1, except for a small minority of outlier values; this indicated that residue amounts of the selected fungicides in the greenhouse cowpeas were larger than those in the open-field cowpeas.

### *3.3. Distribution profiles of fungicides in greenhouse and open-field cowpeas*

In this work, the residue differences of fungicides in different cowpea parts and types were compared, and raw data are shown in Table S3. Fungicide residues in old cowpeas were significantly higher than those in tender cowpeas, including DIF and THI in the greenhouse and open-field cowpeas, and DIM and PYR in the greenhouse cowpeas (Fig. 3). The cowpea samples were divided into two equal parts from the middle, which were the upper and lower parts of the pods. The results suggested that residue concentrations of all selected fungicides in the greenhouse and open-field cowpeas were significantly higher in the upper parts of the pods than in the lower parts of the pods (Fig. 3). In addition, the cowpeas distributed in the upper and lower half parts of the cowpea plants were collected separately. The results suggested that residue concentrations of DIM, PYR and THI in the greenhouse and open-field cowpeas were significantly higher in the lower parts of the plants than in the upper parts of the plants (Fig. 3). Overall, the results indicated that the selected fungicides were not uniformly distributed in different cowpea parts and types, and consuming low-residue cowpeas can help in reducing fungicide intake.

### *3.4. Dietary risk assessment of fungicides in greenhouse and open-field cowpeas*

At present, the maximum residue limits of DIF, DIM, PYR and THI in cowpeas have not been established by the Chinese government. Considering the widespread use of these fungicides and their potential hazards, chronic and acute dietary risk assessments were conducted based on their respective pre-harvest intervals (PHIs) in cowpeas (7 days for DIF and 3 days for DIM, PYR and THI). The RQc values of DIF, DIM, PYR and THI in greenhouse and open-field cowpeas were $<$ 0.001–0.007, $<$ 0.001–0.003, 0.001–0.008 and 0.002–0.02 (Table 3), which were far smaller than 1, indicating that these fungicides in cowpeas posed a negligible chronic health risk to children and adults. Moreover, the RQa values of DIF, DIM and PYR in greenhouse and open-field cowpeas were 0.001–0.007, 0.007–0.025 and 0.046–0.132 (Table 3), i.e. $<$ 1, indicating that acute exposure to these three fungicides from cowpea consumption was within the acceptable limits. THI was absent from the acute dietary risk assessment because its ARfD value was not found in the existing literature. Notably, the RQ values of the fungicides in greenhouse cowpeas were larger than those in open-field cowpeas due to higher fungicide residues in greenhouse cowpeas; therefore, more attention should be given to the use of fungicides in greenhouse cowpeas.

## 4. Discussion

Cowpea is a commonly consumed vegetable variety that is suffering serious problems regarding pesticide residues in China (Duan et al., 2016; Liu et al., 2021; Luo et al., 2023; Ren et al., 2023). Hence, studying the dissipation, accumulation, distribution and risk assessment of fungicides in greenhouse and open-field cowpeas is of vital importance to ensure food safety and protect public health. In this study, the field test results showed that the concentrations of fungicides in the greenhouse cowpeas were higher than those in the open-field cowpeas, and these fungicides dissipated faster in the open field than in the greenhouse. We speculated that the reason for the faster decrease of fungicides under open-field conditions was mainly due to the direct effect of rainfall and solar radiation and possibly higher ultraviolet radiation. Several studies have confirmed the effects of environmental factors on the persistence of pesticide residues in crops (Allen et al., 2015; Fantke and Juraske, 2013; Yang et al., 2022). Several other studies also found higher pesticide residues in protected environments than in open-field conditions (Buddidathi et al., 2016; Chen et al., 2021; Tang et al., 2021; Yang et al., 2022). Moreover, evidence from our study suggested that all surveyed fungicides accumulated in greenhouse and open-field cowpeas after repeated spraying. Similarly, Wang et al. (2021b) verified the RA of four fungicides, i.e. procymidone, cyprodinil, pyrimethanil and pyraclostrobin, on greenhouse strawberries. RA of pesticides is a common phenomenon because pesticides are usually not completely degraded before the next application (Cui et al., 2023b; Wang et al., 2021b). For instance,

