


Research Article

Dietary Risk Assessment and Ranking of Multipesticides in *Dendrobium officinale*

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The presence of pesticide residues in *Dendrobium officinale* (*D. officinale*), a commonly used herbal medicine, has attracted much attention in recent years. Therefore, this study presents the levels of 141 pesticide residues in forty *D. officinale* samples, which were measured by high-performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS). And we used a deterministic estimate model to assess chronic and acute dietary exposure risk, as well as the cumulative risks for adults, children, and specific groups of consumers. Furthermore, the residual risk of individual pesticides was sorted by adapting the matrix-ranking scheme. In 92.5% of the samples, 43 pesticides were detected, of which difenoconazole had the highest detection frequency. Multiple residues were detected in 85.0% of the samples, and one sample contained even up to 17 pesticides. The chronic hazard quotient (HQc) and the acute hazard quotient (HQa) were far below 100%, and both cumulative chronic and acute hazard indices (HI) did not exceed 100%. The risk scoring scheme showed that four pesticides were considered to pose a comparatively potential high risk, including difenoconazole, carbofuran, fipronil, and emamectin benzoate. The results indicated that the occurrence of pesticide residues in *D. officinale* could not pose a serious health problem to the public.

1. Introduction

With more and more people in the world using herbal medicines, the safety of the consumer has attracted international attention [1]. The extensive use of pesticides in the production of herbal medicines, coupled with the lack of good agricultural practices (GAP) and maximum residue limits (MRLs) for pesticides, has led to the accumulation of pesticide residues [2]. To ensure food safety, an assessment of the consumption risks of herbal medicines polluted with pesticides should be conducted.

Dendrobium officinale (*D. officinale*), which is ranked as “the first of the Chinese nine fairy herbs,” has been found to have therapeutic significance. It has shown a variety of pharmacological actions on diabetes [3], tumor [4], and immunomodulatory [5]. Besides, it can be either chewed directly or stewed in dishes or soaked with wine as a high-quality food in diets [6]. However, the wild *D. officinale* was

on the IUCN red list of threatened species because of overexploitation and habitat deterioration [7]. Currently, more than 90% of *D. officinale* is cultivated in greenhouses [8].

In the period of *D. officinale*'s planting, diseases and insect pests are the main factors affecting the yield [9]. The appropriate use of pesticides can guarantee and raise the quantity and quality of crops. However, as a minor crop in China, there are not enough registered pesticides for growing the crop, because of little interest in registering pesticides for pesticide manufacturers. On account of government departments' relaxed pesticides registration regime and lack of MRLs of pesticides on *D. officinale*, some farmers may illegally use pesticides in the process of planting herbs to control harm. Contamination of *D. officinale* occurs from time to time due to indiscriminate use of pesticides. Widespread use of various pesticides can induce associated adverse health effects on consumers [10, 11]. The public is

getting increasingly worried about human health risk through *D. officinale* consumption.

In recent years, research work on the risk assessment of hazardous residues in herbal medicines has been gradually carried out, and it has made some progress. There are a few reports on the risk assessment of pesticide residues in some medicinal and edible plants [2, 12–17]. The results showed that the acute and chronic risks of pesticide residues in most medicinal and edible plants were at an acceptable level. Only a few pesticides, such as pentachloronitrobenzene residues in ginseng, had an acute risk quotient higher than 1 and were considered risky for people [16].

Moreover, there were a few reports that focused on the occurrence of several pesticides in *D. officinale* [18–21]; only one report focused on the risk assessment of pesticide residues in *D. officinale*. The method of dietary risk assessment in the previous research [21] was single; only the deterministic assessment method was used. However, in this paper, the risk ranking method drawing on the ranking matrix developed by the Veterinary Residues Committee of the UK [22] was applied to the pesticide residues in *D. officinale* for the first time. In addition, children, fetus, infants, and pregnant or nursing women, which represent specific subgroups of consumer groups, are particularly vulnerable to pesticide use [23]. Therefore, this study also conducted for the first time the health risk assessment of pesticide residues detected on *D. officinale* to the aforementioned groups.

Thus, the present study was aimed to determine the levels of pesticide residue in *D. officinale* collected from different representative producing regions of China, as well as to assess the health risk of detected residues for various consumer groups. An exposure evaluation was conducted based on the deterministic method, and hazard quotient (HQ) values were utilized, in which a deterministic estimate of the gauged exposure concentration is divided by the toxicity reference dose. In addition, we ranked the pesticide exposure risk by consuming *D. officinale* involving a matrix-ranking scheme and identified the pesticides that should be focused on. Finally, as a relatively complete research system, we hope to provide a reference for responsible government authorities to set residue limits and speed up pesticide registration and ultimately guarantee the quality and food safety of *D. officinale*.

