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Pydiflumetofen in paddy field environments: Its dissipation dynamics and dietary risk

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ABSTRACT

Pydiflumetofen is a broad-spectrum fungicide, the residues of which contaminate crops or are released into the environment, posing a threat to organisms and human health. In this study, pydiflumetofen residues in paddy field ecosystems were determined using quick, easy, cheap, rugged, safe (QuECHERS) sample preparation coupled to high-performance liquid chromatography–mass spectrometry (HPLC–MS) analysis. The dissipation of pydiflumetofen residues was investigated in four Chinese paddy fields over a two-year period (2019 and 2020). The results show that pydiflumetofen dissipation in paddy water occurs faster than those in rice straw and paddy soil, with half-lives of 0.72–2.47, 1.09–9.34, and 6.08–14.38 d, respectively. Linear analysis revealed that the dissipation half-life of pydiflumetofen in different matrices is positively correlated with soil organic matter content and pH and negatively correlated with rainfall and temperature. The final residues of pydiflumetofen in brown rice were determined to assess its dietary-intake risk, and through the household method of soaking for 2–4 h, 28.65–40.24% pydiflumetofen residue can be removed from the rice. The acute and chronic dietary exposure risks of pydiflumetofen in rice were found to be 4.57%–7.14% (acute hazard index) and 0.58%–2.09% (hazard quotient), respectively, indicating that pydiflumetofen poses little or no health risk to Chinese consumers. These results will help guide the practical application of pydiflumetofen and help minimize the environmental risks associated with its global use.

1. Introduction

Pydiflumetofen is a new amide fungicide of the succinate-dehydrogenase-inhibitor class developed by Syngenta Syngenta Crop Protection Co., Ltd. (Switzerland). The chemical formula of pydiflumetofen is $C_{16}H_{16}Cl_3F_2N_3O_2$, and its chemical name is 3-(difluoromethyl)-N-methoxy-1-methyl-N-(1-(2,4,6-trichlorophenyl)propan-2-yl)-1H-pyrazole-4-carboxamide. The chemical has low vapour pressure with relatively non-volatile nature (<1.84×10^{-4} mPa at 25 °C), low water solubility (1.5 mg/L at 25 °C and pH 7.0), Henry's law constant (<1.5 × 10–4 Pam3/mol at 25 °C), octanol–water coefficient (log P = 3.8 and P = 6.31×10^3) and volatilization is not a major factor in disappearance [1]. Pydiflumetofen's mechanism of action is to hinder energy synthesis by interfering with respiratory chain complex II, thereby inhibiting the growth of pathogens [2]. It exhibits a prominent broad-spectrum inhibitory effect on many fungal diseases in crops, such as wheat head blight, rape sclerotium, cucumber powdery mildew, watermelon powdery mildew, leaf spot, brown spot, and bakanae disease. It also plays roles in killing nematodes and improving plant health [3,4]. Considering its excellent in vitro fungicidal effect on *Sclerotinia sclerotiorum* better control efficacy on *Sclerotinia sclerotiorum* in the field, and no cross resistance with current commonly used fungicides. These formulations can be used to control *Fusarium* head blight in wheat [5] and *Sclerotinia sclerotiorum* in rape [6]. Since its release in 2017, pydiflumetofen has been registered in many countries around the world[7]. In China, pydiflumetofen has been registered as the active ingredient in two different formulations, pydiflumetofen standard (purity ≥ 98%) and 20% pydiflumetofen suspension concentrate (SC).

Rice (*Oryza sativa* L.) is one of the most important food crops in the world [8]. In 2020, China's rice planting area was ~ 30.076 million hectares, with a total rice production amounting to ~ 211.8 million tons. China has always been the largest rice consumer in the world [9,10]. However, rice yields can suffer severe losses due to the frequent occurrence of rice diseases, pests, and weeds, resulting in a low average

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yield [11]. In recent years, rice sheath blight has become prevalent in China. Its associated rice yield loss accounts for ~ 10%–30% of total production, and can be as high as 50% in severely affected areas [12]. In order to eliminate such losses, Chinese farmers used to spray synthetic chemicals such as tebuconazole and azoxystrobin onto paddy fields. However, its residues can be toxic to humans in food, and persist in soil and/or migrate to other ecosystems, posing a threat to soil organisms and microbes [13,14]. Moreover, long-term single use of specific chemicals increases pest resistance [15]. Therefore, the use of new fungicides as substitutes has become particularly important.

With the continuous improvement of living standards, people are becoming more aware of the levels of pesticide residues in food, leading to more stringent requirements for pesticide residue testing [16]. The final residues of pesticides in crops such as fruits and vegetables may harm human health. The residue level of a pesticide depends on its rate of dissipation, which is in turn influenced by various factors, such as local climate, soil environment, crop type, and pesticide characteristics [17–19]. Understanding the dissipation dynamics of pesticides and their required pre-harvest intervals is therefore very important for ensuring the quality and safety of agricultural products and for protecting ecological environments. Washing, immersion, and ultrasonication methods are typically used to eliminate pesticide residues from food [20,21]. To date, methods for pydiflumetofen residue determination in grapes [22], tomatoes, wheat, pork, milk, and eggs [23] have been reported. In addition, the environmental behavior of pydiflumetofen enantiomers has been reported too[24]. However, no studies on residue analysis and the dissipation dynamics of pydiflumetofen in paddy field environments have been reported.

Therefore, the purpose of this study was to investigate the dissipation behavior of pydiflumetofen in rice field ecosystems and to evaluate the potential dietary risks it poses to humans based on residue and toxicological data. The factors affecting pydiflumetofen dissipation were also determined, and household methods to eliminate pydiflumetofen residues from brown rice were explored based on the rice consumption habits of the Chinese population. At the same time, the factors affecting the dissipation of pydiflumetofen were analyzed, and found a way to eliminate the residues of pydiflumetofen in brown rice , based on Chinese rice consumption habits. Accordingly, the results of this study will not only provide a fuller picture of the dissipation behavior of pydiflumetofen in paddy field environments, it will also provide guidance for the correct application of pydiflumetofen in pesticide formulations.

2. Experimental

2.1. Reagents and chemicals

Pydiflumetofen standard (purity ≥ 98%) and 20% pydiflumetofen suspension concentrate (SC) were provided by Syngenta Crop Protection Co., Ltd. (Switzerland). Acetonitrile (chromatographic grade) was purchased from Shanghai Anpu Experimental Technology Co., Ltd. (China). Pydiflumetofen standard (0.0100 g) was weighed using an EX224ZH analytical balance (accurate to 0.0001 g; Shanghai Ohaus Instruments Co., Ltd., China) and transferred to a calibrated A-grade volumetric flask (100 mL), where it was dissolved with acetonitrile and diluted to prepare a 100 mg/L stock standard solution. Then, the stock solution was serially diluted with acetonitrile to obtain working standard solutions with different concentrations (0.01, 0.05, 0.1, 0.5, 1, and 5 mg/L). The prepared solutions were stored in a 4-°C freezer until used.

