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Dissipation, Residue Behavior and Dietary Risk Assessment of Difenoconazole on Jujube (*Ziziphus jujuba* Mill.)

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Abstract: Difenoconazole is a triazole germicide that is usually applied to prevent fungal diseases on crops with high efficiency and safety. Jujube is a spiny Rhamnaceous plant that originated in China more than 4000 years ago and is extensively cultivated in northern China nowadays. To evaluate the safety of difenoconazole in jujube, supervised field trials were carried out in six provinces of China, and the final residue and dissipation behavior of difenoconazole on jujube were determined by gas chromatography (GC). The results showed that when addition levels were 0.02, 0.2, and 2 mg·kg^{-1}, average recoveries of the aforementioned method for difenoconazole in jujube can be put into the range of 73–108%, and relative standard deviation (RSD) was 3–9%. The limit of quantitation (LOQ) for this method was 0.02 mg·kg^{-1}. In the final residue test, difenoconazole was sprayed to deal with the jujube at 100 and 150 mg·kg^{-1} doses twice or three times, respectively, while the dissipation test was applied only once at a 150 mg·kg^{-1} dose. Final residue testing results have revealed that when jujube samples were harvested and tested at 7, 14, and 21 days post-application, difenoconazole residues in samples were 0.11–1.59, 0.05–0.77, 0.04–0.63 mg·kg^{-1}, respectively. The dissipation testing results showed that the digestion process of difenoconazole in jujube tends to be a gradual reduction process and the dynamic regularity of the residue dissipation proves consistent with the first-order dynamics reaction equation. The half-life ($t_{1/2}$) for difenoconazole residue dissipation in Qingdao and Yuncheng was 13.1 days and 16.5 days, respectively. The risk quotient (RQ) was 84.9% lower than 100%, showing that dietary intake risk to difenoconazole was acceptable and the maximum residue limit (MRL) of difenoconazole on jujube is recommended to be 2 mg·kg^{-1}.

Keywords: difenoconazole; jujube; gas chromatography; dissipation; residue; dietary risk assessment

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1. Introduction

Jujube (*Ziziphus jujuba* Mill.) is a spiny Rhamnaceous plant that originated in China more than 4000 years ago [1]. Now it is extensively cultivated in northern China. Jujubes are exceedingly rich in protein, amino acids, vitamins, fiber, glucose, and trace substances [2]. As food, jujube can be directly eaten raw or made into dried red jujube. It can also be used in traditional Chinese medicine and processed into food additives and condiments that have a history stretching back thousands of years [3]. China's jujube production accounts for 90% of the world, while domestic consumption occupies a dominant position and just a small part is exported abroad [4]. Disease in jujube is caused by the infection by a pathogen because of its high sugar content (around 0.54 to 1.05 g·kg^{-1}) and its more than 80% water content [5]. Fungal diseases of jujube trees and fruits comprise anthracnose [6], gray mold rot [7,8], and stem rot [9], which can reduce jujube production.

Difenoconazole(1-[2-[2-chloro-4-(4-chloro-phenoxy)phenyl]-4-ethyl[1,3]dioxolan-2-ylmethyl]-1H-1,2,4-triazole) is an efficient and safe triazole germicide. The chemical structural formula is shown in Figure 1. It interferes with the normal growth of a pathogen by

inhibiting ergosterol biosynthesis and the sporogenesis of microorganisms [10,11]. As a broad-spectrum and efficient bactericide, difenoconazole has been widely used to control fungal diseases in grains, vegetables, and fruit trees [11–13]. In China, 796 kinds of difenoconazole and its technical products have been registered for use [14]. Previous studies [15] have shown that difenoconazole entered the water easily through rainwater runoff and accumulates in high concentrations, causing a great toxic effect on fish [16,17], Daphnia [18,19], and other aquatic organisms. It can inhibit zebrafish growth, recess incubation, slow heart rate, and produce teratogenicity [20–22]. Difenoconazole also inhibits the muscle mitochondria of bumblebees, which may reduce their pollinating activity and lifetime [23]. The residue test of difenoconazole has been carried out on many crops, such as peach [12], apple [24], pepper [25], rice [26], etc., and the final residues and half-lives ($t_{1/2}$) of difenoconazole were studied to ensure the safe use in these crops.

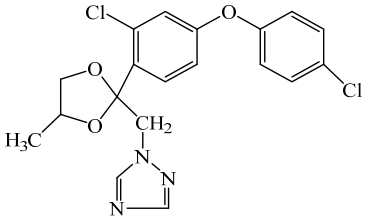


Figure 1. The chemical structural formula of difenoconazole.