2. Materials and Methods

2.1. Sample Collection. In China, *D. officinale* resources are mainly distributed in several provinces south of the Qinling Mountains and the Huaihe River [24]. Through consulting the agricultural management departments of *D. officinale* across the country, we have obtained planting distribution situation messages. We collected samples based on the national *D. officinale* planting area and output information. In addition, it also included farms of different scales, different cultivation models, and special pesticide usage habits. A total of 40 fresh *D. officinale* samples were acquired from all main growing regions of *D. officinale* in China, including Yunnan, Zhejiang, Anhui, Guangdong, Guangxi, Fujian,

Guizhou, and Hunan provinces. Each sample was sealed in an appropriate container and stored at -20°C prior to analysis.

2.2. Determination Method. HPLC-MS/MS method for the determination of pesticides and metabolites was established in our previous study [25]. The method included 141 pesticides and metabolites, which were selected as detected targets through a field survey and literature investigation. All the pesticides had good linear responses with $r > 0.9950$. Moreover, the sensitivity of 100% of the targets reached or was lower than $10\ \mu\text{g}/\text{kg}$. Accuracy and repeatability were investigated, and the recoveries at the spiked level of the 97.20% pesticides were 60.4%–112.4%, $\text{RSD} < 20\%$ in this method, which was validated based on the performance criteria set out by the European Commission Directorate General for Health and Food Safety.

2.3. Health Risk Estimation. The deterministic method is simple, easy to use, and still used for the authorization of pesticides in China [26]. The chronic/acute consumer health risk (hazard quotient, HQ) was calculated based on the residue, food consumption, and toxicology data. The estimated daily intake (EDI) is used to calculate the chronic consumer health risk, while estimated short-term intake (ESTI) is used to predict the acute consumer health risk. For precise evaluation, the values of EDI and ESTI are then compared to the acceptable daily intake (ADI) and acute reference dose (ARfD) of each pesticide [27–29].

2.3.1. Assessment of the Long-Term Intake and Chronic Exposure. The estimated daily intake was calculated by

$$\text{EDI} = \frac{I \times R}{\text{bw}}, \quad (1)$$

where EDI is the estimated daily intake ($\text{mg}/\text{kg}\cdot\text{bw}\cdot\text{d}$), I is the average residue level of pesticide in samples (mg/kg fresh weight), bw is the average body weight, the international default of mean weight was 60 kg for adults and 15 kg for children [30], R is the average daily consumption dose (kg), and this research took 0.045 kg as the average consumption. Because dry *D. officinale* dosage is 0.006 kg–0.012 kg in the 2020 edition of the Chinese Pharmacopoeia [31], the water content of fresh *D. officinale* is about 80% [32].

Chronic/short-term intake risk assessment was calculated by

$$\text{HQ}_C = \% \text{ADI} = \frac{\text{EDI}}{\text{ADI}} \times 100, \quad (2)$$

where HQ_C represents the chronic hazard quotient, $\% \text{ADI}$ is the chronic intake risk assessment, and ADI is the acceptable daily intake ($\text{mg}/\text{kg}\ \text{bw}$), which can be gained from Joint FAO/WHO Meeting on Pesticide Residues (JMPR) [33]. When EDI is less than ADI, that is, $\% \text{ADI} < 100$, we can accept the risk. In cases where $\% \text{ADI}$ is greater than 100, it implies an unacceptable risk. The $\% \text{ADI}$ and the risk are positively correlated.

2.3.2. *Assessment of the Short-Term Intake and Acute Exposure.* Short-term intake of pesticide residues was calculated using

$$\text{ESTI} = \frac{\text{LP} \times \text{HR}}{\text{bw}}, \quad (3)$$

where ESTI is the estimated short-term intake of pesticide residues (mg/kg.bw.d) and LP (kg) is the large portion. This study took 0.06 kg as the maximum daily consumption according to its dosage in Chinese Pharmacopoeia [31] and the water content [32]. HR (mg/kg) represents the highest residue level detected in *D. officinale*, bw is the average body weight, and the international default of mean weight was 60 kg for adults and 15 kg for children [30].

Acute intake risk of pesticide residues was calculated by

$$\text{HQa} = \% \text{ARfD} = \frac{\text{ESTI}}{\text{ARfD}} \times 100, \quad (4)$$

where HQa represents acute hazard quotient, %ARfD is the acute intake risk of pesticide residues, and ARfD is the acute reference dose (mg/kg bw), which is derived from JMPR [33]. When ESTI is not greater than ARfD, that is, %ARfD < 100, we can accept the risk. In cases where %ARfD is greater than 100; it indicates an insufferable risk. The %ARfD and the risk are positively correlated.

