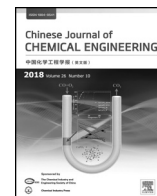




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Article

Distribution and degradation kinetics of cyhalodiamide in Chinese rice field environment☆

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ABSTRACT

Cyhalodiamide is a novel agrochemical which is effective against Lepidoptera pests, including *Cnaphalocrocis medinalis*, *Chilo suppressalis*, *Pieris rapae*, *Plutella xylostella*, *Helicoverpa armigera*, etc. In the study, a fast and accurate analytical method was developed to detect cyhalodiamide in Chinese typical rice field environment by a modified QuEChERS (Quick, Easy, Cheap, Effective, Rugged, Safe) method with UPLC-MS/MS (ultra-high performance chromatography-tandem mass spectrometry). The mean recoveries of cyhalodiamide varied from 73.5% to 107.5%, with the RSDs from 1.2% to 10.7%. The limits of determination (LODs) were 0.0005 mg·kg⁻¹, and the limits of quantitation (LOQs) were from 0.002 to 0.01 mg·kg⁻¹ in all five matrices. This method was used to determine cyhalodiamide residues for studies of the distribution and degradation kinetics in rice field environment. The field trials results showed that cyhalodiamide was easily degradable and the half-lives were 4.2–13.6 d in rice straw, 8.77 d in paddy soil and 5.37–8.45 d in paddy water, respectively. The final residues of cyhalodiamide in brown rice were below 0.35 mg·kg⁻¹. The used dosage of 33.75 g·hm⁻² with pre-harvest interval (PHI) of 21 d and the maximum residue limit (MRL) of cyhalodiamide in rice at 0.1 mg·kg⁻¹ were recommended, which would be safe to human health and environment. The developed analytical method will be useful to monitor cyhalodiamide residues and safety evaluation in rice environment.

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1. Introduction

There are hundreds of the most commonly used agro-chemicals in global agriculture. The rational use of pesticides has become an effective measure for current agricultural production. If pesticides are not used, the yields will be reduced from 30 to 50% by plant pests and diseases. However, improper use can reduce the quality of agricultural products and even cause poisoning accidents, environmental pollution and ecological damage because pesticides are mostly non-natural substances. Therefore, research on distribution and degradation dynamic rules of pesticide in farmland environment, not only improves pesticide efficacy, but also reduces environment pollution and food safety accidents. In current use of pesticides, diamide insecticides are the hot spot on research and market promotion in recent years [1]. There are eight commercialization products from the first diamide insecticide flubendiamide and become the most potential products of pesticide varieties. However, the Chinese government will cancel the registration of flubendiamide on 1st October, 2018 because flubendiamide and

metabolites have a long half-lives in rice fields and unacceptable risk to *Daphnia magna*. The EPA (U.S.) has also issued a notice ready to cancel the registration of flubendiamide [2, 3].

Cyhalodiamide (3-chloro-N²-1-methyl-1-cyano-ethyl-N¹-[2-methyl-4-(1, 2, 2, 2-tetrafluoro-1-trifluoromethyl-ethyl)-phenyl]-phthalimide, ZJ4042) is a novel phthalic diamide insecticide which was independently developed by Zhejiang Research Institute of Chemical Industry, Ltd. [4]. The action mode of cyhalodiamide relies on activating the ryanodine receptors (RyRs) and affecting the release of calcium, which would lead to feeding cessation, emesis, hunger, dehydration and terminal death. Cyhalodiamide exhibits high efficacy to target insects and low toxicity to mammals, and the persistent period and safety of cyhalodiamide showed excellent [5]. Cyhalodiamide is mainly used to control Lepidoptera pests, including *Cnaphalocrocis medinalis* (Guenée), *Chilo suppressalis* (Walker), *Scirpophaga incertulas* (Walker), *Pieris rapae* (L.), *Plutella xylostella* (L.), *Spodoptera exigua* (Hübner), *Prodenia litura* (Fabricius), *Helicoverpa armigera* (Hübner), etc. [6]. The physical and chemical properties of cyhalodiamide were presented in Table 1. The structure of cyhalodiamide was shown in Fig. 1.