Formic acid (88%, chromatographic grade) was purchased from Tianjin Komiou Chemical Reagent Co., Ltd. (China), and a formic acid aqueous solution (0.1%, *v/v*) was prepared immediately before each experiment by adding formic acid (1.0 mL) to ultrapure water (1000 mL). Sodium chloride (NaCl, analytical grade) and anhydrous magnesium sulfate ($MgSO_4$, analytical grade) were purchased from Shanghai Macleans Co., Ltd. (China). Graphitized carbon black (GCB, 60 μm), N-propyl ethylene diamine (PSA, 50 μm), and octadecylsilane (C18, 50 μm) were purchased from Tianjin Agela Technologies (China). Ultrapure water with a resistivity of 18.25 MΩ·cm was obtained from a TST-USB-20 ultrapure water unit (Shijiazhuang Test Instrument Co., Ltd., China) and used for the preparation of all aqueous solutions.

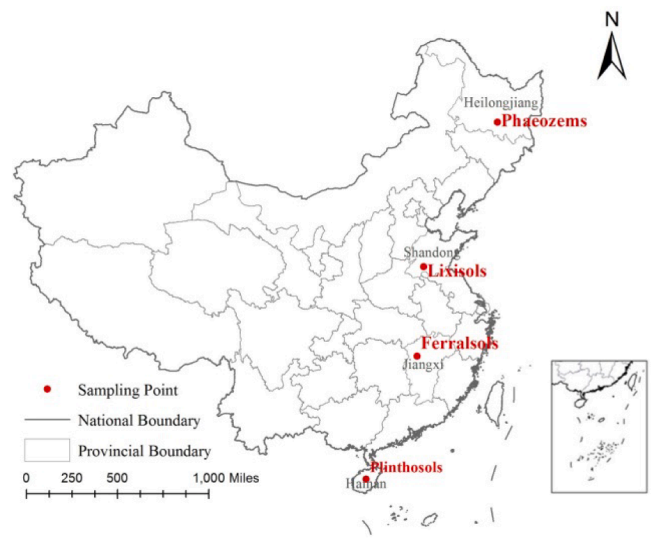


Fig. 1. Locations of the four experimental sites in China.

2.2. Field experiments and sampling procedure

The experimental design followed the "Standard Operating Procedures for Field Efficacy Testing of Pesticide Residues" edited by the Ministry of Agriculture and Rural Affairs of the People's Republic of China, and the latest industry standard "Guideline for the Testing of Pesticide Residues in Crops NY/T 788 −2018″. The field experiments were carried out at four sites in China over two years (August–October in 2019 and 2020). Pydiflumetofen (20% SC) was applied in paddy fields located in Harbin (Heilongjiang Province), Jining (Shandong Province), Yichun (Jiangxi Province), and Haikou (Hainan Province). Blank samples (paddy water, soil, rice straw, and brown rice) were collected from rice planting areas where pydiflumetofen had never been applied (Fig. 1). The soil properties, geographical locations, and climatic conditions of the four experimental sites are provided in Table 1. The soil pH was measured in soil suspensions (soil : water = 1:2.5, w/v) using a pH meter[25]. The dichromate digestion method was utilized to measure the soil organic matter (OM) [26].

2.2.1. Dissipation dynamics analysis

In the dissipation analysis, two treatment plots (Plot 1 and Plot 2) were set up at each experimental site. The application rate of pydiflumetofen in Plot 1 was 200 g /ha (the highest recommended dose) and the application rate in Plot 2 was 300 g /ha (1.5-fold the highest recommended dose). The test site was not<30 m^2 per cell. All the experiments were performed in triplicate. and a buffer zone (1.5 m wide) was set between two adjacent plots to prevent cross-contamination. At the tillering stage of rice production, the plants were evenly sprayed once with pydiflumetofen (20% SC) using an SX-MD16E-2 knapsack electric sprayer (Zhejiang Xia Sprayer Co., Ltd., China). Seven days later, pydiflumetofen was applied again, and samples (paddy water, soil, and rice straw) were collected at 2 h and 1, 2, 3, 5, 7, 14, 21, 28, 35, and 45 days after the second application. In per cell, five to 10 points were selected at random to collect samples (~2 kg each). After collection, water samples were suction-filtered. Each water sample was transferred into a clean beaker after vacuum filtration through a Buchner funnel. Soil samples were air-dried and ground after removing impurities by hand, then passed through a 40 mesh sieve. Rice straw samples (1–2 kg, normal and

Table 1
Soil properties and climatic conditions at the experiment sites in China.

Year	Site	Latitude/Longitude	Soil classification	Organic matter (%)	pH	Total rainfall (Jun–Oct, mm)	Mean temperature (°C)
2019	Haerbin	44°93′ N/127°17′ E	Phaeozems	11.64	6.12	246.4	14.6
	Jining	35°66′ N/117°25′ E	Lixisols	3.96	5.52	435.6	21.8
	Yichun	28°16′ N/115°06′ E	Ferralsols	3.59	5.22	159.5	25.5
	Haikou	19°76′ N/110°51′ E	Plinthosols	1.20	5.79	1122.1	27.2
2020	Haerbin	44°93′ N/127°17′ E	Phaeozems	11.69	6.14	389.9	15.0
	Jining	35°66′ N/117°25′ E	Lixisols	3.88	5.46	511.6	22.0
	Yichun	28°16′ N/115°06′ E	Ferralsols	3.74	5.16	689.5.	23.2
	Haikou	19°76′ N/110°51′ E	Plinthosols	1.21	5.77	1215.3	27.5

Haerbin and Jining (North of China); Yichun and Haikou(South of China)

disease-free) were cut into 0.5 cm pieces and mixed, and retained by the quartering method. The level of pydiflumetofen detected at 2 h was considered as the initial residual level. All samples were stored in a − 20 °C freezer until analysis.

2.2.2. Final residue analysis

In the final residue analysis, two treatment plots (Plot 3 and Plot 4) and one control plot (no pydiflumetofen sprayed) were set up at each experimental site. In Plot 3, pydiflumetofen was first applied to rice plants 35 days before harvest and again seven days later, modelling a pre-harvest interval of 28 days. In Plot 4, pydiflumetofen was first applied 28 days before rice harvest and again seven days later, modelling a pre-harvest interval of 21 days. In each plot, mature rice (2 kg) was collected and hulled using a SATAKE THU35C rice hulling machine (Beijing Bullard Technology Development Co., Ltd., China). Then, brown rice was crushed using a FW80 high-speed universal pulverizer (Beijing Yongguang Medical Instrument Factory, China). The samples were retained by quartering and stored in a − 20-°C freezer.