2.3.3. *Cumulative Risk Assessment.* Cumulative risk assessment (Crisk) is the potential risk of adverse health effects from a mixture of chemical constituents [34]. The hazard index (HI) can be obtained by adding the chronic dietary exposure risk or acute dietary exposure risk value of each pesticide in the diet [35]; the equation is as follows:

$$\text{HI} = C_{\text{risk}} = \sum_{i=1}^n R_i, \quad (5)$$

where HI is the cumulative risk of the detected pesticides, R_i is the long-term exposure risk (%ADI) or the short-term exposure risk (%ARfD) for every pesticide, and n is the whole number of pesticides. If the HI is greater than 100%, this indicates that *D. officinale* should be considered a risk to the consumers, but if HI is below 100%, it indicates that the consumption of *D. officinale* is considered acceptable.

2.3.4. *Risk Ranking Method.* The matrix-ranking scheme was formulated by the Veterinary Residue Committee of UK [22], which has been slightly revised and then accepted to classify the hazardous subcategories of pesticides. This method uses toxicity, potency, dietary proportion, frequency of pesticide use, presence of high exposure population, and residue levels to rank pesticide risk. Table 1 lists the values for each parameter. Data for LD₅₀ and ADI values were obtained from JMPR [33].

The theoretical maximum residual level was calculated by

$$L = \frac{AW}{100M}, \quad (6)$$

where L is the value of the theoretical maximum residual level, A is the ADI, W is the average body weight (kg), generally calculated as 60 kg [30], M is the maximum daily dose (kg) of herbal medicines that can be taken by a human, and 100 is the safety factor.

F is the score of the residue level, which was calculated by

$$F = \frac{(F_0 \times 1 + F_1 \times 2 + F_2 \times 3 + F_3 \times 4)}{n}, \quad (7)$$

where F_0 represents the number of pesticide-free samples, F_1 represents the number of samples in which the pesticide is detected but does not exceed the value of L , F_2 represents the number of samples with the pesticide residue value of 1 L–10 L, F_3 represents the number of samples with the pesticide residue value > 10 L, and n is 40 for all samples of *D. officinale*.

FOD is the score of the usage frequency of the pesticides, which was calculated by

$$\text{FOD} = \frac{T}{P} \times 100, \quad (8)$$

where FOD represents the usage frequency of the pesticides, T is the frequency of pesticide use during cultivation, and P is the growing period (days) of the plant.

Therefore, equation (9) was used to evaluate each pesticide against specific criteria to get the total score (TS):

$$TS = (A + B) \times (C + D + E) \times F, \quad (9)$$

where TS is the total points of the samples with detected pesticide residues; A , B are the score of LD₅₀ and ADI of each pesticide, respectively; C is the score for the ratio of *D. officinale* in daily diet; D is the score of the pesticide using frequency; E is the score about the evidence of high exposure groups; and F is the score of the residual situation. The higher the total score, the greater the risk.

3. Results and Discussion

3.1. *Pesticide Residues' Analysis in D. officinale.* As shown in Figure 1, 43 various pesticides out of 141 were detected in the 40 *D. officinale* samples including 20 insecticides (14.18%), 20 fungicides (14.18%), 2 acaricides (1.42%), and 1 plant growth regulator (PGR) (0.70%). As Figure 1 shows, insecticides and fungicides were the most frequently detected pesticide classes. Because *D. officinale* likes a warm, moist, and semishady growth environment. Similarly, this kind of cultivation environment can easily become a breeding ground for certain pests, such as snails and slugs [36]. Once the growth environment is not well controlled, especially the high temperature and humidity environment, it is also easy to be infected with bacterial and fungal diseases [37]. Residue levels of detected pesticides and their frequencies in *D. officinale* are presented in Table 2. A total of 10 pesticides had a detection rate of more than 20% in 40 samples, 2 were insecticides, and 8 were fungicides; among them, the detection rate of difenoconazole was the highest (70%). In addition, dimethomorph had the highest average residue level and the detection frequency is not low, which is

TABLE 1: Definition and score of A–F indices for risk ranking.

Symbol	Item	Definition	Score	Definition	Score	Definition	Score	Definition	Score
A	Toxicity	Low	2	Moderate	3	High	4	Hypertoxic	5
B	Potency (mg/kg)	>0.01	0	>0.0001–0.001	1	>0.000001–0.0001	2	<0.000001	3
C	Diet proportion (%)	<2.5	0	2.5–20	1	20–50	2	50–100	3
D	Frequency of dosing (%)	<2.5	0	2.5–20	1	20–50	2	50–100	3
E	Evidence of high-exposure groups	No	0	Unlikely	1	Likely	2	Yes or no data	3
F	Residue level (mg/kg)	ND ¹	1	<1L*	2	≥1L*–10L*	3	≥10L*	4

¹ND means not detected. * L represents the theoretical maximum residual level.