However, the migration, distribution and degradation rules of cyhalodiamide in rice fields have not been systematic studied. There are few papers on determination residues of cyhalodiamide in agro-products or environmental samples. To our knowledge, only one HPLC

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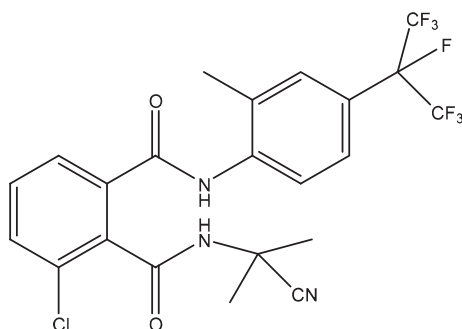
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Table 1

The physical and chemical properties of cyhalodiamide

Compound	Cyhalodiamide
CAS No.	1262605-53-7
Molecular formula	C ₂₂ H ₁₇ ClF ₇ N ₃ O ₂
Molecular weight	523.8
Melting point/°C	215.6–218.8
Water solubility, 25 °C, pH 6/mg·L ⁻¹	0.28
Organic solvent solubility, 25 °C/g·L ⁻¹	Ethyl acetate 19.87, <i>n</i> -hexene 0.004, trichloromethane 2.39, ethyl alcohol 9.41, acetone 39.65, methanol 34.99
Density/g·ml ⁻¹	0.198 (apparent density), 0.338 (bulk density)

**Fig. 1.** The chemical structure of cyhalodiamide.

method [7] and one UPLC-MS/MS method [8] have been used for detecting cyhalodiamide in rice straw, water, soil, and sediments; and our determination method including brown rice and rice husk was simpler, quicker and more sensitive. Furthermore, maximum residue limits (MRLs) of cyhalodiamide in rice have not been established in China or other countries and organizations. This poses a great risk to the consumers' health. In the study, a fast, efficient and practical determination method by using QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) [9–11] and UPLC-MS/MS [12, 13] was established to detect cyhalodiamide residues in all kind of matrixes in rice fields. Moreover, the fate behavior of cyhalodiamide in rice environment could be studied by field experiments and the MRL in rice would be recommended in China. The study results would be considered as a scientific reference for the establishment of the MRL of cyhalodiamide in rice and use specifications in rice fields to protect human health and environmental safety.

2. Materials and Methods

2.1. Standards and reagents

Cyhalodiamide standard substance (96.5%, purity) and suspension concentrated formulation (10%, content) were obtained from Hunan Dafang Agrochemicals Co., Ltd. (Changsha, China). Acetonitrile (chromatography grade) was purchased by American Tedia Reagent Co., Ltd. (Ohio, USA). Analytical grade acetonitrile and sodium chloride were from Changsha Chemical Regent Co., Ltd. (Changsha, China). Cleaning agent C₁₈, Carb were from Agela Technology Co., Ltd. (Tianjin, China) [14].

The standard stock solution of cyhalodiamide (1000 mg·L⁻¹) was prepared by dissolving moderate cyhalodiamide standard substance with acetonitrile. The standard working solutions (0.0005, 0.001, 0.005, 0.01, 0.05, 0.1 and 0.5 mg·L⁻¹) were prepared by diluting from standard stock solution following the order from high to low with acetonitrile. The matrix standard solutions (0.0005 to 0.5 mg·L⁻¹) were obtained by adding blank samples of extracted solutions to each serially diluter standard solution. All solutions were maintained in the dark at 4 °C which kept no degradation in three months [15].

2.2. Field trials

The field trials were operated in different three provinces in China in 2016. Site A was at Meiqiao town in Xiangxiang City, Hunan Province, PR China. Site B was at Baodao New Village, Danzhou City, Hainan Province. Site C was at Zhaodian town, Gaoqing county, Zibo City, Shandong Province. The trials were conducted by “Standard Operation Procedures on Pesticide Registration Residue Field Trials” [16, 17]. Fifteen trial treatments including final residue, degradation kinetic and blank control were prepared; with each treatment having three replicate plots. The details on field trials are listed in Table 2.

The degradation kinetic study was carried out in two treatments. The experiment samples were collected at 2 h, 1, 3, 5, 7, 10, 14, 21, and 30 d after cyhalodiamide suspension concentrate (10% SC) was sprayed at 50.625 g·hm⁻². Rice straw and paddy soil were gathered randomly about 1.0 kg, paddy water samples collected about 500 ml.