To ensure the safety and health of people in the consumption of agricultural products, the maximum residue limit (MRL) of difenoconazole on vegetables, fruits, and other agricultural products has been formulated in various countries and organizations. For example, difenoconazole's MRLs on jujube formulated by the European Union (EU), the United States (US) and Japan were 0.1 [27], 2.5 [28], and 5 mg·kg^{-1} [29], respectively. In China, difenoconazole was registered for use on jujube [14], but the MRL of difenoconazole on jujube has not yet been established. Difenoconazole can effectively control many fungal diseases such as rust and anthracnose of jujube. However, there are few reports on difenoconazole residue and its dissipation in jujube.

Therefore, this study aims to (1) develop a gas chromatography (GC) analytical method for the determination of difenoconazole on jujube; (2) investigate the final residue and dissipation behavior of difenoconazole on jujube after use; (3) evaluate the dietary intake risk of difenoconazole based on the residual data. The study not only provides data support and guidance for the Chinese government to formulate MRL, but also offers a scientific and rational use for difenoconazole on jujube.

2. Materials and Methods

2.1. Chemicals and Reagents

Difenoconazole standards (purity 98.9%) were purchased from Dr. Ehrenstorfer (Augsburg, Germany). The commercial product of difenoconazole (20% microemulsion (ME)) was purchased from Hainan Boswell Agrichemical Co., Ltd. (Haikou, China). Acetonitrile (Analytical grade), ethyl acetate (Analytical grade), and sodium chloride (Analytical grade) were all purchased from Tianjin Hengxin Chemical Reagent Co., Ltd. (Tianjin, China).

2.2. Supervised Field Trials

The experiment was designed following the "guideline for the testing of pesticide residues in crops" issued by China [30]. The field trials including the dissipation trial and final residue trial were completed from May to November 2018. Field trials were carried out in six locations in China, including Beijing (116.44° N, 40.24° E), Dalian (121.97° N, 39.43° E), Jiyuan (112.23° N, 35.10° E), Shijiazhuang (114.31° N, 37.93° E), Qingdao (120.38° N, 36.71° E) and Yuncheng (111.23° N, 34.86° E). All locations have warm and temperate

monsoon climates. The Beijing test site had silty loam with 2.9% soil organic matter content and a 7.2 pH value. The Dalian site had loam soil with 2.4% soil organic matter content and a 6.8 pH value. The Jiyuan site had sandy soil with 2.1% soil organic matter content and a 7.2 pH value. The Shijiazhuang site had calcic cinnamon soil with 1.0% soil organic matter content and an 8.2 pH value. The Qingdao site had sandy soil with 2.0% soil organic matter content and a 6.5 pH value. The Yuncheng site had sandy soil with 1.8% soil organic matter content and a 7.3 pH value. The dissipation field trial was set up in Yuncheng and Qingdao. Each test site was divided into several plots containing four jujube trees, and the blank experimental plots were set the same. To avoid mutual pollution, 1 m spacing was set between adjacent test plots.

Final residue trial: 20% difenoconazole ME was sprayed on the jujube at 100 mg·kg^{-1} (recommended dose of the pesticide, the dilution multiple for 20% difenoconazole ME and water was 1/2000) and 150 mg·kg^{-1} (1.5 times the recommended application rate) doses. Each dose was sprayed twice and three times, respectively, until the leaves dripped, with a spray interval of 7 days, and the preharvest interval (PHIs) was 7, 14, and 21 days post-application.

Dissipation trial: 20% difenoconazole ME was applied to jujube at a dosage of 150 mg·kg^{-1} (spraying once) when the average size of the jujube was approximately 2 cm. Samples were randomly collected on 2 h, 1, 3, 5, 7, 10, 14, 21, 28, 35, and 42 days after spraying.

Three representative normal growing samples (each 1 kg) were picked from each test plot and instantly transported into the pretreatment lab. The core was removed and the pulp was crushed evenly. Two samples (each 200 g) were taken by quartering, packed into a sealed bag and saved at −20 °C for further study.

2.3. Standard Solutions Preparation

In total, 0.0506 g difenoconazole standard (purity 98.9%) was dissolved in 100 mL ethyl acetate (the difenoconazole concentration was 500 mg·L^{-1}) and stored at −20 °C. When used, standard solutions for mass concentrations of 0.01, 0.05, 0.1, 0.5, and 1 mg·L^{-1} were prepared with ethyl acetate by the gradient dilution method. Each standard solution was injected three times, and the average value was taken. All of the solutions were stored in a refrigerator with a temperature of 4 °C in the dark.