2.3. Sample pre-treatment

2.3.1. Sample extraction

A quick, easy, cheap, rugged, safe (QuECHERS) technique was used to extract the samples. In brief, the sample (1.5 g each) was weighed and placed in a 50-mL centrifuge tube. Then, ultrapure water (5 mL) and 0.1% formic acid-acetonitrile solution (10 mL) were added to the tube for the solid samples, whereas only 0.1% formic acid-acetonitrile solution (10 mL) was added to the water sample. The mixture was vortexed at 3000 rpm for 2 min using an NV-30S multi-tube vortex mixer (Suzhou Jiulian Technology Co., Ltd., China). Then, NaCl (1 g, for salting-out and layering) and $MgSO_4$ (2 g, for adsorbing water) were added to the tube. The mixture was vortexed for another 1 min and then centrifuged at 9000 × *g* for 5 min in a Digicen 21R bench refrigerated centrifuge (Wiggens, Germany). The supernatant was collected for purification.

2.3.2. Sample cleanup

After extraction, the supernatant (1.5 mL each) was placed in a 2.5-

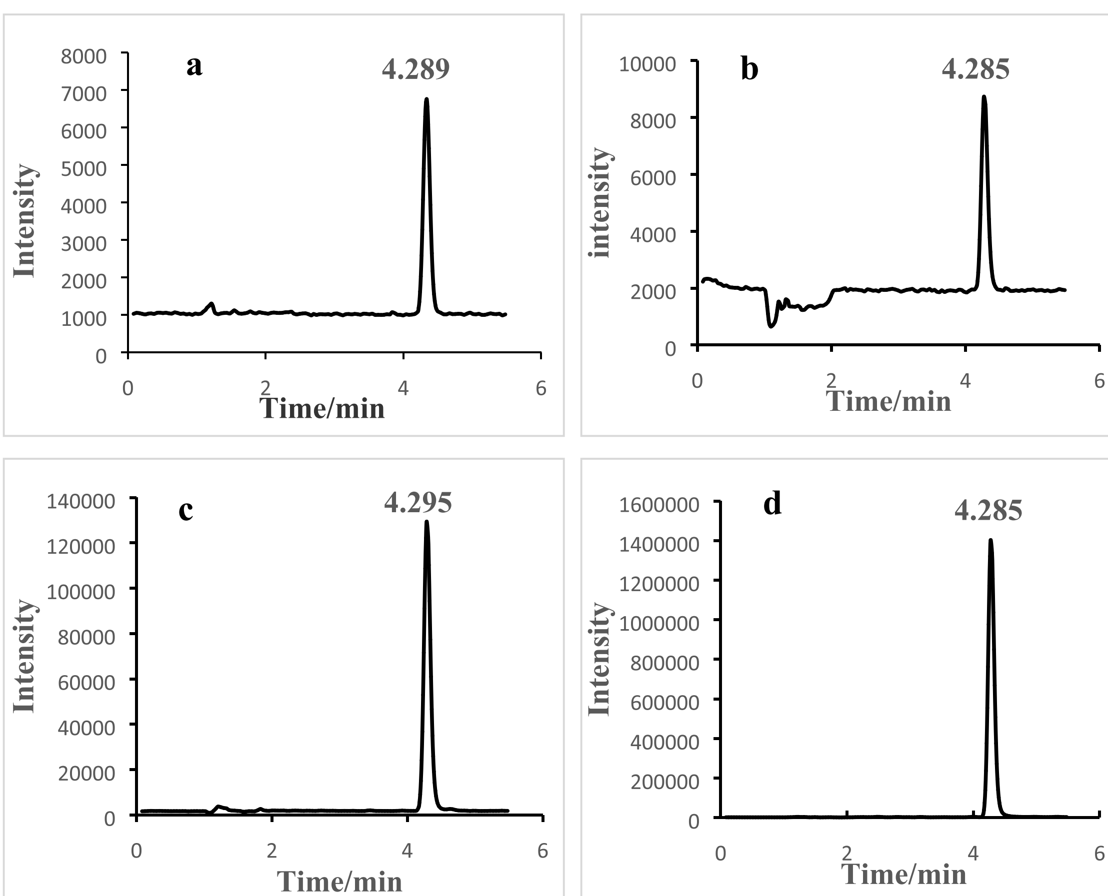


Fig. 2. Chromatogram of standard solution(a, 0.1 mg/L) and residual of pydiflumetofen in paddy water (b), soil (c), and rice straw (d).

mL centrifuge tube. For the paddy water and soil matrices, the tube contained 150 mg $MgSO_4$ and 50 mg C18; for the rice straw matrix, the tube contained 150 mg of $MgSO_4$, 100 mg PSA, and 10 mg GCB; for the brown rice matrix, the tube contained 150 mg of $MgSO_4$ and 50 mg of PSA. The mixture was vortexed for 1 min and then centrifuged at 6000 × *g* for 5 min. The supernatant was passed through a 0.22-μm filter membrane using a sterile syringe and collected for by high-performance liquid chromatography–mass spectrometry (HPLC–MS) analysis.

2.4. Instrumental analysis

The detection of pydiflumetofen was carried out on 1260 series HPLC unit (Agilent Technologies, USA) equipped with an automatic sampling device, a single-stage four-bar mass spectrometer (6120 series, Agilent Technologies), and an Agilent Zorbax Eclipse XDB-C18 chromatographic column (4.6 mm × 150 mm, 5 μm; Agilent Technologies). The following HPLC parameters were used: sample injection volume, 10 μL; mobile phase, acetonitrile and 0.1% formic acid aqueous solution (75:25, *v/v*); left and right column temperature, 35 °C; and flow rate, 1 mL/min. The MS parameters were as follows: ESI ion source, positive ion scan mode (ESI +); dwell time, 590 ms; relative dwell, 100.0%; collision-induced dissociation voltage, 105 V; gain, 10.00; mass-to-charge ratio (*m/z*) in selective ion monitoring (SIM) mode, 426.0; capillary voltage, ±3000 V; drying gas temperature, 350 °C; drying gas flow rate, 12.0 L/min; and atomizing gas pressure, 35 psig. Under these conditions, the retention time of pydiflumetofen was ~ 4.289 min (Fig. 2).

2.5. Method validation

After pre-treatment by the QuECHERS technique, blank matrix solutions of pesticide-free samples (paddy water, soil, rice straw, and brown rice) were obtained. The blank matrix solutions were used to dilute the pydiflumetofen standard solution (100 mg/L) and prepare a series of matrix standard solutions (0.01–5 mg/L). The prepared solutions were stored in a 4-°C freezer until used. HPLC–MS was used to determine the pydiflumetofen concentrations of the prepared solutions multiple times. A standard curve was drawn using OriginPro v2018 (OriginLab Corp., USA), with mass concentration as the abscissa (x), and the peak area corresponding to each concentration as the ordinate (y). Then, the linear regression equation and the coefficient of determination (R^2) were obtained.