The final residue experiments were implemented in twelve treatments. Cyhalodiamide (10% SC) was sprayed at 33.75 and 50.625 g·hm⁻² for one or two times. All the samples were gathered with the pre-harvest intervals of 14, 21, and 28 d and stored in a –20 °C freezer before analyzed.

2.3. Sample preparation

The analytical method for determination of cyhalodiamide residues in rice straw, rice husk, brown rice, paddy soil, and paddy water was derived from the reference methods using the modified QuEChERS extraction and cleanup technique [18–23]. Rice straw, rice husk and brown rice samples were smashed before treatment.

Rice straw and rice husk samples: 5.0 g samples were weighted into a 100 ml polypropylene centrifuge tube. 10 ml water was added and mixed evenly. 50 ml acetonitrile was added and vortex extracted on the oscillator for 2 min. 5 g NaCl was added and vortexed vigorously for 2 min and then centrifuged for 6 min at 5000 r·min⁻¹. Then, 1.0 ml of the supernatant was transferred into a 4 ml small centrifuge tube which contains 50 mg C₁₈ and 10 mg Carb cleaning agents. The tube was vortexed vigorously for 30 s and centrifuged at 12000 r·min⁻¹ for 5 min. The supernatant was passed through 0.22 μm organic syringe filters to sample vials for HPLC-MS/MS determination.

Brown rice, paddy soil and paddy water samples: 10.0 g samples (10.0 ml for paddy water) were weighted into a 100 ml polypropylene centrifuge tube. 10 ml water was added in brown rice and paddy soil samples and mixed evenly. The samples were extracted with 20 ml acetonitrile and vortexed on the oscillator for 2 min. 5 g NaCl was added and vortexed vigorously for 2 min and then centrifuged for 6 min at 5000 r·min⁻¹. Then, 1.0 ml of the supernatant was transferred into a 4 ml small centrifuge tube which containing 50 mg C₁₈ cleaning agents. The tube was vortexed vigorously for 30 s and centrifuged at 12000 r·min⁻¹ for 5 min. The supernatant was passed through a 0.22 μm organic syringe filters to sample vials for determination.

2.4. Instrumentation conditions

Analysis of cyhalodiamide was used by Waters Acquity UPLC instrument with BEH C₁₈ column (2.1 mm × 50 mm, 1.7 μm particle, USA). Mobile phase consists of acetonitrile (a) and aqueous solution (b). The initial gradient of mobile phase was set to 90% aqueous solution and kept for 0.5 min before starting a linear gradient that decreased to 10% aqueous solution at 1.0 min and maintained for 3.0 min. At 4.0 min, the gradient was returned to the original gradient to re-equilibrate the column for 1.0 min [24]. The run time was 5.0 min and the flow rate was kept at 0.30 ml·min⁻¹.

The triple-quadrupole mass spectrometer (XEVO TQ MS, Waters, USA) and ESI- (electrospray negative ionization) mode was used to analyze cyhalodiamide. The extractor voltage was kept at 35 V and the capillary voltage was kept at 3.0 kV, respectively. The desolvation temperature

Table 2

Field trials design of cyhalodiamide in rice fields in China

Field trials projects	Plots number	Plots area/m ²	Application dosage/g·hm ⁻²	Application times ^①	Pre-harvest intervals/d	Sampling objects
Final residue trials	1, 2, 3	30	33.75	1	14	Rice straw, brown rice, rice husk and paddy soil
	4, 5, 6	30	33.75	1	21	
	7, 8, 9	30	33.75	1	28	
	10, 11, 12	30	33.75	2	14	
	13, 14, 15	30	33.75	2	21	
	16, 17, 18	30	33.75	2	28	
	19, 20, 21	30	50.625	1	14	
	22, 23, 24	30	50.625	1	21	
	25, 26, 27	30	50.625	1	28	
	28, 29, 30	30	50.625	2	14	
	31, 32, 33	30	50.625	2	21	
	34, 35, 36	30	50.625	2	28	
	37, 38, 39	50	50.625	1	2 h, 1, 3, 5, 7, 10, 14, 21, 30 d	
	40, 41, 42	50	50.625	1	2 h, 1, 3, 5, 7, 10, 14, 21, 30 d	
Degradation kinetic trials						Rice straw
						Paddy soil and paddy water
Blank control	43	50	0	0	0 h, 28 d	Rice straw, brown rice, rice husk, paddy soil and paddy water