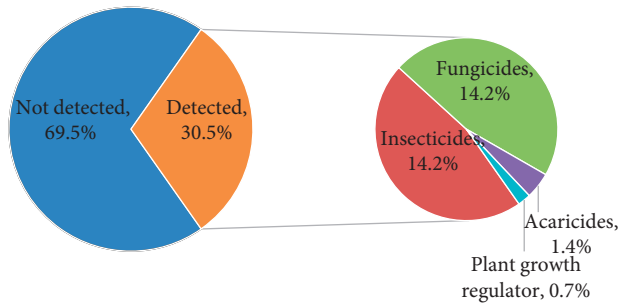


FIGURE 1: Detection ratio of different types of pesticides in *Den-drobium officinale*.

45.0%. In the study performed by Xu et al. [21], the highest residue was measured for dimethomorph in *D. officinale* as well. Moreover, dimethomorph is a registered pesticide on *D. officinale*; the work of formulating its MRL on *D. officinale* becomes more and more urgent. Of banned pesticides, fipronil (the sum of fipronil, fipronil desulfanyl, fipronil sulfone, and fipronil sulfide), carbofuran, and methomyl were found in 12.5%, 2.5%, and 5.0% of the total samples, respectively. And the maximum detected values of these three pesticides were up to 0.039, 0.014, and 0.16 mg/kg, respectively. According to the 2020 edition of the Chinese Pharmacopoeia [38], the MRL values of fipronil and carbofuran are 0.02 mg/kg and 0.05 mg/kg, respectively. Only one of the 40 samples of *D. officinale* contained fipronil residues exceeding the standard, with an exceed multiple of 0.955. There is currently no clear MRL value for methomyl, but the Ministry of Agriculture of the People's Republic of China stipulated that methomyl cannot be used in traditional Chinese medicine. The reason for the detection of banned pesticides could be that some farmers are still using these prohibited pesticides or that pesticide residues from previous years are still very high and active in the soil.

For crops, it is easy to get access to approved pesticides and MRLs on them but there are few standards for MRLs on medicinal plants. Of all detected pesticide residues, only the MRL of prochloraz, carbofuran, and fipronil was established in *D. officinale* according to GB 2763-2019 [39] and Chinese Pharmacopoeia of the 2020 version [38].

The co-occurrence of pesticide residues is shown in Figure 2. Of the 40 *D. officinale* samples analyzed, 7.5% of the samples were residue-free, 7.5% of the samples were found to contain one residue, and the detection rate for multiple residues was 85.0%. The total detection rate of multiresidue samples was the highest. Soil uptake, spray drift from

neighbouring plots, and cross-contamination in the processing of the crops may explain the occurrence of multi-residues [23].

3.2. Intake Risk Assessment. A total of 43 pesticides and metabolites were detected in *D. officinale*. According to GB 2763-2019 [39], fipronil represents the sum of fipronil, fipronil sulfone, fipronil sulfide, and fipronil desulfanyl; carbendazim represents the sum of thiophanate-methyl and carbendazim in the following risk assessment. The risk assessment and risk ranking of detected pesticides in *D. officinale* are as follows.

3.2.1. Risk Assessment of Acute and Chronic Intake. Long-term intake risk for adults and children was evaluated according to equations (1) and (2). As can be seen from Table 3, the HQc never exceeded 100% for adults and children, implying that pesticide residues in *D. officinale* were within the acceptable level. The reason for the highest exposure for children is that they ingest more food per unit body weight compared to adults [23, 40].

Short-term exposure risk estimate could not be conducted for azoxystrobin, metalaxyl, chlorantranilprole, trifloxystrobin, oxadixyl, fludioxonil, lufenuron, pyridaben, propargite, hexaconazole, pyrimethanil, hexaflumuron, paclobutrazol, and piperonyl butoxide, because ARfD values are unnecessary for these pesticides, or because ARfD data is not available in the JMPR database [33]. Table 3 shows the ARfD values of the other 25 pesticides and their HQa, which were calculated according to equations (3) and (4). It turned out that the HQa values for people were all acceptable with ESTI between 0.0003% and 5.760%. All the ESTIs were much less than the ARfD value, which meant there was a negligible acute risk with exposure to the detected pesticides via *D. officinale* consumption for children and adults. For both adults and children, carbofuran posed the highest risk. However, it was only detected in one sample out of forty. It also indicates that even though some pesticides were detected in many samples, the acute exposure risks were still acceptable, that is, difenoconazole, pyraclostrobin, and tebuconazole. The detection rates of such pesticides were generally above 50%, but the HQa values were less than 6.0%.