**Table 2**
Residues (μg/kg), dissipation dynamic, residue accumulation (RA) and $C_{GH}$ / $C_{OF}$ (concentrations in the greenhouse / concentrations in the open field) of DIF, DIM, PYR and THI in cowpeas after repeated spraying.

| Fungicide | Time | Open Field | | | | Greenhouse | | | | $C_{GH}$ / $C_{OF}$ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1st | 2nd | 3rd | RA | 1st | 2nd | 3rd | RA | 1st | 2nd | 3rd |
| DIF | 2 h | $429.66^{a} \pm 29.16$ | $510.08^{b} \pm 5.04$ | $867.99^{a} \pm 3.31$ | 1: 1.19: 1.70 | $566.3^{b} \pm 18.64$ | $745.64^{a} \pm 8.22$ | $1110.8^{b} \pm 15.03$ | 1: 1.32: 1.49 | 1.32 | 1.46 | 1.28 |
| | 1 d | $258.32^{c} \pm 22.58$ | $539.46^{a} \pm 14.3$ | $518.87^{b} \pm 12.6$ | 1: 2.09: 0.96 | $586.48^{a} \pm 6.61$ | $735.4^{a} \pm 9.61$ | $1350.53^{a} \pm 8.94$ | 1: 1.25: 1.84 | 2.27 | 1.36 | 2.60 |
| | 3 d | $386.04^{b} \pm 16.61$ | $335.17^{c} \pm 1.38$ | $360.21^{c} \pm 8.14$ | 1: 0.87: 1.07 | $353.49^{c} \pm 10.07$ | $674.68^{b} \pm 4.07$ | $1066.13^{c} \pm 20.8$ | 1: 1.91: 1.58 | 0.92 | 2.01 | 2.96 |
| | 5 d | $119.22^{d} \pm 3.71$ | $157.41^{d} \pm 5.82$ | $192.87^{d} \pm 11.86$ | 1: 1.32: 1.23 | $221.14^{d} \pm 1.65$ | $538.81^{c} \pm 1.57$ | $573.41^{d} \pm 3.7$ | 1: 2.44: 1.06 | 1.85 | 3.42 | 2.97 |
| | 7 d | $21.32^{e} \pm 0.63$ | $33.52^{e} \pm 1.48$ | $73.53^{e} \pm 3.9$ | 1: 1.57: 2.19 | $28.38^{e} \pm 1.88$ | $161.1^{d} \pm 7.51$ | $152.58^{e} \pm 3.83$ | 1: 5.68: 0.95 | 1.33 | 4.81 | 2.08 |
| | Mean | 242.91 | 315.13 | 402.69 | 1: 1.30: 1.28 | 351.16 | 571.13 | 850.69 | 1: 1.63: 1.49 | 1.45 | 1.81 | 2.11 |
| | Dynamic equation | $y = 560.25e^{-0.387x}$ | $y = 750.66e^{-0.385x}$ | $y = 861.20e^{-0.331x}$ | – | $y = 861.37e^{-0.402x}$ | $y = 944.21e^{-0.196x}$ | $y = 1673.69e^{-0.282x}$ | – | – | – | – |
| | R2 | 0.7896 | 0.8964 | 0.9745 | – | 0.8351 | 0.7348 | 0.8104 | – | – | – | – |
| | t1/2 (d) | 1.79 | 1.80 | 2.09 | – | 1.72 | 3.54 | 2.46 | – | – | – | – |
| | Mean t1/2 (d) | 1.89 | | | – | 2.57 | | | – | – | – | – |
| DIM | 2 h | $854.66^{a} \pm 8.11$ | $1115.26^{a} \pm 4.46$ | $1133.92^{a} \pm 6.02$ | 1: 1.30: 1.02 | $1007.75^{b} \pm 5.9$ | $1247.9^{a} \pm 3.68$ | $1490.23^{a} \pm 3.44$ | 1: 1.24: 1.19 | 1.18 | 1.12 | 1.31 |
