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Uptake and Translocation of Triflumezopyrim in Rice Plants

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ABSTRACT: A new type of mesoionic insecticide triflumezopyrim is mainly used to control rice planthoppers, leafhoppers, etc. In order to study the uptake and translocation characteristics of this new insecticide in rice (*Oryza sativa*), a method for the detection of triflumezopyrim in rice, soil, and water was established using liquid−liquid extraction and QuEChERS sample pretreatment combined with liquid chromatography−triple quadrupole tandem mass spectrometry. The distribution of triflumezopyrim in rice was investigated after hydroponic treatment and foliar treatment at the concentrations of 2.5 and 5 mg·L^{-1} within the ranges of 24, 48, and 72 h. The results showed that triflumezopyrim could be absorbed by roots and form a systematic distribution in rice by hydroponic treatment; meanwhile, it could also be absorbed by leaves and transported to the bottom leaves under foliar treatment, but no triflumezopyrim was detected in the roots. Thus, triflumezopyrim exhibited high acropetal translocation within the rice plant. This study provides an important scientific basis for the development of an application strategy of triflumezopyrim to control planthoppers and leafhoppers as well as for the residue detection method and safety evaluation.

KEYWORDS: *triflumezopyrim, Oryza sativa, QuEChERS, liquid chromatography−triple quadrupole tandem mass spectrometry, systemicity*

1. INTRODUCTION

Triflumezopyrim is a new type of mesoionic insecticide,[1−3] which acts on nicotinic acetylcholine receptor.[4] Ihara et al.[5] proposed that most of the insecticides currently acted on nicotinic acetylcholine receptor, which might be harmful to beneficial insect species (including pollinators), poultry, and mammals. For triflumezopyrim, its mechanism of action is different from existing neonicotinoids. Neonicotinoids act on nicotinic acetylcholine receptor (nAChR) resulting in acute excitatory symptoms, while triflumezopyrim is the only agent that has an inhibitory effect on the nAChR resulting in lethargic poisoning among planthoppers.[6] Nowadays, pymetrozine-based insecticides and imidacloprid are still the main insecticides against rice planthoppers in China. However, the resistance of planthoppers to pymetrozine insecticides has been increasing in recent years.[7] Triflumezopyrim has the characteristics of high efficiency with low dosage, which can be used in crops such as cotton, rice, corn, and soybean crops.[8] It is mainly used to control rice planthoppers, leafhoppers, etc.[9] Zhu et al.[10] proposed that triflumezopyrim was more effective against planthoppers than imidacloprid. The former was harmless to parasitoid wasp and some predatory spider species such as *Pardosa pseudoannulata* and *Ummeliata insecticeps*, but it was still slightly active against *Theridion octomaculatum*. The emergence of triflumezopyrim is bound to become the main product to control rice planthoppers in the future. Some studies indicated that the longevity, fecundity, and egg hatch ability of the F_0 and F_1 generations were not significantly affected by the LC_{30} of triflumezopyrim, while the developmental stages (except for the third stage), the adult preoviposition period, the total preoviposition period, and the average duration of life were significantly prolonged. Moreover, no significant differences were observed in the survival rates of different stages.[11]

The rice planthoppers develop specialized stylets for sucking the nutrient-rich phloem sap, and they mainly pierce the leaf sheath at the stem base.[12] The traditional spray application is generally hard to spray pesticide onto the leaf sheath part of the stem base. Therefore, the translocation ability of triflumezopyrim in rice is vital for its insecticidal efficacy against planthoppers. In addition, only a small percentage of applied pesticides reached the target.[13] Due to various environmental factors, the utilization rate of pesticides was only about 0.1%, and a large proportion of off-targeted pesticides caused a series of environmental pollution.[14,15] The living environment of rice was generally in paddy fields, so if rice plants could absorb triflumezopyrim in the water through their roots, it could not only improve the utilization of pesticides but also avoid waste and protect the environment. Thus, it was of great significance to study the systemicity of triflumezopyrim in rice, especially to a new pesticide.

Nowadays, Yu et al.[16] and Peng et al.[17] have established a high-performance liquid chromatography method for the analysis of triflumezopyrim. In this study, liquid chromatography−triple quadrupole tandem mass spectrometry (LC−MS/MS) was used to establish a method for the determination of triflumezopyrim in rice, water, and soil. The mortality of *Nilaparvata lugens* at different sites of the plant were calculated

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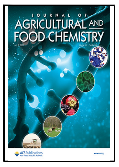

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by simulating the application of triflumezopyrim on rice to determine whether triflumezopyrim has been transmitted in rice, and then the absorption and distribution of triflumezopyrim were investigated by detecting the residue of triflumezopyrim in various parts of rice. The transfer factor (TF) value was to evaluate and compare the transfer ability of triflumezopyrim in rice under two treatments. The uptake, translocation, and distribution characteristics of triflumezopyrim within rice plants are largely unknown. Therefore, by determining the distribution and accumulation of triflumezopyrim in rice within the effective insecticidal time, it is helpful to provide an important directive to formulate the application strategy of controlling *N. lugens* in production practice as well as for the residue detection method and safety evaluation.