2.4. Sample Preparation

In total, 10.0 g of the prepared jujube sample was weighed and placed into a 250 mL conical triangular flask, with 50 mL acetonitrile added in for extraction. The sample was shaken at a constant temperature (30 °C) oscillator at 150 rpm for 30 min and left for 10 min, and then was filtered through a Buchner funnel relying on decompression. All the filtrate was collected and transferred into a separating funnel with 5 g sodium chloride, then shaken for 1 min. After standing for stratification, the upper solution was separated and concentrated until nearly dry on a rotary evaporator (50 °C). The residues were dissolved with ethyl acetate to 5 mL and then were filtered with a 0.22-micron membrane, transferred to an autosampler vial, and analyzed by GC.

2.5. GC/ECD Conditions

Residues of difenoconazole in jujube samples and standard solutions were analyzed on a GC (7890A, Agilent Technologies Co., Ltd Santa Clara, America) equipped with an electron capture detector (ECD) and an Agilent HP-5 capillary chromatography column (30 m × 0.25 mm i.d. ×0.25 μm). The injection volume was 1 μL (splitless mode). The temperature for the injector port was 280 °C and the ECD detector was 300 °C. The column oven temperature was first maintained at 180 °C for 2 min, raised to 280 ℃ with the rate of 30 °C·min^{-1}, and retained for 4 min. Ultra-high pure nitrogen was used as a carrier gas with a flow speed of 3 mL·min^{-1} and the tail gas flow spend was 45 mL·min^{-1}. The total

running time of the method was 9.33 min, and the relative retention time of difenoconazole was 7.87 ± 0.2 min.

2.6. Recovery Study

For the accuracy validation, the working standard solutions of difenoconazole were added to the jujube blank sample. The addition levels for difenoconazole in jujube were 0.02, 0.2, and 2 mg·kg^{-1}, respectively. Each addition level was repeated 5 times, and the recovery and relative standard deviation (RSD) were calculated. The precision of the method was reflected by the RSD and the interference of impurities was evaluated through analysis of the blank sample.

2.7. Data Calculation and Analysis

2.7.1. Dietary Risk Assessment

To ensure the scientific and safe application of difenoconazole, the risk quotients (RQ) method [31–33] was used to represent the long-term (chronic) dietary risk assessment. RQ was determined based on the national estimated daily intake (NEDI) and the acceptable daily intake (ADI), which were calculated in the following equation [34–36].

$$\text{NEDI} = \sum (STMR_i \times F_i)$$

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

where STMR$_i$ (mg·kg^{-1}) stands for supervised trial's median residue of difenoconazole in a certain kind of tested crop, Fi (kg) represents residents' daily consumption of a certain agricultural product (kg), and bw represents the average weight for Chinese adults (63 kg). When there is no applicable STMR, MRL can be used instead. RQ < 100%, which means that the impact of pesticide residues on the health of the general population is considered to be at an acceptable risk level. On the contrary, RQ ≥ 100%, which means that the pesticide residues are unacceptable. The smaller the RQ, the lower the risk.

2.7.2. Dissipation Kinetics

The degradation residue trend for difenoconazole on jujube was demonstrated by the first-order kinetic equation [37,38].

$$C_t = C_0 \times e^{-kt} \quad (1)$$

$$t_{1/2} = \ln \frac{2}{k} \quad (2)$$

where C_0 (mg·kg^{-1}) stands for the initial residue of difenoconazole, C_t (mg·kg^{-1}) stands for the residue of difenoconazole at time t (day), k represents the degradation rate constant, and $t_{1/2}$ is the half-life.

3. Results and Discussion

3.1. Method Validation

The applicability of the method was verified by linearity, recovery, accuracy, and precision. In the range 0.01–1 mg·L^{-1}, there was good linearity between the mass concentration of difenoconazole (x, mg·L^{-1}) and response peak area (y). The standard curve equation was $y = 39321x + 182$, with the determination coefficient (R^2) greater than 0.999. When the mass concentration of addition levels were 0.02, 0.2, and 2 mg·kg^{-1} (concentrations of the extracts were 0.04, 0.4, and 4 mg·L^{-1}), difenoconazole average recoveries on jujube were 83–105%, with the RSD (n = 5) in the range of 3–9%. The specific data are listed in Table 1. The limit of quantification (LOQ) is used to measure the accuracy of the method and is defined as the lowest amount of analyte in a sample which can be quantitatively

determined with suitable precision and accuracy. According to the above conditions, the LOQ of this method was 0.02 mg·kg^{-1}. So, the linearity, recovery, RSDs, and LOQ of the method all meet the requirements of the "Guideline for the testing of pesticide residues in crops" [30]. Representative chromatograms are shown in Figure 2.