In addition, fetuses, infants, pregnant women, or breastfeeding women are a special group of people. The potential toxicity, integrity of the exposure, and toxicity database should be taken into account [30]. The US

TABLE 2: Frequencies and residue levels of detected pesticides in *D. officinale*.

Pesticide	Frequencies (%)	Min-max (mg/kg)	Mean (mg/kg)
Difenoconazole	70	ND-582.67	76.36
Pyraclostrobin	62.5	ND-249.09	58.15
Tebuconazole	52.5	ND-425.44	49.44
Azoxystrobin	50	ND-263.94	32.27
Dimethomorph	45	ND-4439.92	231.59
Metalaxyl	45	ND-55.49	10.15
Propamocarb	37.5	ND-406.8	59.43
Chlorantraniliprole	32.5	ND-533.58	54.09
Famoxadone	25	ND-2798.59	127.92
Imidacloprid	22.5	ND-156.14	14.40
Fenbuconazole	17.5	ND-574.36	39.62
Emamectin benzoate	17.5	ND-26.03	1.80
Flubendiamide	15	ND-141.67	8.68
Prochloraz	15	ND-278.44	8.36
Carbendazim	12.5	ND-242.76	13.73
Fipronil	12.5	ND-16.78	1.15
Fenpropathrin	10	ND-400	28.95
Trifloxystrobin	10	ND-112.87	4.94
Myclobutanil	10	ND-51.39	3.14
Oxadixyl	10	ND-47.42	2.99
Triadimenol	10	ND-61.49	2.56
Fipronil sulfone	10	ND-15.04	0.55
Fipronil desulfinyl	10	ND-4.67	0.41
Chlorpyrifos	7.5	ND-295.65	20.35
Cyromazine	7.5	ND-406.9	11.31
Thiophanate-methyl	7.5	ND-140	7.14
Acetamiprid	7.5	ND-193.2	6.76
Fludioxonil	7.5	ND-51.59	1.59
Lufenuron	7.5	ND-15.14	0.64
Propargite	5	ND-718.37	18.48
Methomyl	5	ND-160.73	4.38
Carbaryl	5	ND-215.38	5.50
Pyridaben	5	ND-67.32	2.63
Clothianidin	5	ND-35.71	1.38
Hexaconazole	5	ND-8.96	0.27
Fipronil sulfide	5	ND-2.58	0.10
Pyrimethanil	2.5	ND-149.38	3.73
Propiconazole	2.5	ND-40	1.00
Hexaflumuron	2.5	ND-26.45	0.66
Carbofuran	2.5	ND-14.44	0.36
Paclobutrazol	2.5	ND-16.02	0.40
Piperonyl butoxide	2.5	ND-4.7	0.12
Buprofezin	2.5	ND-1.39	0.03

ND means not detected.

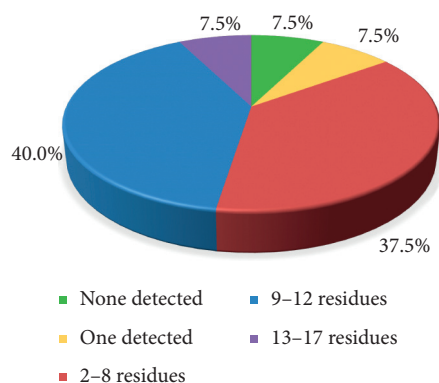


FIGURE 2: Distribution of detected pesticide residues in analyzed *Dendrobium officinale* samples.

Environmental Protection Agency has formulated the “Food Quality Protection Act” (FQPA) safety factor (1-10X) to target specific groups of people (fetuses, infants, pregnant, or nursing women) [41]. In the worst case, we believe that the FQPA safety factor of all detected pesticides is 10x. That is, the HQa and HQc of a certain population are ten times that of adults. Table 3 demonstrates that the HQa and HQc values for certain populations were less than 100%.

3.2.2. Cumulative Dietary Risk Assessment. The human body is an ultimate accumulator of chemical pollutants, which can cause health problems [42]. In this study, 85% of samples contained more than one pesticide residue, which requires us to consider the cumulative risk for a mixture of pesticides in one sample.

TABLE 3: Results of the chronic, acute, and cumulative exposure risk for children, adults, and the specific population.