^① Intervals between application was 10 days.

was maintained in 350 °C and the source temperature was maintained in 120 °C, respectively. The flow rate of desolvation gas (N₂) was held at 650 L·h⁻¹ and the collision gas (Ar) was set to 0.15 ml·min⁻¹. The MRM transitions were m/z 522 > 254 at collision energy of 23 eV (quantitative) and m/z 522 > 194 at collision energy of 50 eV (qualitative). The retention time of cyhalodiamide was approximately 2.93 min.

2.5. Calculations

The degradation kinetics [25] of cyhalodiamide in rice field environment were described by the first-order model. The degradation concentration and half-life were calculated using Eqs. (1) and (2), respectively.

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

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

C_t is the residue concentration (mg·kg⁻¹) at time t , C_0 is the initial concentration (mg·kg⁻¹), k is the degradation coefficient, and $T_{1/2}$ is the required time of pesticide residue level decreased to half of the initial residues concentration after application.

3. Results and Discussion

3.1. Method validation

The linear of the method [26, 27] was measured by analyzing the standard solutions and different matrices in triplicate within the concentration range of 0.0005–0.5 mg·L⁻¹. Matrix effects (ME) followed the equation: $ME = (\text{slope}_{\text{matrix}} - \text{slope}_{\text{solvent}}) / \text{slope}_{\text{solvent}} \times 100\%$, with $\text{slope}_{\text{matrix}}$ and $\text{slope}_{\text{solvent}}$ as the slopes [12, 28, 29] of the calibration curves for matrices and solvent, respectively. The linear regression equations of solvent and different matrices were calculated. For satisfactory linear relationship obtained between solvent and different matrixes, all the correlation coefficients (r) were above 0.9933. The ME ranged from 16% to 27%, and rice straw, rice husk and paddy water presented medium effects while brown rice and paddy soil were a mild signal effect [30–32].

The limits of detection (LODs) of cyhalodiamide was 0.0005 mg·kg⁻¹ and set as the lowest concentration from the calibration curves. The limits of quantification (LOQs) were generally considered to be the lowest acceptable recovery level according to NY/T 788–2004 [33]. Therefore, the LOQs of brown rice, paddy soil and paddy water samples were 0.002 mg·kg⁻¹, and 0.01 mg·kg⁻¹ for rice straw and rice husk.

The spiked recoveries at different concentrations (0.002 to 5.0 mg·kg⁻¹) in different matrices were used to represent accuracy.

The relative standard deviation (RSD) of spiked samples recoveries were used to describe precision. The mean recoveries of cyhalodiamide were 73.5%–96.0% for rice straw, 83.9%–107.5% for brown rice, 89.7%–107.3% for rice husk, 88.7%–100.1% for paddy soil and 95.6%–99.5% for paddy water, respectively. The RSDs of cyhalodiamide were 1.2%–5.6% for rice straw, 2.7%–7.6% for brown rice, 1.3%–5.3% for rice husk, 2.9%–9.3% for paddy soil and 2.1%–10.7% for paddy water, respectively. The above results demonstrated that the satisfactory sensitivity, recovery and precision were achieved by this analytical method. The average recoveries and RSDs of cyhalodiamide in all matrices were listed in Table 3. The typical chromatograms of cyhalodiamide in standard solution and spiked samples were shown in Fig. 2.