2. MATERIALS AND METHODS

2.1. Instruments and Reagents. An Agilent 1200 Series HPLC system equipped with an Agilent 6460 Triple Quadrupole LC/MS system from Agilent Co. (USA); Telstar Lyoquest-55 freeze-dryer from Telstar, Spain; AUY120 electronic balance from Shimadzu, Japan; RXZ-type intelligent artificial climate box from Ningbo Jiangnan Instrument Factory; MX-F vortex stirrer from Beijing Cobser Shanghai Mengrui Biotechnology; desktop high-speed centrifuge from Hunan Hexi Instrument Equipment Co., Ltd.; and Milli-Q ultrapure water machine from Millipore Co., Ltd were used.

The 97% triflumezopyrim standard was prepared and purified by Pesticide Research Institute of Yangzhou University. PSA (primary secondary amine) and C18 from Chemical Reagent Co., Ltd. of China Pharmaceutical Group and acetonitrile (chromatographic purity) from Tedia Company of America were used.

2.2. Test Materials. Rice (*Oryza sativa*) cultivar Nanjing 9108 was planted in a greenhouse of the Wenhui Road Campus of Yangzhou University. Water and soil were taken from the paddy field of the experimental farm of Yangzhou University. There was no use of insecticide triflumezopyrim in the paddy field.

2.3. Test Method. *2.3.1. Preparation of Standard Solution.* The standard triflumezopyrim was accurately weighed (0.0103 g) and dissolved in 10 mL of chromatographic pure acetonitrile to a volume of 100 mL. The standard triflumezopyrim solution with a concentration of 100 mg·L^{-1} was obtained and stored at −4 °C for reserve. When in use, 2 mL of standard solution was taken and diluted with acetonitrile solution to prepare 25 mL of standard solution. Then, the above solution was diluted with acetonitrile to prepare a series of solutions of 12.5, 3.12, 1.56, 0.78, and 0.02 mg·L^{-1}, which were to be used.

2.3.2. Greenhouse Trial, Hydroponic Treatment, and Foliar Treatment. The test concentrations were prepared according to its insecticidal activity,[18] with solutions of 2.5 and 5 mg·L^{-1}. In addition, Tween-80 with a volume fraction of 0.1% was added to ensure the expansion of the agent on rice leaves. When the rice was grown to the third-leaf stage, the following two methods were used to treat the rice (Figure 1). Twenty-four, forty-eight, and seventy-two hours after treatment, the whole plant was collected and divided into four parts: root, first leaf, second leaf, and third leaf. Then, they were stored in a refrigerator at −20 °C for reserve. (1) For the hydroponic treatment, rice was cultured by the hydroponic method, and the hydroponic nutrient solution was formulated according to the method of the International Rice Research Institute.[19] The rice was cultured in an artificial climate chamber (temperature, 28 °C; light 8000 lx). The rice roots were immersed in 2.5 and 5 mg·L^{-1} triflumezopyrim solution (Figure 1a), and the whole rice and 10 mL of the culture solution were taken after 24, 48, and 72 h. The rice roots were cleaned with methanol and ultrapure water in turn. (2) For the foliar treatment, the rice was wrapped with a plastic film and sprayed evenly on the third leaf surface with 2.5 and 5 mg·L^{-1} triflumezopyrim solution until sprayed onto the leaf surface without dropping droplets (Figure 1b). After that, the rice was placed in the artificial climate box. Twenty-four, forty-eight, and seventy-two hours after treatment, the rhizosphere soil and the whole rice were taken. The rice leaves were washed with methanol and ultrapure water in turn.

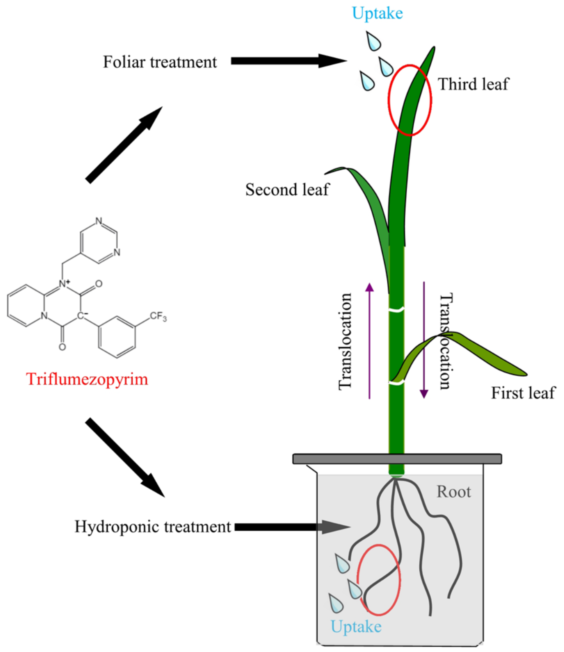

Figure 1. Schematic diagram of different parts of rice (root, first leaf, second leaf, and third leaf) and application methods (a, hydroponic treatment site; b, foliar treatment site). The plants were cultivated for 15 days to the third-leaf stage before treatment and harvested 3 days after treatment. The beaker was covered with aluminum foil to avoid photolysis of triflumezopyrim. Each treatment had three replicates.