Pesticide	Long-term risk assessment				Short-term risk assessment			
	ADI (mg/kg bw)	HQc (%)			ARfD (mg/kg bw)	HQa (%)		
		Adults	Children	Specific population		Adults	Children	Specific population
Difenoconazole	0.0100	0.5730	2.2920	5.7300	0.3000	0.1942	0.7769	1.9423
Pyraclostrobin	0.0300	0.1455	0.5820	1.4550	0.7000	0.0356	0.1423	0.3559
Tebuconazole	0.0300	0.1235	0.4940	1.2350	0.3000	0.1418	0.5672	1.4180
Azoxystrobin	0.2000	0.0121	0.0485	0.1211	Unnecessary	—	—	—
Dimethomorph	0.2000	0.0869	0.3474	0.8685	0.6000	0.7400	2.9599	7.3998
Metalaxyl	0.0800	0.0096	0.0383	0.0956	—	—	—	—
Propamocarb	0.4000	0.0111	0.0446	0.1114	2.0000	0.0203	0.0814	0.2034
Chlorantraniliprole	2.0000	0.0020	0.0081	0.0203	Unnecessary	—	—	—
Famoxadone	0.0060	1.5988	6.3950	15.9875	0.6000	0.4664	1.8657	4.6643
Imidacloprid	0.0600	0.0180	0.0720	0.1800	0.4000	0.0390	0.1561	0.3903
Fenbuconazole	0.0300	0.0990	0.3960	0.9900	0.2000	0.2872	1.1488	2.8720
Emamectin benzoate	0.0005	0.2700	1.0800	2.7000	0.0200	0.1300	0.5200	1.3000
Flubendiamide	0.0200	0.0326	0.1305	0.3263	0.2000	0.0709	0.2834	0.7085
Prochloraz	0.0100	0.0630	0.2520	0.6300	0.1000	0.2784	1.1136	2.7840
Carbendazim ¹	0.0300	0.0520	0.2080	0.5200	0.1000	0.3561	1.4244	3.5610
Fipronil ²	0.0002	0.8250	3.3000	8.2500	0.0030	1.3033	5.2133	13.0333
Fenpropathrin	0.0300	0.0725	0.2900	0.7250	0.0300	1.3333	5.3333	13.3333
Trifloxystrobin	0.0400	0.0092	0.0368	0.0919	Unnecessary	—	—	—
Myclobutanil	0.0300	0.0078	0.0310	0.0775	0.3000	0.0171	0.0685	0.1713
Oxadixyl	0.0100	0.0225	0.0900	0.2250	—	—	—	—
Triadimenol	0.0300	0.0065	0.0260	0.0650	0.0800	0.0769	0.3075	0.7688
Chlorpyrifos	0.0100	0.1523	0.6090	1.5225	0.1000	0.2957	1.1828	2.9570
Cyromazine	0.0600	0.0141	0.0565	0.1413	0.1000	0.4069	1.6276	4.0690
Acetamiprid	0.0700	0.0073	0.0291	0.0729	0.1000	0.1932	0.7728	1.9320
Fludioxonil	0.4000	0.0003	0.0012	0.0030	Unnecessary	—	—	—
Lufenuron	0.0150	0.0030	0.0120	0.0300	Unnecessary	—	—	—
Propargite	0.0100	0.1388	0.5550	1.3875	Unnecessary	—	—	—
Methomyl	0.0200	0.0165	0.0660	0.1650	0.0200	0.8035	3.2140	8.0350
Carbaryl	0.0080	0.0516	0.2063	0.5156	0.2000	0.1077	0.4308	1.0770
Pyridaben	0.0100	0.0195	0.0780	0.1950	—	—	—	—
Clothianidin	0.1000	0.0011	0.0042	0.0105	0.6000	0.0060	0.0238	0.0595
Hexaconazole	0.0050	0.0045	0.0180	0.0450	—	—	—	—
Pyrimethanil	0.2000	0.0014	0.0056	0.0139	Unnecessary	—	—	—
Propiconazole	0.0700	0.0011	0.0043	0.0107	0.3000	0.0133	0.0533	0.1333
Hexaflumuron	0.0200	0.0026	0.0105	0.0263	—	—	—	—
Carbofuran	0.0010	0.0300	0.1200	0.3000	0.0010	1.4400	5.7600	14.4000
Paclobutrazol	0.1000	0.0003	0.0012	0.0030	—	—	—	—
Piperonyl butoxide	0.2000	0.0000	0.0002	0.0004	Unnecessary	—	—	—
Buprofezin	0.0090	0.0000	0.0000	0.0000	0.5000	0.0003	0.0011	0.0028
HI		4.4847	17.9390	44.8475		8.7572	35.0288	87.5719

The symbol “—” suggests that there was no authorized value for ARfD and the corresponding risk index could not be calculated. ¹Carbendazim is the sum of thiophanate-methyl and carbendazim. ²Fipronil is the sum of fipronil, fipronil sulfone, fipronil sulfide, and fipronil desulfinyl.