3.2. Degradation kinetic of cyhalodiamide in rice field environment

The degradation kinetics of cyhalodiamide in rice field environment were calculated with the first-order kinetic equation [34], the results as shown in Table 4. The original deposition of cyhalodiamide in rice straw was 1.121 mg·kg⁻¹ at 2 h in Hunan, and the residues were degraded to 0.019 mg·kg⁻¹ at 21 d. The residues were decreased from 0.172 mg·kg⁻¹ in the beginning to less than LOQ at 21 d in Hainan rice straw. It was degraded from 0.887 mg·kg⁻¹ to 0.172 mg·kg⁻¹ at 30 d in Shandong rice straw. The degradation rates of cyhalodiamide in rice straw in Hunan and Hainan were faster than those in Shandong, which were 98.91%, 98.85% and 80.61% at 30 d and the half-lives were 4.2, 4.3 and 13.6 d, respectively. The residues of cyhalodiamide in paddy soil were not detected (less than LOQ, 0.002 mg·kg⁻¹) in Hainan. The residues were lower than 0.01 mg·kg⁻¹ in Hunan paddy soil, and

Table 3The average recoveries and RSDs of cyhalodiamide in different matrix ($n = 5$)

Samples	Spiked level/mg·kg ⁻¹	Average Recoveries/%	RSD _s /%
Rice straw	0.01	73.5	5.6
	0.1	88.2	3.2
	5	96.0	1.2
Brown rice	0.002	83.9	7.2
	0.02	107.5	2.7
	0.2	104.5	7.6
Rice husk	0.01	89.7	5.3
	0.1	107.3	2.9
	5	97.8	1.3
Paddy soil	0.002	88.7	9.3
	0.02	99.3	2.9
	0.2	100.1	4.3
Paddy water	0.002	95.6	10.7
	0.02	99.5	4.0
	0.2	96.6	2.1

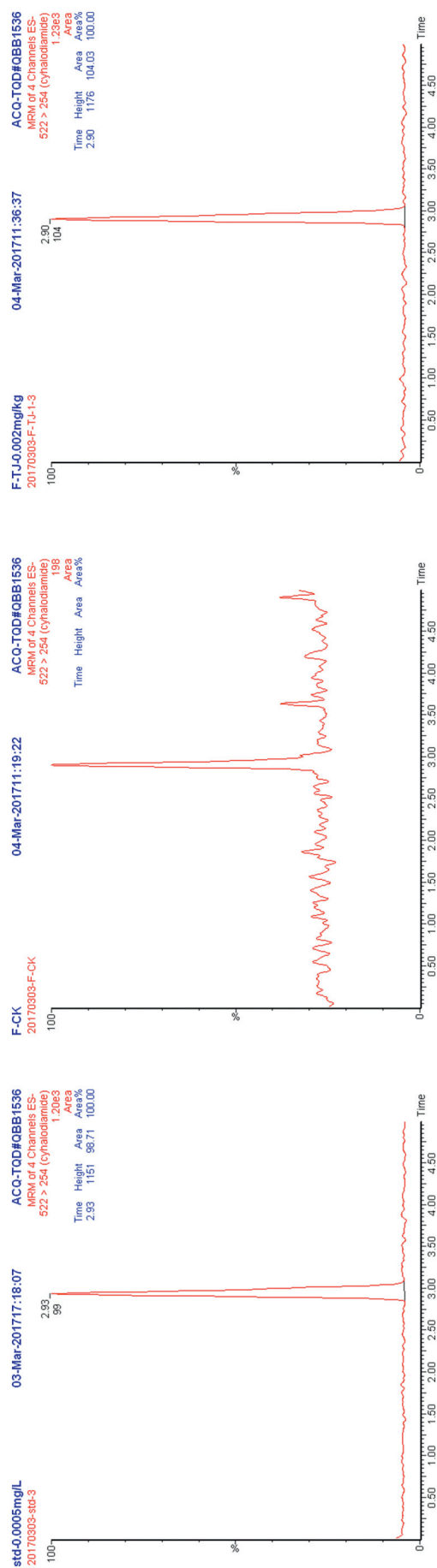


Fig. 2. The MRM chromatograms of cyhalodiamide in (a) standard solution (0.0005 mg·L⁻¹), (b) blank brown rice, (c) fortified brown rice (0.002 mg·kg⁻¹).