The pydiflumetofen concentration yielding a signal-to-noise ratio of three in the prepared matrix solution was defined as the limit of detection (LOD) of the method. Similarly, the pydiflumetofen concentration yielding a signal-to-noise ratio of 10 was defined as the limit of quantification (LOQ) of the method. The matrix effect for each matrix was calculated using Eq. 1:

$$ME=(B-A)/A \times 100\% \quad (1)$$

where *ME* is the matrix effect; *A* is the slope of the standard curve for pydiflumetofen in acetonitrile solution, and *B* is the slope of the standard curve for pydiflumetofen in the matrix sample.

The method 2.3 was used to pre-treatment the samples, and the recovery rate of the blank sample was repeated 5 times at three spike levels (0.01, 0.1 and 0.5 mg/kg). The recovery of pydiflumetofen (Eq. 2) and the coefficient of variation (CV) were obtained by an external standard method. The results for a blank reagent sample were compared with those for standard sample to verify the specificity of the method [27].

$$R(\%)=(S_2-S_0)/S_1 \times 100 \quad (2)$$

where R is the recovery rate of pydiflumetofen residues in the sample; S_2 and S_1 are respectively the peak area of the analyte obtained in the matrix sample and that of the standard in acetonitrile solution at the same concentration; and S_0 is the peak area of the blank matrix with no pydiflumetofen added [28].

2.6. Dissipation dynamics analysis

A first-order kinetic model was used to describe the dissipation process in the field soil environment [29]. Here, the dissipation kinetic parameters of pydiflumetofen were obtained OriginPro v2018 (OriginLab Corp.) based on a non-linear fitting method as follows:

$C_t = C_0 \times \exp^{-kt}; t_{0.5} = ln_2/k$ (3)$C_t = C_0 \times \exp^{-kt}; t_{0.5} = \frac{\ln 2}{k}$where C_t is the concentration of pydiflumetofen residues at time t (mg/kg); C_0 is the initial concentration of pydiflumetofen residues after application (mg/kg); K is the coefficient of dissipation; t is the time after application (d); and $t_{0.5}$ is the dissipation half-life [30].

2.7. Dietary-risk assessment

The acute dietary-intake risk (acute hazard index; aHI) and chronic dietary-intake risk (hazard quotient; HQ) of pydiflumetofen were evaluated based on the maximum residues in the four experimental sites over the two-year study period. The aHI and HQ values were estimated for dietary exposure and risk assessment using Eqs. 4–7 [31]:

$$NESTI = HR \times LP/bw \quad (4)$$

$$aHI = NESTI/ARfD \times 100\% \quad (5)$$

$$NEDI = STMR \times Fi/bw \quad (6)$$

$$HQ = NEDI/ADI \times 100\% \quad (7)$$

where *NESTI* is the national estimated short-term intake; *HR* is the highest residue (mg/kg); *LP* is the majority of consumption (0.40 kg/d) of commodities obtained from the World Health Organization (WHO, 2019); *bw* is the average weight of an adult in China (60 kg); *ARfD* is the acute reference dose (0.30 mg/kg/d); *NEDI* is the national estimated daily intake; *STMR* is the median residual (mg/kg) derived from a supervised trial; *Fi* is the average daily intake of rice (0.30 kg/d); and *ADI* is the acceptable daily intake (0.1 mg/kg/d).

2.8. Rice decontamination

The effectivenesses of different household technologies for removing pydiflumetofen residues from brown rice were evaluated with selected samples. Each sample was divided into six parts: one part received no treatment (control), and the other parts were rinsed with water or soaked with water for 0.5, 1, 2, and 4 h. After treatment, the water was removed and the samples were dispersed on filter paper and air-dried. Subsequently, the samples were prepared by using the QuECHERS technique and then analyzed by HPLP–MS.

3. Results and discussion

3.1. HPLC–MS optimization

The optimal HPLC–MS conditions were determined using a standard 1-mg/L pydiflumetofen solution. First, chromatographic separation was optimized using two mobile phases, acetonitrile–0.1% formic acid aqueous solution and methanol–0.1% formic acid aqueous solution. The results showed that when acetonitrile–0.1% formic acid aqueous solution is used as the mobile phase, the pydiflumetofen retention time is shorter and the resolution is better. Therefore, the volume ratio of components in the mobile phase was optimized on this basis, and the optimal volume ratio of acetonitrile and 0.1% formic acid aqueous solution was determined to be 75:25 (*v/v*). Under the same chromatographic conditions, ESI (+/–) simultaneous scan mode was selected to perform a full scan of the standard sample (*m/z* = 100–1000), and the strongest effective peak was obtained at *m/z* 426.0. Then, using SIM

Table 2
Linear equation, coefficient of determination $(R)^2$, limit of detection (LOD), limit of quantification (LOQ), and matrix effect of pydiflumetofen in different matrices.

Matrix	Linear equation	R^2	LOD (μg/kg)	LOQ (μg/kg)	Matrix effect (%)
Acetonitrile	$y = 421,804.80x - 9,168.32$	0.9998	–	–	–
Paddy water	$y = 395,146.95x + 4,537.86$	0.9999	1.9	6.87	–0.79
Paddy soil	$y = 406,594.48x - 3,095.12$	0.9999	2.2	7.86	–3.61
Rice straw	$y = 466,511.86x + 5,609.83$	0.9999	2.0	7.20	10.6
Brown rice	$y = 497,605.48x + 1,461.35$	0.9999	3.2	11.16	17.97

mode, the collision-induced dissociation voltage and other parameters were optimized and adjusted to maximize the instrument response value. Finally, the optimal HPLC–MS conditions were obtained as described (*section 2.4*).