The HI values were calculated to assess the cumulative effect of multiple pesticide residues by equation (5). As shown in Table 3, the chronic hazard index (HIc) and the acute hazard index (HIa) of all detected pesticides for adults, children, and the specific population were 4.49%, 17.94%, 44.85%, 8.76%, 35.03%, and 87.57%, respectively. It can be concluded that the cumulative intake risk of multipesticides through *D. officinale* consumption was acceptable to consumers' health.

3.2.3. Risk Ranking of Detected Pesticides. Using formula (9) and the matrix-ranking scheme in Table 1, the risk of

pesticide intake in *D. officinale* was ranked. According to the LD₅₀, pesticides were classified into 4 classes, including hypertoxic, high, moderate, and low toxicity, which was found by the China Pesticide Information Network [43]. In terms of the maximum dosage of *D. officinale* in the Chinese Pharmacopoeia of the 2020 version [31] and the water content of fresh *D. officinale* [32], the estimated intake from *D. officinale* for an adult per day is 0.06 kg, and the consumption of certain foods of the general population was 1.03 kg [44]. We estimated that the ratio of *D. officinale* dietary intake to the total diet was 5.83%. According to Table 1, the dietary proportion score was assigned to 1. According to GB/T 8321.1-2000 [45], each pesticide was

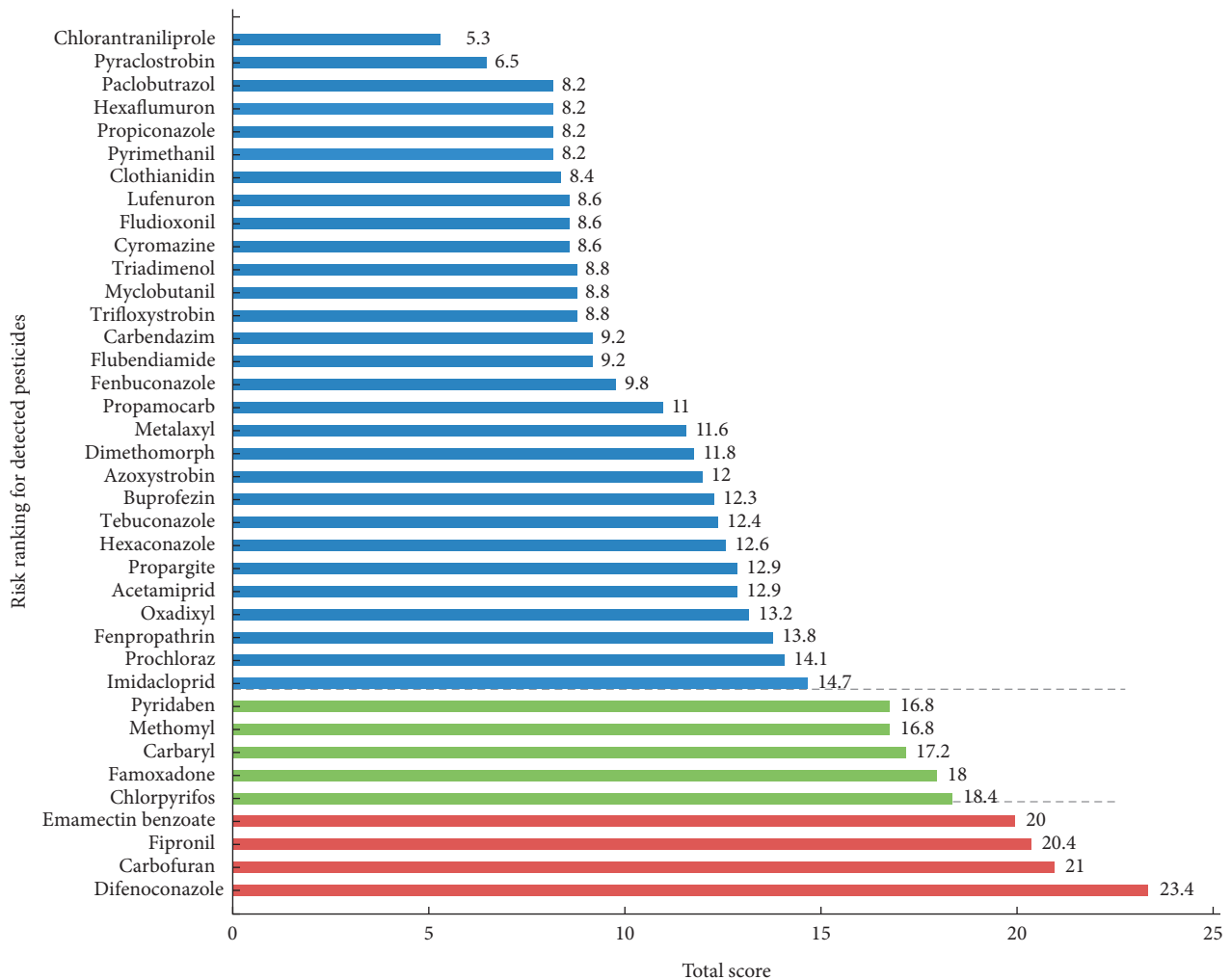


FIGURE 3: Risk ranking score for 38 pesticide residues in *D. officinale* samples.

used up to 3 times in the crop. The Chinese Pharmacopoeia of the 2020 version [31] pointed out that *D. officinale* was harvested from November to March of the next year. The harvest period is about 5 months, that is 150 days. By using equation (8), we can calculate the frequency of dose of pesticides (FOD) of *D. officinale* which was 2%; accordingly, the *D* was assigned the score of 0, according to Table 1. There is no data on *D. officinale* intake in highly exposed people in China. Therefore, we set the score for this parameter to 3. The toxicity classification of piperonyl butoxide cannot be known, so its risk score was not calculated. The risk score of the other thirty-eight pesticides was calculated and is shown in Figure 3.

Among these pesticides, difenoconazole, carbofuran, fipronil, and emamectin benzoate had a relatively high total score of 20–23.4. Followed by famoxadone, chlorpyrifos, methomyl, carbaryl, and pyridaben with risk scores of 18.0, 18.4, 16.8, 17.2, and 16.8, respectively. Compared with those, most of the other pesticides have relatively low-risk scores, which are between 5.3 and 14.7.

From the results shown above, we know that for those pesticides with a relatively high total score, difenoconazole

and emamectin benzoate pose higher long-term risk than short-term risk, and the rate of difenoconazole detection was the highest in all detected samples. However, the acute risk of carbofuran was the highest with the HQa value of 14.4% for the specific population, while the chronic risk was low, which was only found in one sample. The results indicated the risk ranking score was not always consistent with the detection rate, short-term or long-term dietary exposure risk, signifying that the overall risk of pesticides depends on the combined effects of multiple factors.