Table 4

The degradation kinetics regression equation and half-lives of cyhalodiamide in rice fields

Matrixes	Locations	Regression equation	Correlation coefficient (R^2)	$T_{1/2}$ /d
Rice straw	Hunan	$C_t = 1.0777e^{-0.165t}$	0.9621	4.20
	Hainan	$C_t = 0.1785e^{-0.161t}$	0.9596	4.30
	Shandong	$C_t = 0.8671e^{-0.051t}$	0.9632	13.59
Paddy soil	Hunan	–	–	–
	Hainan	–	–	–
	Shandong	$C_t = 0.0663e^{-0.079t}$	0.8906	8.77
Paddy water	Hunan	$C_t = 0.0163e^{-0.129t}$	0.8673	5.37
	Hainan	–	–	–
	Shandong	$C_t = 0.0501e^{-0.082t}$	0.9587	8.45

the residues in Shandong paddy soil were degraded from the initial deposition $0.076 \text{ mg} \cdot \text{kg}^{-1}$ to $0.009 \text{ mg} \cdot \text{kg}^{-1}$ at 30 d with the half-life of 8.77 days. The residues of cyhalodiamide in paddy water were also undetected except the original deposition in Hainan. The initial residues were reduced from $0.025 \text{ mg} \cdot \text{kg}^{-1}$ at 0 d to below the LOQ ($0.002 \text{ mg} \cdot \text{kg}^{-1}$) at 14 d in Hunan paddy water. The residues were reduced from $0.056 \text{ mg} \cdot \text{kg}^{-1}$ in the beginning to $0.005 \text{ mg} \cdot \text{kg}^{-1}$ at 30 d in Shandong paddy water. The degradation rates were 97.20% and 91.07% at 30 d in Hunan and Shandong, and the half-lives were 5.37 d and 8.45 d, respectively. The degradation kinetic curves for rice straw and paddy water were plotted in Fig. 3.

The original deposition of cyhalodiamide in rice straw, paddy soil and paddy water was in descending order; the maximum values were $1.121 \text{ mg} \cdot \text{kg}^{-1}$, $0.076 \text{ mg} \cdot \text{kg}^{-1}$ and $0.056 \text{ mg} \cdot \text{kg}^{-1}$, respectively. This differences may be related to the plant surface easy to adhere the molecules, and the absorption and migration in the soil and water would be easy to occur. The residues of cyhalodiamide gradually decreased with the extension of time, and decreased significantly within one week after application, and then degraded at a relatively slow rate. The degradation rates of rice straw samples exceed 50% at 5 d in Hunan and Hainan, but it exceeds 50% at 14 d in Shandong. The degradation rates of soil samples exceed 50% at 7 d in Shandong. The residues of cyhalodiamide in Hunan soil samples were between 0.003 and $0.01 \text{ mg} \cdot \text{kg}^{-1}$, and it increased in the period of 0–5 days, which indicated that the adsorption equilibrium of cyhalodiamide between water and soil occurred in the rice field ecosystem [35]. The paddy water samples of Hunan and Shandong exceed 80% and 50% at 7 d, respectively.

From the perspective of different substrates, the half-lives of cyhalodiamide in paddy water and paddy soil are shorter than rice straw in Shandong and the degradation speed is faster, and the hydrolysis and soil degradation may be the main degradation approach of cyhalodiamide in rice fields [36]. However, the degradation rate was much faster in rice straw in Hunan, the metabolism on the rice plant surface is the main degradation approach, which may be related to the

rapid growth and plant surface photolysis at the tillering stage of rice plant [37]; and the growth dilution is also an important factor of rapid elimination of agricultural chemicals in ecosystem [38]. From the perspective of different regions, the degradation rate of cyhalodiamide was faster in Hainan and Hunan, but it was relatively slower in Shandong, which may be related to the climate differences in different regions: Hainan and Hunan are tropical and subtropical regions with warm and wet climates; the microbial community in rice field is much easier to grow, the annual average temperature, illumination duration and organic matter content in soil are higher than those in Shandong, and the precipitation is more. Furthermore, three and two times of rice can be planted in Hainan and Hunan respectively, and the rice varieties, growing period and planting habits, etc. may be the key influence factors [19, 39]. By investigating the soil degradation, hydrolysis and photolysis test results under indoor single condition, the cyhalodiamide can hardly be degraded in such situations. However, the cyhalodiamide can be degraded rapidly in rice fields due to the influence of comprehensive external conditions, such as soil microorganism, rain, high temperature, high humidity, illumination, etc.