3.2. Method validation

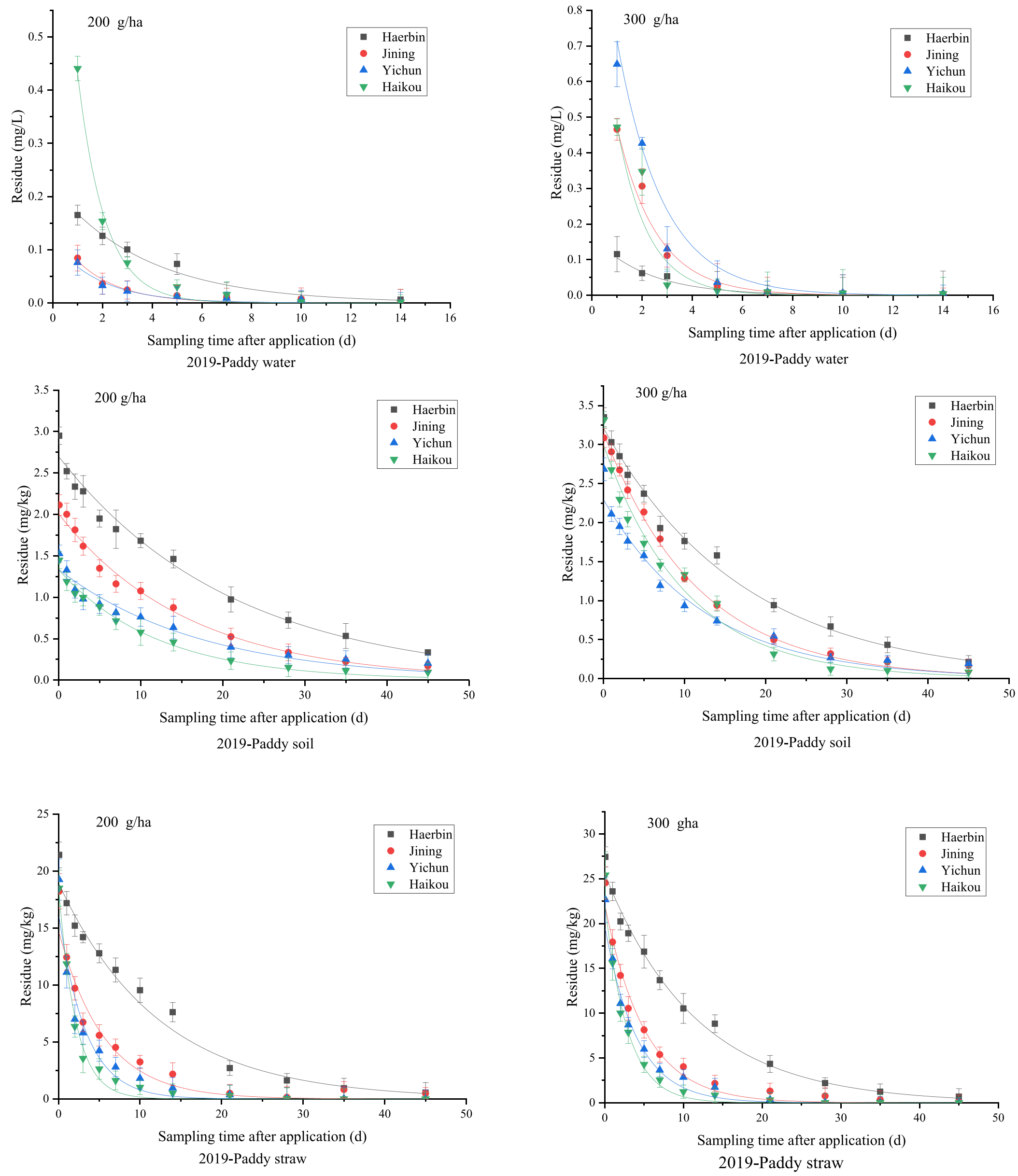
The linear regression equation showed that there is a good linear relationship between the concentration of pydiflumetofen and the peak area of different matrices ($R^2 > 0.999$). The LODs for pydiflumetofen detection are 1.9–3.2 μg/kg, and the LOQs are 6.87–11.16 μg/kg. Here, the matrix effects for the five different matrices range from –0.79% to 17.94% ($|ME| < 20\%$, Table 2), which can be ignored [32]. The recoveries of pydiflumetofen from the spiked samples range from 84.23% to 105.10% and the CV values are 1.07%–9.99% (<15%), indicating that this method is feasible in terms of accuracy and precision. By comparing the results of the reagent blank and the pydiflumetofen standard sample, it was established that the blank matrix presents no

Table 3
Initial residual concentrations (mg/kg, mg/L) of pydiflumetofen in paddy water, soil, and rice straw at different sites.

Year	Site	Paddy water		Paddy soil		Rice straw	
		200 g/ha	300 g/ha	200 g/ha	300 g /ha	200 g/ha	300 g/ha
2019	Haerbin	0.1651	0.1154	2.9493	3.3505	21.4232	27.4387
	Jining	0.0844	0.4659	2.1132	3.0849	18.2273	24.5419
	Yichun	0.0760	0.6487	1.5260	2.6833	19.2529	22.6646
	Haikou	0.4407	0.4722	1.4483	3.3174	18.5021	25.4150
2020	Haerbin	0.3642	0.9136	2.5642	3.0152	16.4794	21.1067
	Jining	0.3363	0.7864	1.9017	2.7762	15.4077	22.2098
	Yichun	0.0760	0.1177	1.3733	2.4147	16.2746	20.5110
	Haikou	0.4254	0.5544	1.3033	2.9854	15.6400	19.5500

Table 4
Dissipation of pydiflumetofen in paddy water, soil, and rice straw.

Year	Site	Pydiflumetofen dose(g/ha)	Paddy water			Paddy soil			Rice straw		
			Dissipation equation	R2	$t_{0.5}$ (d)	Dissipationequation	R^2	$t_{0.5}$ (d)	Dissipation equation	R^2	$t_{0.5}$ (d)
2019	Haerbin	200	$Ct = 0.2228e^{-0.2802t}$	0.9653	2.47	$Ct = 2.6832e^{-0.0482t}$	0.9824	14.38	$Ct = 18.9667e^{-0.0816t}$	0.9816	8.49
		300	$Ct = 0.1704e^{-0.4261t}$	0.9821	1.63	$Ct = 3.2124e^{-0.0587t}$	0.9918	11.81	$Ct = 25.5763e^{-0.0865t}$	0.9928	8.01
	Jining	200	$Ct = 0.1504e^{-0.6159t}$	0.9521	1.13	$Ct = 2.0561e^{-0.0673t}$	0.9891	10.30	$Ct = 14.7675e^{-0.1784t}$	0.942	3.89
		300	$Ct = 0.8811e^{-0.6076t}$	0.9828	1.14	$Ct = 3.1428e^{-0.0839t}$	0.9978	8.26	$Ct = 22.1783e^{-0.1982t}$	0.9799	3.50
	Yichun	200	$Ct = 0.1355e^{-0.6158t}$	0.9521	1.13	$Ct = 1.3279e^{-0.0569t}$	0.9476	12.18	$Ct = 16.3453e^{-0.3019t}$	0.9446	2.30
		300	$Ct = 1.2625e^{-0.6348t}$	0.9764	1.09	$Ct = 2.4212e^{-0.0879t}$	0.9747	7.89	$Ct = 19.7694e^{-0.2453t}$	0.982	2.83
	Haikou	200	$Ct = 1.1409e^{-0.9585t}$	0.9935	0.72	$Ct = 1.3282e^{-0.0823t}$	0.9851	8.42	$Ct = 18.6671e^{-0.4729t}$	0.9773	1.47
		300	$Ct = 0.6028e^{-0.5778t}$	0.9151	0.99	$Ct = 3.0201e^{-0.992t}$	0.9776	6.99	$Ct = 22.4340e^{-0.3482t}$	0.9782	1.99
2020	Haerbin	200	$Ct = 0.5683e^{-0.5119t}$	0.9286	1.35	$Ct = 2.4682e^{-0.0623t}$	0.9934	11.13	$Ct = 14.3170e^{-0.0742t}$	0.9823	9.34
		300	$Ct = 1.6965e^{-0.5905t}$	0.9859	1.17	$Ct = 2.9084e^{-0.0576t}$	0.9942	12.03	$Ct = 19.9350e^{-0.0874t}$	0.9928	7.93
	Jining	200	$Ct = 0.6164e^{-0.6444t}$	0.9442	1.08	$Ct = 1.7992e^{-0.0837t}$	0.9769	8.28	$Ct = 14.4317e^{-0.2397t}$	0.9486	2.89
		300	$Ct = 1.4996e^{-0.6692t}$	0.9766	1.04	$Ct = 2.8311e^{-0.0831t}$	0.9986	8.34	$Ct = 20.2763e^{-0.2069t}$	0.9769	3.35
	Yichun	200	$Ct = 0.1355e^{-0.6158t}$	0.9521	1.13	$Ct = 1.1800e^{-0.0803t}$	0.9571	8.63	$Ct = 15.9086e^{-0.3965t}$	0.9685	1.75
		300	$Ct = 0.2275e^{-0.6588t}$	0.9876	1.05	$Ct = 2.1893e^{-0.0871t}$	0.9874	7.96	$Ct = 19.8320e^{-0.2883t}$	0.9833	2.40
	Haikou	200	$Ct = 0.9209e^{-0.7183t}$	0.9077	0.96	$Ct = 1.2181e^{-0.1140t}$	0.9754	6.08	$Ct = 16.3499e^{-0.6382t}$	0.9958	1.09
		300	$Ct = 1.1043e^{-0.6873t}$	0.9940	1.01	$Ct = 2.5778e^{-0.0976t}$	0.9730	7.10	$Ct = 19.8076e^{-0.4569t}$	0.9886	1.52