Table 1. Recoveries and RSDs for difenoconazole on jujube (n = 5).

Sample	Spiked Level (mg·kg^{-1})	Recovery (%)					Average Recovery (%)	RSD (%)
		1	2	3	4	5		
Jujube	0.02	84	79	86	73	94	83	9
	0.2	106	107	104	99	108	105	3
	2	82	94	87	88	90	88	5

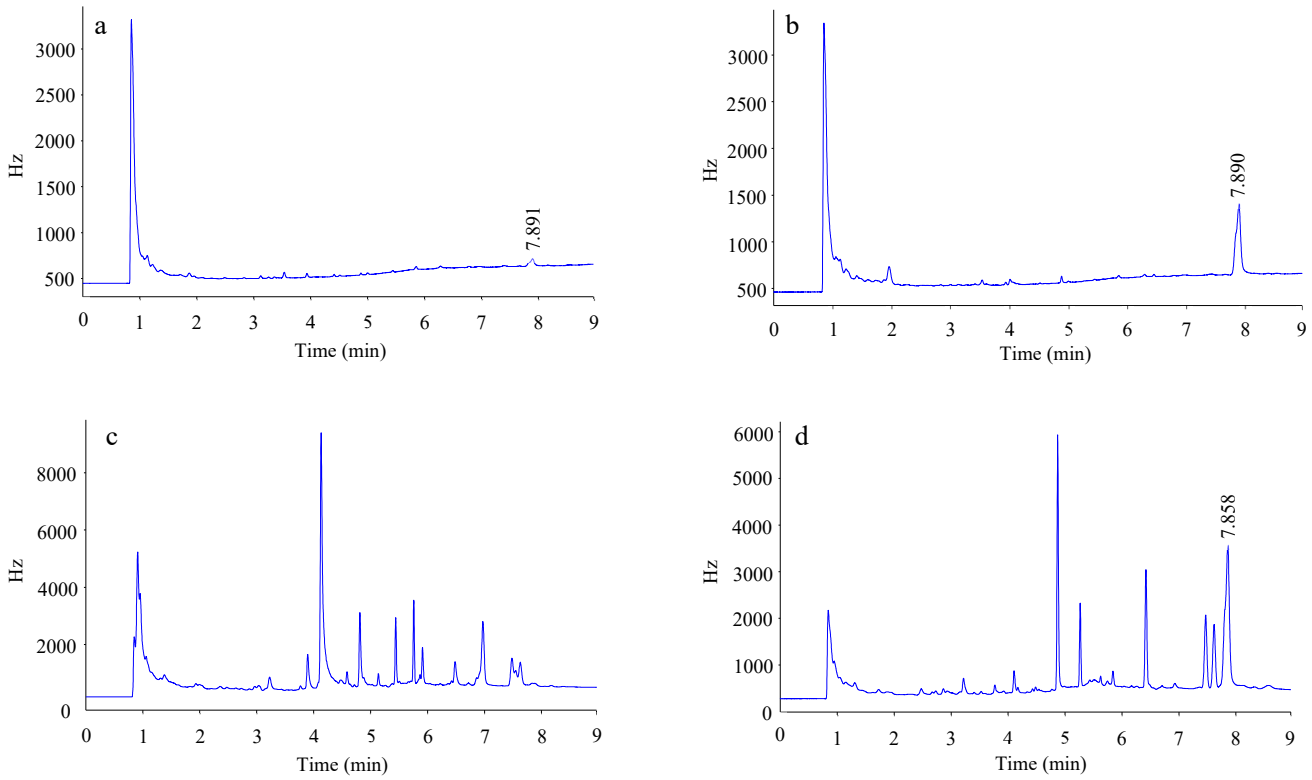


Figure 2. Representative chromatogram ((**a**). difenoconazole standard solution was 0.01 mg·L^{-1}, (**b**). difenoconazole standard solution was 0.1 mg·L^{-1}, (**c**). jujube blank sample, (**d**). addition concentration for difenoconazole in jujube was 0.2 mg·kg^{-1}).