3.3. Distribution of cyhalodiamide in rice field environment

The final residual tests of cyhalodiamide in rice fields in Hunan, Hainan and Shandong were sprayed one and two times with the dosage of $33.75 \text{ g} \cdot \text{hm}^{-2}$ (the recommended dosage) and $50.625 \text{ g} \cdot \text{hm}^{-2}$ (1.5 times of recommended dosage), and the pre-harvest intervals were 14, 21 and 28 d. The final residual distribution results are shown in Table 5. According to the table, the residues in brown rice with the PHI of 14, 21 and 28 d were $0.003\text{--}0.035 \text{ mg} \cdot \text{kg}^{-1}$, $<0.002\text{--}0.032 \text{ mg} \cdot \text{kg}^{-1}$, and $<0.002\text{--}0.018 \text{ mg} \cdot \text{kg}^{-1}$, respectively. The residues in rice straw with the PHI of 14, 21 and 28 d were $0.059\text{--}1.010 \text{ mg} \cdot \text{kg}^{-1}$, $0.023\text{--}0.837 \text{ mg} \cdot \text{kg}^{-1}$, and $0.021\text{--}0.658 \text{ mg} \cdot \text{kg}^{-1}$, respectively. The residues in rice husk with the PHI of 14, 21 and 28 d were $0.094\text{--}2.890 \text{ mg} \cdot \text{kg}^{-1}$, $0.011\text{--}2.693 \text{ mg} \cdot \text{kg}^{-1}$, and $<0.01\text{--}$

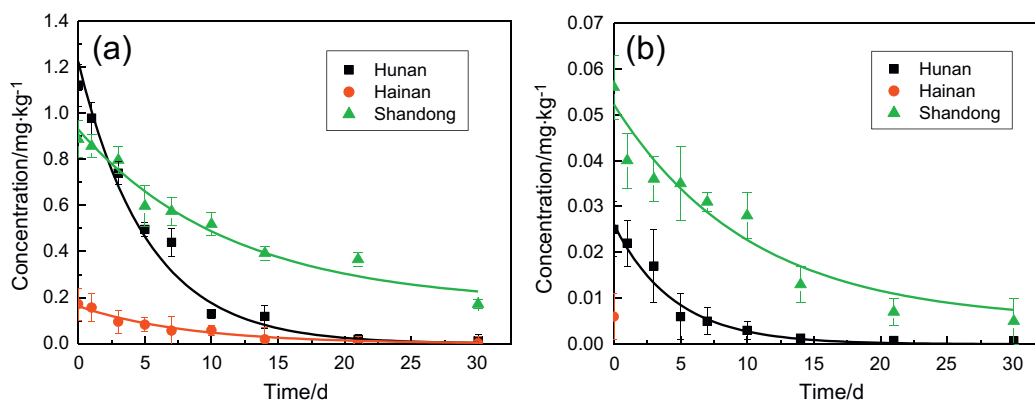
**Fig. 3.** The degradation kinetic curves of cyhalodiamide (a) rice straw, (b) paddy water.

Table 5

The final residues of cyhalodiamide in brown rice, rice straw, paddy soil and husk samples

Trial sites	Application dosage/g·hm ⁻²	Spraying times	Brown rice			Rice straw			Paddy Soil			Rice husk		
			14 d	21 d	28 d	14 d	21 d	28 d	14 d	21 d	28 d	14 d	21 d	28 d
Hunan	33.75	1	0.010	0.006	<0.002	0.125	0.061	0.036	0.003	0.002	<0.002	0.506	0.221	0.056
		2	0.012	0.006	0.002	0.180	0.083	0.039	0.012	0.007	0.006	0.583	0.261	0.081
	50.625	1	0.023	0.007	0.002	0.185	0.075	0.039	0.009	0.002	<0.002	0.950	0.195	0.082
		2	0.025	0.012	0.004	0.573	0.131	0.106	0.033	0.007	0.003	1.231	0.459	0.116
Hainan	33.75	1	0.003	<0.002	<0.002	0.059	0.023	0.022	0.008	0.007	0.005	0.094	0.011	<0.01
		2	0.004	<0.002	<0.002	0.098	0.059	0.025	0.022	0.015	0.008	0.216	0.018	<0.01
	50.625	1	0.005	<0.002	<0.002	0.082	0.031	0.021	0.009	0.007	0.005	0.173	0.026	<0.01
		2	0.009	<0.002	<0.002	0.213	0.119	0.029	0.031	0.017	0.006	0.357	0.067	<0.01
Shandong	33.75	1	0.021	0.020	0.010	0.340	0.095	0.082	0.009	0.007	0.003	1.722	1.431	0.993
		2	0.026	0.022	0.017	0.672	0.562	0.298	0.016	0.013	0.003	2.229	1.952	1.523
	50.625	1	0.029	0.023	0.012	0.985	0.387	0.375	0.020	0.010	0.006	2.172	1.825	1.187
		2	0.035	0.032	0.018	1.010	0.837	0.658	0.051	0.020	0.012	2.890	2.693	2.165