(a)

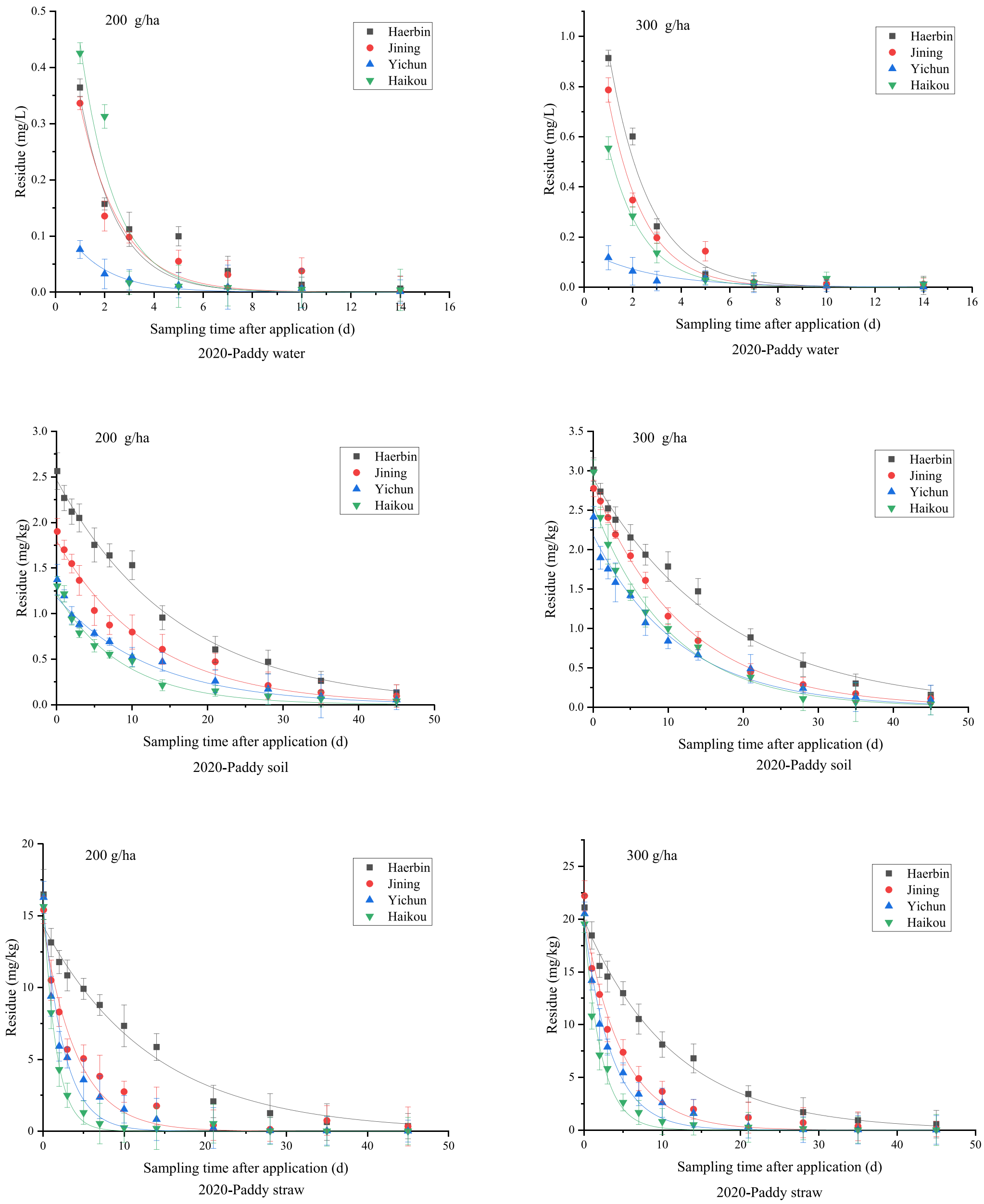
Fig. 3. Dissipation dynamics of pydiflumetofen in paddy water, soil, and straw in 2019 (a) and 2020 (b).

peaks in near the retention time of the standard product, which demonstrates that the specificity of the method is satisfactory.

3.3. Deposition and dissipation of pydiflumetofen in paddy water, soil, and straw

The residual concentrations of pydiflumetofen detected in different matrices 2 h after application were taken as the initial deposition values, and the deposition amount values were found to decrease in the order rice straw > paddy soil > paddy water (Table 3). The initial residual concentrations of pydiflumetofen in rice straw are the highest (18.2273–27.4387 mg/kg in 2019, and 15.4077–22.2098 mg/kg in 2020), followed by those in paddy soil (1.4483–3.3505 mg/kg in 2019, and 1.3033–3.0152 mg/kg in 2020). The lowest initial residual concentrations are observed for paddy water (0.0760–0.6487 mg/L in 2019 and 0.0760–0.9136 mg/L in 2020).The results of the two-year measurement are consistent. Because pydiflumetofen is sprayed in the afternoon and the weather is not raining, most of it would be absorbed by the leaves on the contacted rice straw. Therefore, the initial concentration of pydiflumetofen in rice straw was the highest. The remainder will fall into the paddy field water and soil. Meanwhile, the low solubility of pydiflumetofen in the water, most of the fungicide will settle in the soil, and then may be absorbed and transferred by the rice roots. So the initial concentration in the paddy water is the lowest.