3.3. Future Work. Firstly, in this study, the unprocessed monitoring data was directly used as the raw data for exposure assessment; however, in the actual use of *D. officinale*, people do not just simply consume raw *D. officinale*. Boiling and brewing are usually employed in household *D. officinale* processing. Processing methods will affect pesticide residues in food to varying degrees. If the dietary exposure assessment does not consider the impact of processing factors on pesticide residues, it will overestimate or underestimate the exposure risk of pesticide residues [46]. For example, Xiao

et al. [2] found that TCM processing could be useful for the partial removal of several pesticide residues. Lentza-Rizos et al. found that the drying and concentration process of grapes to produce raisins increased the level of pesticide residues and the risk due to the loss of moisture content and weight [47]. Therefore, when calculating the actual consumption of *D. officinale*, the amount lost during processing, storage, and export should not be considered. Secondly, dietary pesticide exposure estimated in this study considered only exposure through consumption of *D. officinale* and did not include other food products. To carry out more accurate risk assessment work, it is also necessary to establish relevant databases, such as processing factor of food and risk assessment for other food products. Finally, we used the recommended daily amount of the Pharmacopoeia of People's Republic of China [31] for the consumption data of *D. officinale*, instead of employing population-based methods, household-based methods, or individual-based methods [48]. There would be errors in the level of risk estimation results. Thus, when exact consumption data are obtainable, a comprehensive and more accurate risk assessment would be carried out.

4. Conclusions

In this study, 43 pesticides and metabolites were detected in the *D. officinale* samples. Thirty-seven out of 40 *D. officinale* samples contained at least one pesticide residue. Most pesticide residues were detected at low levels, but a few banned highly toxic pesticides (e.g., fipronil, carbofuran, and methomyl) were detected. Intake risks were assessed using the deterministic method, which implied that the short-term, long-term, and cumulative risks of adults, children, and certain population to pesticides in *D. officinale* were all negligible. In addition, a risk scoring system was used to prioritize chemical hazards for *D. officinale* samples. Difenconazole, carbofuran, fipronil, and emamectin benzoate had a higher residual risk ranking score according to the research results. It is recommended to carry out more monitoring programs so that a proper database regarding pesticides contamination could be created for possible policy decisions.

Data Availability

All the data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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