2.165 mg·kg⁻¹, respectively. The residues in soil with the PHI of 14, 21 and 28 d were 0.003–0.051 mg·kg⁻¹, 0.002–0.020 mg·kg⁻¹, and <0.002–0.012 mg·kg⁻¹, respectively. The residues of cyhalodiamide were decreased with the extension of pre-harvest intervals, and the decreased order of residues in each substrate was: rice husk > rice straw > paddy soil > brown rice. The residues of cyhalodiamide were higher with the sprayed times increased under the conditions of the same dosage. The results of final residues of cyhalodiamide from different districts were basically consistent with the results of residual degradation dynamics, Shandong was the highest and Hainan was the lowest, the residual degradation rates in Hunan and Hainan were relatively faster than Shandong. Therefore, the differences of residues were related to the regional differences in illumination, temperature, humidity, rain, surface wash-off, spatial variability, growth dilution, soil properties, rice varieties, growth cycle, planting habits, etc. [39–46].

The final residual test results indicate that 10% cyhalodiamide suspension concentrated was sprayed one or two times with the low dosage of 33.75 g·hm⁻² and high dosage of 50.625 g·hm⁻² respectively, The maximum residue of cyhalodiamide was 0.035 mg·kg⁻¹ in brown rice samples with the PHI of 14 d. Therefore, it is safe to public health and ecosystem when the recommended sprayed dosage of cyhalodiamide was 33.75 g·hm⁻² and the PHI was 21 days. The MRL of cyhalodiamide in brown rice has not been established in China and other countries and organizations, so the MRL of cyhalodiamide in brown rice is recommended to be 0.1 mg·kg⁻¹ based on the final residual test results.

4. Conclusions

The study was developed a quick and accurate determine method, and investigate the final residue distribution and degradation kinetics of cyhalodiamide in rice field environment in China. The average recoveries of cyhalodiamide in all matrices were from 73.5% to 107.5%, and the RSDs of cyhalodiamide were from 1.2% to 10.7%. The LODs were 0.0005 mg·kg⁻¹, and the LOQs were from 0.002 to 0.01 mg·kg⁻¹ in different matrix samples, respectively. Cyhalodiamide was easily degradable due to the half-lives of cyhalodiamide which were 4.2–13.6 d in rice straw, 8.77 d in paddy soil of Shandong and 5.37–8.45 d in paddy water, respectively. The residues of cyhalodiamide in brown rice samples were below 0.35 mg·kg⁻¹. Furthermore, the dosage of 33.75 g·hm⁻² with the PHI at 21 d was also proven safe in rice environment. The MRL of cyhalodiamide was suggested to be 0.1 mg·kg⁻¹ in brown rice in China. The developed analytical method and relative study results would contribute to establish MRLs and reasonable usage specification, and carry out risk assessment to protect consumer health and environmental safety.

Nomenclature

C_t	residue concentration at time t , mg·kg ⁻¹
C_0	the initial concentration, mg·kg ⁻¹
k	degradation coefficient
LODs	limits of detection
LOQs	limits of quantitation
MRLs	maximum residue limits
ME	the matrix effects
PHI	pre-harvest intervals
QuEChERS	quick, easy, cheap, effective, rugged, safe method
RSD	relative standard deviation
slope _{matrix}	the slope of matrix
slope _{solvent}	the slope of solvent
$T_{1/2}$	half-lives, d
t	the time of sampling, d
UPLC-MS/MS	ultrahigh performance liquid chromatography–tandem mass spectrometry

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