| | 1 d | $676.04^{c} \pm 13.26$ | $1022.47^{b} \pm 12.11$ | $1146.72^{a} \pm 8.88$ | 1: 1.51: 1.12 | $1081.97^{a} \pm 13.85$ | $1252.97^{a} \pm 1.98$ | $1207.17^{b} \pm 4.85$ | 1: 1.16: 0.96 | 1.60 | 1.23 | 1.05 |
| | 3 d | $740.23^{b} \pm 21.4$ | $822.37^{c} \pm 3.32$ | $417.16^{c} \pm 27.63$ | 1: 1.11: 0.51 | $771.39^{c} \pm 8.91$ | $1194.62^{b} \pm 3.31$ | $1005.63^{d} \pm 40.9$ | 1: 1.55: 0.84 | 1.04 | 1.45 | 2.41 |
| | 5 d | $174.38^{d} \pm 2.86$ | $302.59^{d} \pm 3.55$ | $503.16^{b} \pm 14.52$ | 1: 1.74: 1.66 | $535.49^{d} \pm 6.31$ | $487.44^{c} \pm 3.27$ | $1083.95^{c} \pm 3.53$ | 1: 0.91: 2.22 | 3.07 | 1.61 | 2.15 |
| | 7 d | $133.68^{e} \pm 4.41$ | $62.28^{e} \pm 1.11$ | $65.11^{e} \pm 3.36$ | 1: 0.47: 1.05 | $112.54^{e} \pm 1.47$ | $278.79^{d} \pm 14.99$ | $486.74^{e} \pm 60.19$ | 1: 2.48: 1.75 | 0.84 | 4.48 | 7.48 |
| | Mean | 515.80 | 665.00 | 653.21 | 1: 1.29: 0.98 | 701.83 | 892.34 | 1054.75 | 1: 1.27: 1.18 | 1.36 | 1.34 | 1.61 |
| | Dynamic equation | $y = 1005.56e^{-0.288x}$ | $y = 1627.22^{e-0.402x}$ | $y = 1486.88e^{-0.374x}$ | – | $y = 1422.6e^{-0.295x}$ | $y = 1580.85e^{-0.228x}$ | $y = 1513.10e^{-0.132x}$ | – | – | – | – |
| | R2 | 0.8592 | 0.881 | 0.8228 | – | 0.8125 | 0.8785 | 0.7779 | – | – | – | – |
| | t1/2 (d) | 2.41 | 1.72 | 1.85 | – | 2.35 | 3.04 | 5.25 | – | – | – | – |
| | Mean t1/2 (d) | 1.99 | | | | 3.55 | | | – | | | |
| PYR | 2 h | $276.85^{a} \pm 18.38$ | $394.95^{a} \pm 14.56$ | $447.92^{a} \pm 4.27$ | 1: 1.43: 1.13 | $320.24^{b} \pm 1.18$ | $471.19^{a} \pm 23.14$ | $787.1^{b} \pm 11.09$ | 1: 1.47: 1.67 | 1.16 | 1.19 | 1.76 |
| | 1 d | $218.66^{b} \pm 15.27$ | $351.95^{b} \pm 16.04$ | $415.33^{b} \pm 8.18$ | 1: 1.61: 1.18 | $502.49^{a} \pm 25.93$ | $431.37^{a} \pm 15.4$ | $1112.97^{a} \pm 8.07$ | 1: 0.86: 2.58 | 2.30 | 1.23 | 2.68 |
| | 3 d | $253.77^{a} \pm 12.66$ | $222.6^{c} \pm 17.47$ | $229.69^{c} \pm 13.25$ | 1: 0.88: 1.03 | $249.85^{c} \pm 7.59$ | $242.77^{b} \pm 83.02$ | $520.96^{c} \pm 1.82$ | 1: 0.97: 2.15 | 0.98 | 1.09 | 2.27 |
| | 5 d | $98.08^{c} \pm 9.59$ | $72.22^{d} \pm 2.74$ | $101.29^{d} \pm 5.06$ | 1: 0.74: 1.40 | $120.76^{d} \pm 1.27$ | $145.28^{c} \pm 1.12$ | $405.27^{d} \pm 6.08$ | 1: 1.20: 2.79 | 1.23 | 2.01 | 4.00 |