The fitting results for the pydiflumetofen-dissipation equations for each matrix are in all in accordance with first-order kinetics (Table 4), and the dissipation dynamics are shown in Fig. 3. In the results for 2019, the dissipation half-lives of pydiflumetofen in paddy water, paddy soil, and rice straw are 0.72–2.47, 6.99–14.38, and 1.47–8.49 d, respectively. In 2020, the corresponding dissipation half-lives are 0.96–1.35, 6.08–12.03, and 1.09–9.34 d, respectively. The dissipation rates decrease in the order paddy water > rice straw > paddy soil. The



(b)

Fig. 3. (*continued*).

difference in climate and soil organic matter between the north and the south is the decisive factor leading to the different half-lives of pesticides in different substrates[33]. Since the dissipation half-lives are < 30, pydiflumetofen is classified as an easily degradable pesticide. At 45 d after application, there are still pydiflumetofen residues in rice straw and paddy soil, indicating that it has a long-lasting effect.

$t_{0.5}$ indicates dissipation half-life.

3.4. Factors influencing pydiflumetofen dissipation

The dissipation of pesticides depends on many factors, such as local climate, soil type, and crop species [34,35]. Here, the effects of different soil properties and climatic conditions on the dissipation half-life of pydiflumetofen in paddy water, paddy soil, and rice straw were evaluated by linear regression (Table 5).

In paddy water, the dissipation of pesticides is closely related to their thermodynamic diffusion in the surrounding soil and plants as well as other factors such as light, heat, and pH [36]. In the present study, the dissipation half-life of pydiflumetofen in paddy water was found to be positively correlated with soil organic matter content (r = 0.9740–0.9993) and pH (r = 0.4586–0.7001) and negatively correlated with total rainfall (r = − 0.8916 to − 0.5870) and mean temperature (r = − 0.9676 to − 0.9145).In paddy soil, the dissipation of pesticides is mainly affected by the physical and chemical properties of the soil, such as surface vegetation, leaching, adsorption–desorption, and microbial degradation, and is the result of various driving forces, such as temperature, pH, organic matter content, and microbial composition [37]. Here, linear regression analysis revealed that the dissipation half-life of pydiflumetofen in paddy soil is positively correlated with soil organic matter content (r = 0.8988–0.9978) and negatively correlated with total

Table 5
Linear regression analysis of the degradation half-life of pydiflumetofen in soil with the main soil properties and climatic conditions.

Year	Influencing factor	Pydiflumetofen dose(g/ha)	Paddy water		Paddy soil		Rice straw	
			Linear equation	r	Linear equation	r	Linear equation	r
2019	Organic matter/%	200	y = 0.1684x + 0.5042	0.9993	y = 0.5065x + 8.7392	0.8988	y = 0.6819x + 0.5592	0.9845
		300	y = 0.0351x + 0.9512	0.9740	y = 0.4331x + 6.3222	0.9493	y = 0.8278x − 0.4528	0.9892
	Soil pH	200	y = 1.2697x − 5.8269	0.6383	y = 1.7996x + 1.1306	0.2706	y = 5.6681x − 28.0600	0.6932
		300	y = 0.1949x + 0.0262	0.4586	y = 1.9599x − 2.5678	0.3639	y = 7.3054x − 37.6000	0.7395
	Total rainfall	200	y = −0.001x + 1.8666	−0.5870	y = −0.0049x + 13.734	−0.8400	y = −0.0037x + 5.8641	−0.5180
		300	y = −0.0003x + 1.2661	−0.7417	y = −0.0039x + 10.422	−0.8137	y = −0.0041x + 5.7764	−0.4712
	Mean temperature/°C	200	y = −0.1312x + 4.2847	−0.9611	y = −0.3678x + 19.514	−0.8057	y = −0.5589x + 16.485	−0.9959
		300	y = −0.0267x + 1.7242	−0.9145	y = −0.3363x + 16.021	−0.9099	y = −0.662x + 18.5120	−0.9764
2020	Organic matter/%	200	y = 0.0626x + 0.8916	0.9962	y = 0.4650x + 6.3500	0.9978	y = 0.5891x + 1.0594	0.9939
		300	y = 0.0155x + 0.9882	0.9968	y = 0.4785x + 6.4042	0.9973	y = 0.6228x + 0.6055	0.9915
	Soil pH	200	y = 0.4753x − 1.4648	0.7001	y = 3.4041x − 10.4380	0.6755	y = 4.5366x − 21.4710	0.7078
		300	y = 0.1079x + 0.4598	0.6437	y = 3.5595x − 11.19	0.6862	y = 4.7586x − 23.0020	0.7006
	Total rainfall	200	y = −0.197x + 1.7050	−0.8916	y = −1.4839x + 12.445	−0.9049	y = −1.8739x + 8.7665	−0.8985
		300	y = −0.047x + 1.185	−0.8617	y = −1.5179x + 12.653	−0.8992	y = −2.0187x + 8.8473	−0.9133
	Mean temperature/°C	200	y = −0.0532x + 2.3794	−0.9676	y = −0.3985x + 17.472	−0.9761	y = −0.5024x + 15.097	−0.9676
		300	y = −0.0131x + 1.3542	−0.9629	y = −0.4087x + 17.819	−0.9725	y = −0.5349x + 15.527	−0.9720

Table 6
Final residual concentrations of pydiflumetofen in brown rice harvested from the four experimental sites during 2019 and 2020 ($n = 5$).