3.2. Dissipation Residue

The dissipation field trial was set up in Yuncheng and Qingdao and the dissipation dynamics of difenoconazole in jujube were analyzed.

The dissipation residue amount for difenoconazole in jujube decreased along with time. Two hours after application, the initial concentration of difenoconazole on jujube was 0.14 mg·kg^{-1} in Qingdao and 0.26 mg·kg^{-1} in Yuncheng. On the 42nd day, the difenoconazole residue in jujube was <0.02 mg·kg^{-1} (indicating that the residue for difenoconazole on jujube was less than its LOQ) in Qingdao and 0.03 mg·kg^{-1} in Yuncheng. The dissipation kinetic equations for difenoconazole on jujube in Yuncheng was $C_t = 0.2298e^{-0.042t}$ and in Qingdao was $C_t = 0.1319e^{-0.053t}$. The half-life ($t_{1/2}$) of difenoconazole in jujube in Yuncheng and Qingdao were, respectively, 16.5 and 13.1 d, with correlation coefficients (R)

of, respectively, 0.992 and 0.959. Dissipation kinetic parameters are listed in Table 2 and the dissipation kinetics curve is shown in Figure 3.

Table 2. Dissipation kinetic parameters of difenoconazole on jujube.

Crop	Experimental Site	Dissipation Dynamics Equation	*R*	$t_{1/2}$ (d)
Jujube	Yuncheng	$C_t = 0.2298e^{-0.042t}$	0.992	16.5
	Qingdao	$C_t = 0.1319e^{-0.053t}$	0.959	13.1

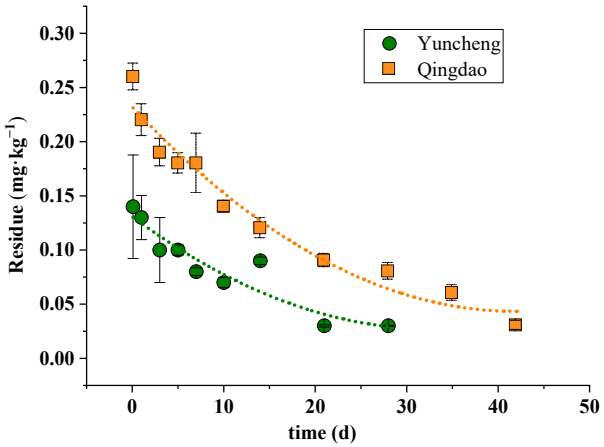


Figure 3. Dissipation dynamic curve of difenoconazole in jujube.

In field conditions, the process of pesticide residue dissipation was influenced by various factors, for instance, natural action (volatilization, wash-off, photodegradation), climatic conditions (sunlight, temperature, humidity, and wind), exposure stability, application dosage of pesticides, the period for pesticide application, type of crops, sampling time and so on. The dissipation rate for difenoconazole was dissimilar on different crops. Literature study results showed that difenoconazole digested quickly in the straw of grain, e.g., the half-life ($t_{1/2}$) of the dissipation in wheat straw was 3.6–5.5 days [13] and in rice plants was 4.7–5.9 days [26]. In vegetable crops, the half-life was 2.4–3.8 days in carrots [39], 6.6–7.8 days in Chinese cabbage [40], and 6.0–11.5 days in pepper [41]. In fruits, the half-life was 6.3 days in strawberry [10], 3.2–8.8 days in watermelon [42], 6.4–8.4 days in pomegranate [43], 4.4–13 days in peach [12], 9.4–12.6 days in apple [24], and 12.2–13.3 days in banana [24].

In this experiment, the half-life for difenoconazole in jujube is longer than that of other crops. Because the experimental site is located in North China, the meteorological records show that there is almost no rain during the period from spraying to harvest. Besides, the increase in fruit weight during the growth period was the predominant reason for the significant decrease in pesticide residue level according to the weight ratio [44]. In the experiment, the growth of jujube was in the period of almost maximum size when spraying, so the degradation rate for difenoconazole on jujube was slower than that on other fruits mentioned above. It has also been confirmed that the half-life ($t_{1/2}$) for tebuconazole in jujube was comparatively larger than that of other crops [45].