| | 7 d | $11.36^{d} \pm 0.29$ | $24.2^{e} \pm 0.58$ | $32.04^{e} \pm 1$ | 1: 2.13: 1.32 | $19.11^{e} \pm 0.72$ | $57.32^{d} \pm 5.07$ | $97.66^{e} \pm 0.58$ | 1: 3.00: 1.70 | 1.68 | 2.37 | 3.05 |
| | Mean | 171.74 | 213.18 | 245.25 | 1: 1.24: 1.15 | 242.49 | 269.59 | 584.79 | 1: 1.11: 2.17 | 1.41 | 1.26 | 2.38 |
| | Dynamic equation | $y = 422.94e^{-0.415x}$ | $y = 523.11e^{-0.409x}$ | $y = 577.55e^{-0.382x}$ | – | $y = 590.61e^{-0.414x}$ | $y = 554.46e^{-0.301x}$ | $y = 1184.96e^{-0.302x}$ | – | – | – | – |
| | R2 | 0.7727 | 0.9561 | 0.9634 | – | 0.8389 | 0.9731 | 0.8432 | – | – | – | – |
| | t1/2 (d) | 1.67 | 1.69 | 1.81 | – | 1.67 | 2.30 | 2.30 | – | – | – | – |
| | Mean t1/2 (d) | 1.72 | | | | 2.09 | | | – | | | |
| THI | 2 h | $293.02^{a} \pm 18.58$ | $472.46^{a} \pm 16.75$ | $489.97^{b} \pm 1.93$ | 1: 1.61: 1.04 | $371.74^{b} \pm 15.81$ | $616.68^{a} \pm 17.2$ | $1158.11^{a} \pm 13.26$ | 1: 1.66: 1.88 | 1.27 | 1.31 | 2.36 |
| | 1 d | $284.52^{a} \pm 17.11$ | $384^{b} \pm 11.14$ | $503.27^{a} \pm 5.09$ | 1: 1.35: 1.31 | $534.18^{a} \pm 27.78$ | $543.04^{b} \pm 12.19$ | $698.63^{b} \pm 13.15$ | 1: 1.02: 1.29 | 1.88 | 1.41 | 1.39 |
| | 3 d | $220.8^{b} \pm 15.48$ | $277.96^{c} \pm 6.79$ | $287.62^{c} \pm 11.82$ | 1: 1.26: 1.03 | $289.68^{c} \pm 4.45$ | $425.34^{c} \pm 25.89$ | $624.91^{c} \pm 24.01$ | 1: 1.47: 1.47 | 1.31 | 1.53 | 2.17 |
| | 5 d | $112.11^{c} \pm 3.47$ | $125.99^{d} \pm 3.73$ | $135.15^{d} \pm 8.07$ | 1: 1.12: 1.07 | $152.03^{d} \pm 8.72$ | $229.9^{d} \pm 2.72$ | $449.97^{d} \pm 19.38$ | 1: 1.51: 1.96 | 1.36 | 1.82 | 3.33 |
| | 7 d | $43.33^{d} \pm 2.12$ | $14.17^{e} \pm 0.47$ | $41.06^{e} \pm 2.44$ | 1: 0.33: 2.90 | $37.43^{e} \pm 1.61$ | $116.08^{e} \pm 5.29$ | $222.41^{e} \pm 11.12$ | 1: 3.10: 1.92 | 0.86 | 8.19 | 5.42 |
| | Mean | 190.76 | 254.91 | 291.42 | 1: 1.34: 1.14 | 277.01 | 386.21 | 630.81 | 1: 1.39: 1.63 | 1.45 | 1.52 | 2.16 |
| | Dynamic equation | $y = 373.23e^{-0.273x}$ | $y = 695.56e^{-0.466x}$ | $y = 663.76e^{-0.360x}$ | – | $y = 603.13e^{-0.342x}$ | $y = 707.87e^{-0.239x}$ | $y = 1070.86e^{-0.207x}$ | – | – | – | – |