Year	Site	Pre-harvest interval(d)	Pydiflumetofen dose 200g/ha	300g/ha	Year	Site	Pre-harvest interval	Pydiflumetofen dose 200g/ha	300g/ha
			Final residues /mg·kg^{-1}					Final residues /mg·kg^{-1}	
2019	Haerbin	21	2.1210	3.1242	2020	Haerbin	21	2.0132	3.2109
		28	1.2346	2.0544			28	1.1482	1.4683
	Jining	21	0.4351	1.1073		Jining	21	0.4021	1.1704
		28	0.1298	0.7248			28	0.1103	0.6682
	Yichun	21	0.3123	0.3455		Yichun	21	0.2121	0.3263
		28	0.0431	0.0423			28	0.0402	0.0356
	Haikou	21	0.2163	0.2934		Haikou	21	0.5125	0.2466
		28	0.0211	0.0258			28	0.0213	0.1201

rainfall ($r = -0.9049$ to -0.8137) and mean temperature ($r = -0.9761$ to -0.8057). In particular, the coefficients of correlation between the dissipation half-life of pydiflumetofen and soil organic matter content, total rainfall, and mean temperature are relatively high in paddy soil and water, low correlation with pH. In contrast, the dissipation rate in paddy soil and water in South of China is higher than that in North of China. This may be attributed to the following reasons: First, due to the relatively low soil organic matter content in the south region, paddy soil has a poor ability to adsorb pydiflumetofen into the paddy water; second, the total rainfall in the south of China is higher than that in the north, and the fungicide may penetrates into the ground through leaching. In addition, the temperature in the south region are higher than those in the north, so paddy soil may harbor a higher diversity and abundance of active microorganisms. These microbial drivers could accelerate the dissipation of pydiflumetofen, leading to faster dissipation in the south than in the north. The pH values of the four locations are not much different, and the effect on dissipation is small. The application method is spraying, and the dissipation of pydiflumetofen in two years is similar.

In rice straw, the dissipation of a pesticide is closely relationship to the nature of the pesticide itself, rainfall, and temperature [38]. Rice straw is the above-ground part of rice plants, in which the dissipation half-life of pydiflumetofen was found to be negatively correlated with total rainfall ($r = -0.9133$ to -0.4712) and mean temperature ($r = -0.9959$ to -0.9676). These strong correlations indicate that pydiflumetofen is easily washed away by rainfall. Owing to the abundant rainfall and high temperature in South China, pydiflumetofen dissipates more quickly in rice straw there.

Table 7
Acute and chronic dietary intake risk assessment of pydiflumetofen in rice samples ($n = 5$).

PHI (d)	HR(mg/kg)	NESTI(mg/kg bw/d)	aHI (%)	STMR (mg/kg)	NEDI(mg/kg bw/d)	HQ (%)
21	3.2109	0.0214	7.14	0.4186	0.0021	2.09
28	2.0544	0.0137	4.57	0.1152	0.0006	0.58

PHI, pre-harvest interval; HR, the highest residue; *NESTI,* national estimated short-term intake; aHI, acute hazard index; *STMR*, median residual; *NEDI*, national estimated daily intake; HQ, hazard quotient.

3.5. Final residues and dietary risk assessment for pydiflumetofen in rice

The detection of final residues in rice is of great significance for safety assessment of pesticides in paddy fields. Based on the established HPLC–MS method, the final residues of pydiflumetofen in brown rice were detected at the harvest stage across the four sites. In Harbin, Jining, Yichun, and Haikou, the final residual concentrations of pydiflumetofen in brown rice were found to range from 0.0211 to 3.2109 mg/kg over the two-year study period (Table 6). China has not yet established a

Table 8
Decontamination of pydiflumetofen residues from brown rice by different household methods.

Treatment	200 g/ha		300 g/ha	
	Residue (mg/kg)	Removal (%)	Residue (mg/kg)	Removal (%)
Untreated control	0.2105		0.3151	
Rinsing with running water	0.1711	18.72	0.2701	14.28
Soaking for 0.5 h	0.1722	18.19	0.2485	21.14
Soaking for 1 h	0.1637	22.23	0.2355	25.26
Soaking for 2 h	0.1502	28.65	0.2104	33.23
Soaking for 4 h	0.1297	38.38	0.1883	40.24

maximum residue limit for pydiflumetofen in rice. Nevertheless, the maximum residues of pydiflumetofen detected in the harvested rice do not exceed the maximum residue limit (4 mg/kg) specified by the United Nations Food and Agriculture Organization (FAO) and the World Health Organization (WHO) in grains [39].

The risk assessment results for acute and chronic dietary intake of pydiflumetofen via rice consumption are summarized in Table 7. The aHI values are 4.57%–7.14% and the HQ values are 0.58%–2.09%. An HQ value higher than 1 indicates that the risk is unacceptably high; when $HQ < 1$, the risk is acceptable [40]. Here, both aHI and HQ are much<1, indicating that the risks of residents consuming large amounts of rice containing pydiflumetofen over a short time and of long-term consumption of rice containing pydiflumetofen are low and acceptable.

3.6. Decontamination of pydiflumetofen residues in rice

After the application of pesticides, their residues may persist in food crops and cause harm to consumers. In order to reduce the abundance of pydiflumetofen residues in rice, household methods were used to remove pydiflumetofen and other impurities from brown rice. The results showed that compared with the untreated control, rinsing with running water removes 14.28%–18.72% of the pydiflumetofen residues on the surface of rice (Table 8). In addition, soaking with water for 0.5 h removes 18.19%–21.14% of the residues, while soaking for 4 h removes 38.38%–40.24% of the residues. This result indicates that the longer the soaking time, the better the effect in terms of removing the fungicide. However, a longer soaking time may also reduce the nutrient content or increase the bacterial occurrence in rice [41,42]. Moreover, the effect on pesticides absorbed by rice plants is not good, and the recommended soaking time is 2–4 h. This result provides a scientific basis for people seeking to reduce pydiflumetofen residues in rice or other foods.

4. Conclusions

In this study, the dissipation of pydiflumetofen residues in rice field ecosystems was described by a first-order kinetic model. In different matrices investigated, pydiflumetofen dissipates the fastest in paddy water and the slowest in rice straw. Across different experimental sites, pydiflumetofen dissipates quickly in the south of China and slowly in the north region. Soil organic matter content and pH have positive effects on the dissipation half-life of pydiflumetofen, whereas total rainfall and mean temperature negatively affect it. Pydiflumetofen is proven to be a long-lasting component in the soil, and thus may harm organisms inhabiting the soil. This phenomenon could be due to the high content of organic matter in the soil, which adsorbs most of the pesticide residues. The final residual concentrations of pydiflumetofen in brown rice are lower than the maximum residual limit in grains, while the acute and chronic dietary intake risks via rice consumption are relatively low and at a safe level. However, this study only considered the dietary intake risk of residual pydiflumetofen in rice not the impact of pydiflumetofen ingested through other pathways into the human body. Therefore, the safety risk of pydiflumetofen requires further study. Investigation of the decontamination of pydiflumetofen-contaminated brown rice by different household methods demonstrated that soaking for ~ 2 h effectively removes more than one-third of the residual pydiflumetofen. Thus, the results of this study not only provide data on the dissipation behavior of pydiflumetofen but also useful information for the rational application of this fungicide in paddy fields.

CRediT authorship contribution statement

Chuanfei Bian: Data curation, Writing – original draft. **Juan Luo:** Investigation, Visualization. **Meizhu Gao:** Investigation, Visualization. **Xugen Shi:** Software, Validation. **Yuqi Li:** Investigation, Visualization. **Baotong Li:** Funding acquisition, Supervision, Writing – review & editing. **Limei Tang:** Software, 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.

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