3.3. Final Residue

Difenoconazole was applied twice and three times at 100 mg·kg^{-1} and 150 mg·kg^{-1} doses on jujube, respectively, with a spray interval of 7 days; the final residue data of difenoconazole in jujube are shown in Table 3 and Figure 4. When the PHI was on the 7th day, the residue for difenoconazole on jujube was between 0.11 and 1.59 mg·kg^{-1}, with STMR being 0.52 mg·kg^{-1}, and the highest residue (HR) was 1.59 mg·kg^{-1}. On the 14th day, the final residue for difenoconazole in jujube was 0.05–0.77 mg·kg^{-1}, with STMR and HR being 0.36, 0.77 mg·kg^{-1}, respectively. On the 21st day, the final residue was 0.04–0.63

mg·kg^{-1}, with STMR being 0.28 mg·kg^{-1} and HR 0.63 mg·kg^{-1}. Aggregated data for STMR and HR are shown in Table 4. The above residues were lower than the MRL of difenoconazole in jujube formulated by the US (2.5 mg·kg^{-1}) and Japan (5 mg·kg^{-1}), but higher than that formulated by the EU (0.1 mg·kg^{-1}).

Table 3. Final residue data of difenoconazole on jujube (n = 3).

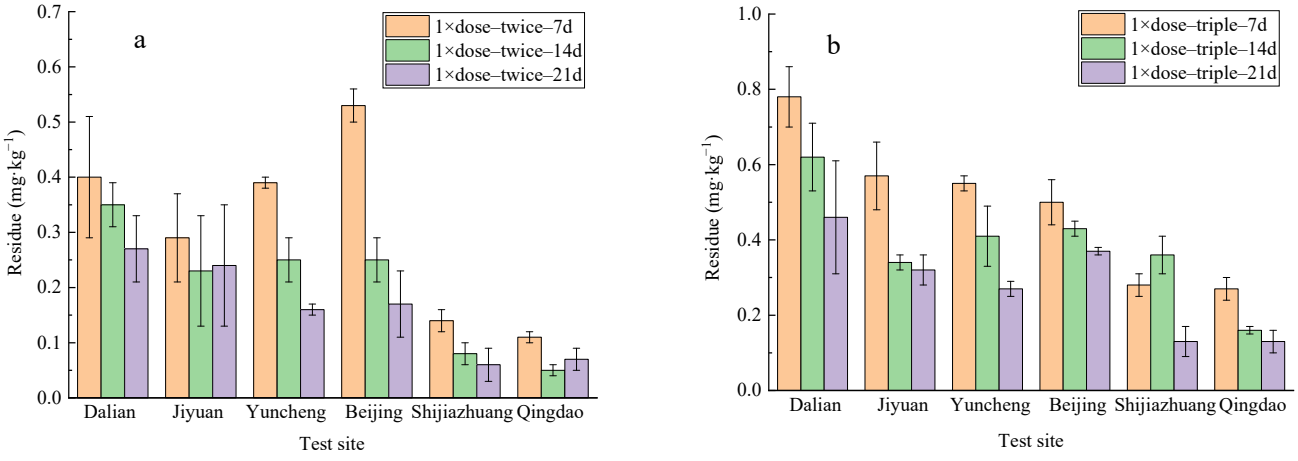
Dosage (mg a.i.·kg^{-1})	Spray Times	PHI (Day)	Final Residue * (mg·kg^{-1})					
			Dalian	Jiyuan	Yuncheng	Beijing	Shijiazhuang	Qingdao
100	2	7	0.40 ± 0.11	0.29 ± 0.08	0.39 ± 0.01	0.53 ± 0.03	0.14 ± 0.02	0.11 ± 0.01
		14	0.35 ± 0.04	0.23 ± 0.10	0.25 ± 0.04	0.25 ± 0.04	0.08 ± 0.02	0.05 ± 0.01
		21	0.27 ± 0.06	0.24 ± 0.11	0.16 ± 0.01	0.17 ± 0.06	0.06 ± 0.03	0.07 ± 0.02
	3	7	0.78 ± 0.08	0.57 ± 0.09	0.55 ± 0.02	0.50 ± 0.06	0.28 ± 0.03	0.27 ± 0.03
		14	0.62 ± 0.09	0.34 ± 0.02	0.41 ± 0.08	0.43 ± 0.02	0.36 ± 0.05	0.16 ± 0.01
		21	0.46 ± 0.15	0.32 ± 0.04	0.27 ± 0.02	0.37 ± 0.01	0.13 ± 0.04	0.13 ± 0.03
150	2	7	1.29 ± 0.10	0.78 ± 0.03	0.58 ± 0.08	0.83 ± 0.01	0.33 ± 0.02	0.11 ± 0.03
		14	0.56 ± 0.04	0.71 ± 0.06	0.48 ± 0.00	0.54 ± 0.02	0.28 ± 0.03	0.05 ± 0.01
		21	0.63 ± 0.11	0.56 ± 0.02	0.28 ± 0.05	0.31 ± 0.01	0.21 ± 0.02	0.04 ± 0.01
	3	7	1.59 ± 0.26	0.63 ± 0.04	0.77 ± 0.14	0.73 ± 0.06	0.44 ± 0.01	0.18 ± 0.02
		14	0.68 ± 0.07	0.77 ± 0.05	0.59 ± 0.01	0.66 ± 0.04	0.32 ± 0.04	0.21 ± 0.06
		21	0.63 ± 0.05	0.50 ± 0.02	0.31 ± 0.02	0.47 ± 0.03	0.38 ± 0.05	0.11 ± 0.01