(*continued on next page*)

**Table 2** (*continued*)

| Fungicide | Time | Open Field |  |  |  | Greenhouse |  |  |  | $C_{GH}$ / $C_{OF}$ |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  | 1st | 2nd | 3rd | RA | 1st | 2nd | 3rd | RA | 1st | 2nd | 3rd |
|  | R2 | 0.9165 | 0.8588 | 0.9428 | – | 0.8625 | 0.958 | 0.9277 | – | – | – | – |
|  | t1/2 (d) | 2.54 | 1.49 | 1.93 | – | 2.03 | 2.90 | 3.35 | – | – | – | – |
|  | Mean t1/2 (d) | 1.99 |  |  |  | 2.76 |  |  | – |  |  |  |

Note: Values of different letters (a–e) are significantly different ($P < 0.05$).

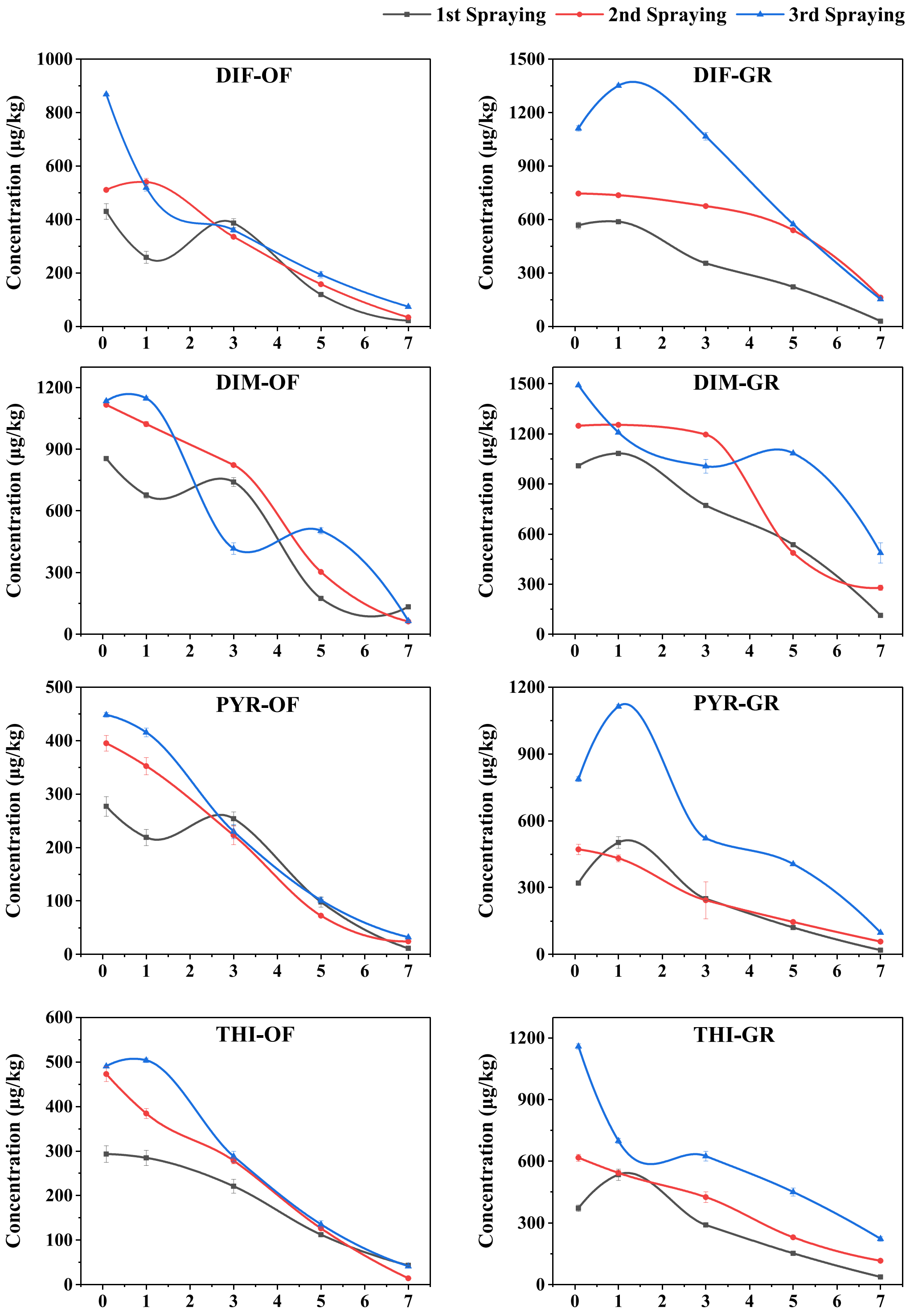


**Fig. 2.** Dissipation of DIF, DIM, PYR and THI in the greenhouse (GR) and open-field (OF) cowpeas after three sprays.

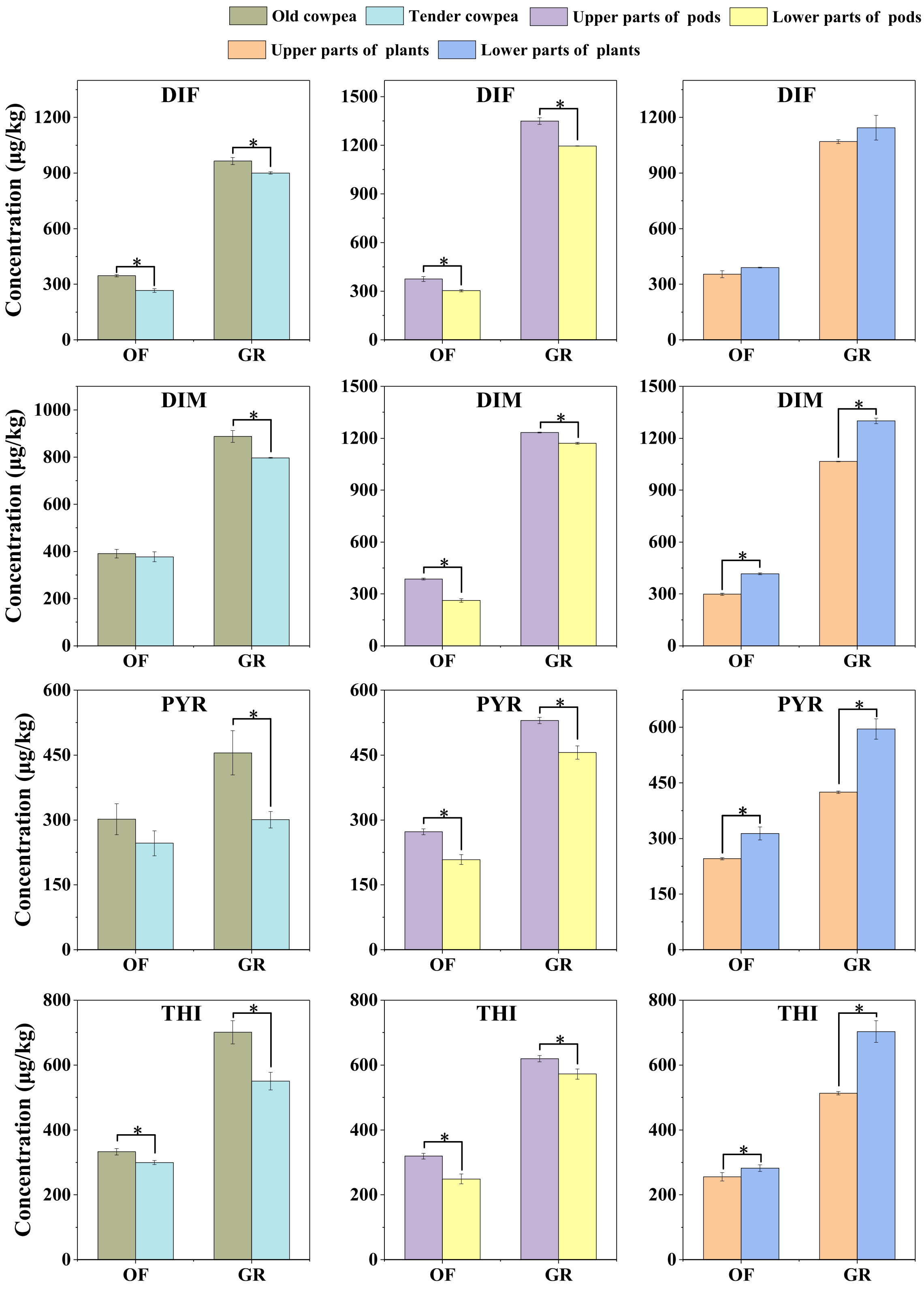


**Fig. 3.** Distribution of DIF, DIM, PYR and THI in different cowpea parts and types in the greenhouse (GR) and open field (OF). (* indicates significant differences, Student's *t*-test, P < 0.05.).

our previous study found that fluxapyroxad residues were 23.22 μg/kg and 86.30 μg/kg in cucumbers before the second and third spray, respectively, whereas those in cowpeas were 908.73 μg/kg and 1439.94 μg/kg, respectively (Cui et al., 2023b). We need to apply various fungicides on cowpeas to ensure the effectiveness of pathogen control, but at the same time, we should try to reduce application times to minimise the dietary exposure risk due to their potential RA.

Fungicide residues in different cowpea parts and types were significantly different. The first difference is that fungicide residues were higher in old cowpeas than in tender cowpeas. The growth dilution

**Table 3**
Chronic and acute risk quotients of DIF, DIM, PYR and THI in the greenhouse and open-field cowpeas for children and adults.

| Fungicide | Planting position | Spraying time | NEDI (μg/kg bw/d) | | RQc | | IESTI (μg/kg bw/d) | | RQa | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Children | Adults | Children | Adults | Children | Adults | Children | Adults |
| DIF | Open field | 1 | 0.010 | 0.003 | 0.001 | <0.001 | 0.276 | 0.209 | 0.001 | 0.001 |
| | | 2 | 0.015 | 0.004 | 0.001 | <0.001 | 0.444 | 0.336 | 0.001 | 0.001 |
| | | 3 | 0.034 | 0.010 | 0.003 | 0.001 | 0.955 | 0.723 | 0.003 | 0.002 |
| | Greenhouse | 1 | 0.013 | 0.004 | 0.001 | <0.001 | 0.376 | 0.285 | 0.001 | 0.001 |
| | | 2 | 0.074 | 0.022 | 0.007 | 0.002 | 2.095 | 1.586 | 0.007 | 0.005 |
| | | 3 | 0.069 | 0.021 | 0.007 | 0.002 | 1.963 | 1.486 | 0.007 | 0.005 |
| DIM | Open field | 1 | 0.336 | 0.102 | 0.002 | 0.001 | 9.502 | 7.193 | 0.016 | 0.012 |
| | | 2 | 0.368 | 0.112 | 0.002 | 0.001 | 10.390 | 7.865 | 0.017 | 0.013 |
| | | 3 | 0.180 | 0.055 | 0.001 | <0.001 | 5.656 | 4.282 | 0.009 | 0.007 |
| | Greenhouse | 1 | 0.343 | 0.104 | 0.002 | 0.001 | 9.846 | 7.454 | 0.016 | 0.012 |
| | | 2 | 0.535 | 0.162 | 0.003 | 0.001 | 15.076 | 11.412 | 0.025 | 0.019 |
| | | 3 | 0.441 | 0.134 | 0.002 | 0.001 | 13.261 | 10.038 | 0.022 | 0.017 |
| PYR | Open field | 1 | 0.115 | 0.035 | 0.004 | 0.001 | 3.328 | 2.519 | 0.067 | 0.050 |
| | | 2 | 0.097 | 0.029 | 0.003 | 0.001 | 3.054 | 2.312 | 0.061 | 0.046 |
| | | 3 | 0.100 | 0.030 | 0.003 | 0.001 | 3.085 | 2.335 | 0.062 | 0.047 |
| | Greenhouse | 1 | 0.112 | 0.034 | 0.004 | 0.001 | 3.243 | 2.455 | 0.065 | 0.049 |
| | | 2 | 0.129 | 0.039 | 0.004 | 0.001 | 3.687 | 2.791 | 0.074 | 0.056 |
| | | 3 | 0.233 | 0.071 | 0.008 | 0.002 | 6.588 | 4.987 | 0.132 | 0.100 |
| THI | Open field | 1 | 0.098 | 0.030 | 0.007 | 0.002 | 2.981 | 2.256 | – | – |
| | | 2 | 0.124 | 0.038 | 0.009 | 0.003 | 3.594 | 2.720 | – | – |
| | | 3 | 0.126 | 0.038 | 0.009 | 0.003 | 3.795 | 2.872 | – | – |
| | Greenhouse | 1 | 0.129 | 0.039 | 0.009 | 0.003 | 3.708 | 2.807 | – | – |
| | | 2 | 0.187 | 0.057 | 0.013 | 0.004 | 5.722 | 4.331 | – | – |
| | | 3 | 0.283 | 0.086 | 0.020 | 0.006 | 8.111 | 6.140 | – | – |