Notes: * Values represent the mean ± SD (n = 3).

Table 4. Summary of final residues.

Crop	PHI (Day)	Final Residue * (mg·kg^{-1})	STMR (mg·kg^{-1})	HR (mg·kg^{-1})
Jujube	7	0.11, 0.11, 0.14, 0.18, 0.27, 0.28, 0.29, 0.33, 0.39, 0.40, 0.44, 0.50, 0.53, 0.55, 0.57, 0.58, 0.63, 0.73, 0.77, 0.78, 0.78, 0.83, 1.29, 1.59	0.52	1.59
	14	0.05, 0.05, 0.08, 0.16, 0.21, 0.23, 0.25, 0.25, 0.28, 0.32, 0.34, 0.35, 0.36, 0.41, 0.43, 0.48, 0.54, 0.56, 0.59, 0.62, 0.66, 0.68, 0.71, 0.77	0.36	0.77
	21	0.04, 0.06, 0.07, 0.11, 0.13, 0.13, 0.16, 0.17, 0.21, 0.24, 0.27, 0.27, 0.28, 0.31, 0.31, 0.32, 0.37, 0.38, 0.46, 0.47, 0.50, 0.56, 0.63, 0.63	0.28	0.63

Notes: * Final residues data are sorted from small to large.



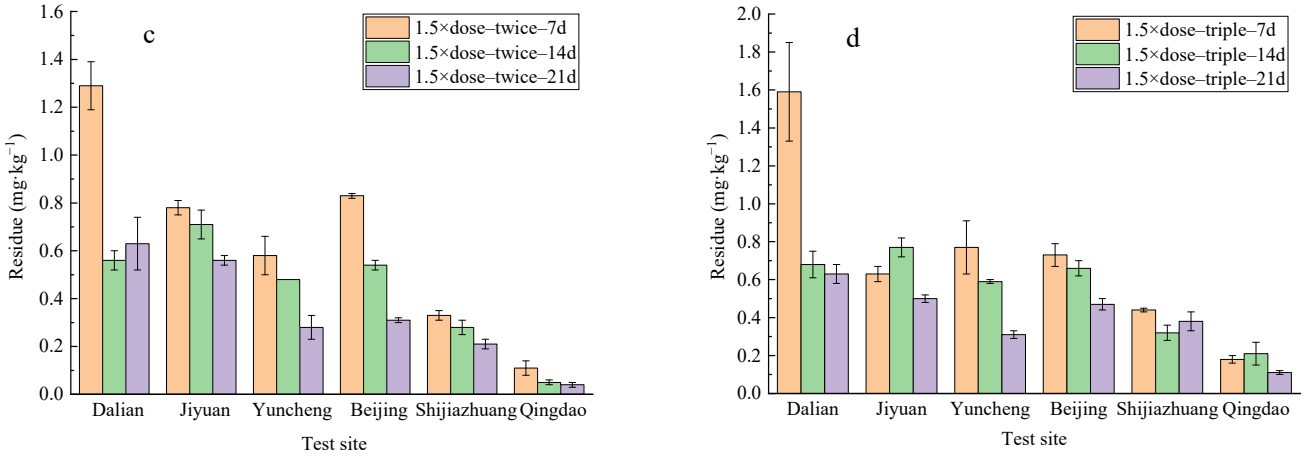


Figure 4. Difenoconazole final residues on jujube in six field trials under different treatments ((**a**). 1× dose twice, (**b**). 1× dose triple, (**c**). 1.5× dose twice, (**d**). 1.5× dose triple).