effect may be the main reason for fungicide decrease in tender cowpeas, where fungicides are typically diluted with cowpea growth (Li, 2023; Zongmao and Haibin, 1988). Similar to our results, emamectin benzoate, an insecticide, also dissipated faster in tender cowpeas than in old cowpeas and presented higher residue amounts in old cowpeas (Wang et al., 2021a). Moreover, we found that, even in the same cowpea pods, the upper parts had significantly higher fungicide residues than the lower parts. Cowpea pods elongate from the tips at the lower parts of the pods; we speculate that the lower pod growth may result in the fungicide dilution. In addition, the cowpeas that were distributed in the lower parts of the cowpea plants had significantly higher fungicide residues than the upper parts of the plants. After application, fungicides in the atmosphere tended to deposit down to the lower portion of the plants. Moreover, solar radiation intensity was higher in the upper portion of the plants, accelerating the degradation of fungicides in the upper cowpeas (Sandoval et al., 2022). These reasons may result in higher fungicide residues in cowpeas in the lower parts of the cowpea plants. Therefore, choosing low-residue cowpea parts and types for consumption can help in reducing pesticide intake and decreasing the dietary exposure risk.

The RQ values (RQc range, < 0.001–0.02; RQa range, 0.001–0.132) of the fungicides of this study were much less than 1, indicating that chronic and acute exposure to the surveyed fungicides from cowpea consumption are at low levels for both children and adults. Previous studies also found an acceptable dietary exposure risk for PYR and THI from cowpea consumption based on field trials at eight locations in China (Han et al., 2022). Despite the low health risk, the potential hazards of dietary exposure to fungicides should raise more public attention. In contrast, these fungicides maintained high residue levels even at PHIs. Moreover, other daily-consumed foods by the citizens, such as fruits, vegetables cereals, and aquatic products, may also contain these fungicides to increase the dietary exposure risk (Kim et al., 2023; Khazaal et al., 2022; Rodríguez-Ramos et al., 2023). However, these fungicides are often repeatedly sprayed, depending on the personal experience of farmers and disease severity in cowpea management (Bagheri et al., 2021; Pan et al., 2021), resulting in higher fungicide residues in the really case in the field than those of our supervised field trials. In addition, different fungicides coexisted in agricultural products and potentially resulted in cumulative toxicity (Tsatsakis et al., 2019; Wang et al., 2023). Remarkably, the dietary intake risk of fungicides from the greenhouse cowpeas was much larger than those from the open-field cowpeas, and this required us to ensure the scientific and standardised use of fungicides in cowpea planting in the greenhouse.

## 5. Conclusions

In this study, the dissipation, accumulation, distribution and risk assessment of four commonly used fungicides were comprehensively explored in relation to greenhouse and open-field cowpeas. Our results suggest that fungicides dissipated faster in the open-field cowpeas than in the greenhouse cowpeas, and their residues in greenhouse cowpeas were higher than those in open-field cowpeas. All surveyed fungicides had the RA potentials after repeated spraying in both the greenhouse and open-field cowpeas. The fungicide residues in old cowpeas were higher than in tender cowpeas, while those in the upper half parts of cowpea pods were higher than those in the lower half parts. Moreover, cowpeas distributed in the lower half parts of the plants had higher fungicide residues than those in the upper half parts. Therefore, the consumption of the lower half parts of tender cowpea pods that distribute the lower half parts of the plants may help reduce fungicide intake. The chronic and acute dietary risk assessment results based on the supervised field trials indicate that the dietary intake risk of the surveyed fungicides from cowpea consumption was considered to be at an acceptable level for human health. This study described and compared the residue fate of four fungicides in greenhouse and open-field cowpeas, and the results provide a scientific basis for establishing the maximum residue limits and guiding the standard use of these fungicides.

## CRediT authorship contribution statement

**Kai Cui:** Formal analysis, Funding acquisition, Investigation, Methodology, Software, Validation, Writing – original draft, Writing – review & editing. **Guoping Ma:** Writing – original draft, Writing – review & editing. **Shengying Zhao:** Supervision, Validation. **Shuai Guan:** Investigation, Methodology. **Jingyun Liang:** Investigation, Methodology. **Liping Fang:** Software, Validation. **Ruiyan Ding:** Data curation. **Teng Li:** Resources. **Qian Hao:** Conceptualization, Resources,

Validation. **Zhan Dong:** Conceptualization, Funding acquisition, Supervision, Writing – review & editing. **Jian Wang:** Conceptualization, Resources, Validation.

## 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

No data was used for the research described in the article.

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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.2024.101172.

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