These research data showed that the difenoconazole residues in jujube are mainly affected by spraying dose, spraying frequency, and PHI. Higher dosage, more application frequency, and shorter PHI caused the residual concentrations in jujube to be higher. There were some slight differences in the final residue data among the six experimental sites. The residue of difenoconazole in Qingdao is lower than that in other places, which may be because the climate has a significant marine characteristic by the sea. The air is more humid, which leads to the degradation of difenoconazole in the jujube relatively quickly. These residual results will then be further used to assess the dietary risk of difenoconazole.

3.4. Dietary Risk Exposure

The guidelines for the approval and registration of pesticides vary from country to country. Each country should conduct exposure risk assessments according to its national eating habits and crop registration. In China, difenoconazole has been registered in 41 crops, such as rice, wheat, corn, and so on [14]. By default, it was assumed that difenoconazole was applied to all registered crops or crops in the process of being registered. For food classification, only the crop with the largest STMR or MRL was selected. The ADI for difenoconazole was 0.01 mg·kg^{-1} bw [46]. On the basis of the research report for the Chinese Nutrition Society, the per capita weight of Chinese adults was 63 kg [47]. Following the risk maximization principle, STMR with a PHI of 7 days was used to calculate the dietary risk. For other crops without STMR, the corresponding MRL was used to calculate the dietary risk. MRL was preferred to China, followed by Codex Alimentarius Commission (CAC), the US, the EU, and Japan. Dietary risk assessments are shown in Table 5; the results show that the NEDI of difenoconazole for ordinary consumers was 0.541 mg and the RQ was 84.9%. The RQ was less than 100%, indicating that the risk was at an acceptable level.

Table 5. Long-term dietary risk assessment for difenoconazole.

Registration Crops	Food Classification	Fi (kg)	Reference Residue Limits (mg·kg^{-1})	Sources	NEDI (mg)	ADI (mg)	RQ (%)
Rice	Rice and its products	0.2399	0.5	MRL(China)	0.11995		
Wheat	Noodles and its products	0.1385	0.1	MRL(China)	0.01385		
Corn	Other grains	0.0233	0.1	MRL(China)	0.00233		
Potato	Tubers	0.0495	0.02	MRL(China)	0.00099		
Soybean	Dried beans and bean products	0.016	0.05	MRL(China)	0.0008		
Celery	Dark vegetables	0.0915	3	MRL(China)	0.2745		
Cucumber	Light vegetable	0.1837	0.02	STMR (China)	0.003674	ADI × 63	
Jujube	Fruits	0.0457	0.52	STMR	0.018737		
Hazelnut	Nuts	0.0039	0.03	MRL(CAC)	0.000117		
Peanut	Vegetable oil	0.0327	0.2	MRL(China)	0.00654		
Sugar cane	Sugar, starch	0.0044	0.05	MRL(EU)	0.00022		
Wolfberry	Salt	0.012	0.81	STMR(China)	0.000972		
Sanchi	Soy sauce	0.009	10	MRL(China)	0.09		
	Other foods *	0.2191					
	Total	1.0286			0.541	0.63	84.9

Notes: * The unregistered food types of difenoconazole were merged into other foods.

According to the "Guidelines for maximum residue limits of pesticides in food" [48], the recommended MRLs are usually set to values of 1, 2, 3, 5, 7, and 10. Based on the above evaluation conclusions and combined with an HR value of 1.59 mg·kg^{-1} (PHI = 7 days), it is suggested that the MRL for difenoconazole on jujube can be set at 2 mg·kg^{-1}.

4. Conclusions

In this paper, the final and dissipation residue for difenoconazole on jujube was analyzed by GC, and the dietary risk exposure for difenoconazole was evaluated. The dissipation results indicated that the degradation rate of difenoconazole on jujube was comparatively slower than that on other fruits, with the half-life ($t_{1/2}$) of difenoconazole on jujube in Yuncheng and Qingdao being 16.5 and 13.1 days, respectively. The final residue test showed that when PHI was 7 days, 14 days, and 21 days, difenoconazole residues in jujube were 0.11–1.59, 0.05–0.77, and 0.04–0.63 mg·kg^{-1}; STMR was 0.52, 0.36, and 0.28 mg·kg^{-1}; HR was 1.59, 0.77, and 0.63 mg·kg^{-1}. According to the risk evaluation result, the NEDI of difenoconazole for ordinary consumers was 0.541 mg, and RQ was 84.9%, not more than 100%, indicating that the hazard caused by chronic dietary intake for difenoconazole was acceptable. Hence, the recommended MRL for difenoconazole on jujube is 2 mg·kg^{-1}.

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