2.3.3. Insecticidal Activity of Triflumezopyrim. Rice leaf dipping and hydroponic treatment were used to determine the insecticidal activity of triflumezopyrim against *N. lugens*. In the test, we only applied to the roots and third leaves of the rice and isolated the *N. lugens* from the application site. The detailed processing is included in the Supporting Information. In this test, nine concentrations of 20, 10, 5, 2.5, 1.25, 0.62, 0.31, 0.16, and 0.08 mg·L^{-1} were prepared by half dilution with a 0.1% Tween-80 aqueous solution for future use. The third instar nymphs with the same feeding and physiological status were selected for testing, and 15 were placed in each test tube. The culture conditions were 25 °C and 80% relative humidity, and the photoperiod was L:D = 16:8. All data were statistically analyzed by SPSS (IBM SPSS Statistics 21.0).

2.3.4. Extraction and Cleanup Procedure. The extraction and cleanup method of triflumezopyrim in water used the liquid−liquid extraction method. Ten milliliters of filtered water sample was put in a 50 mL centrifuge tube, and then 4 mL of $V_{(\text{dichloromethane})}:V_{(\text{ethyl acetate})} = 1:1$ mixed solution was added to the extract. Two grams of NaCl was added to be vibrated and centrifuged for 5 min at 6000 rpm, and then 2 mL of supernatant was extracted. The centrifuge tube was shaken thoroughly after an appropriate amount of anhydrous sodium sulfate was added. One milliliter of supernatant was taken, which was to be dried under a gentle nitrogen stream and dissolved in acetonitrile, and then the extract was filtered through a 0.22 μm membrane into a sample vial for analysis. The concentration of triflumezopyrim in water was 1, 0.5, and 0.05 mg·kg^{-1}.

The extraction and cleanup procedure of triflumezopyrim in soil and rice referred to Meng et al.[20] The QuEChERS method was used to extract and cleanup samples. Five grams of soil samples was collected in a 50 mL centrifuge tube. NaCl (1 g), anhydrous magnesium sulfate (2 g), and acetonitrile (10 mL) were added and centrifuged for 5 min at 6000 rpm after vibrating. After that, 4 mL of supernatant was taken. Anhydrous magnesium sulfate (50 mg) and $m_{(\text{PSA})}:m_{(\text{C18})} = 1:1$ (100 mg) were added to the supernatant and centrifuged for 5 min at 6000 rpm. Two milliliters of supernatant was taken, which was to be dried under a gentle nitrogen stream and dissolved in acetonitrile, and then the extract was filtered through a 0.22 μm membrane into a sample vial for analysis. The concentration of triflumezopyrim in water was 1, 0.5, and 0.05 mg·kg^{-1}.

2.3.5. LC–MS/MS Method for the Determination of Triflumezopyrim. HPLC analysis was performed with an Agilent 1200 HPLC system equipped with a binary pump, auto plate sampler, column oven, and diode array detector. Separation was performed on Agilent Eclipse Plus chromatographic columns C$_{18}$ (2.1 mm × 150 mm (i.d.), 5 μm) at 35 °C, with mobile solvents consisting of acetonitrile (A) and 0.5% formic acid solution (B) at gradient elution. 0 min, A:B = 40:60 (V:V); 0−3 min, A:B = 90:10 (V:V); 3−10 min, A:B = 40:60 (V:V), isocratic at 0.3 mL·min^{-1}. Aliquots of 5 μL were injected directly to the LC−MS/MS system to test triflumezopyrim and quantified with the external standard peak area. Mass spectra were recorded on an Agilent 6460 triple quadrupole (QQQ) mass spectrometer equipped with an ESI source. System control and data acquisition were controlled by Agilent Mass Hunter software.

Detailed MS conditions were as follows: a cluster voltage of −120 V, gas temperature of 300 °C, gas flow of 10 L·min^{-1}, nebulizer pressure of 15 psi, sheath gas temperature of 250 °C, sheath gas flow of 7 L·min^{-1}, capillary voltage of 4 KV, and nozzle voltage of 500 V. ESI was operated in positive ion mode in the MRM (multiple reaction monitoring).

3. RESULTS

3.1. Optimization of Mobile Phase. The parent compound of triflumezopyrim was subjected to collision-induced dissociation in MRM positive mode. The electrospray capillary potential as well as the shield and needle voltage was optimized for triflumezopyrim. The collision energy was optimized to achieve the highest sensitivity. Fragmentation ions at m/z 279 and 306 were observed by the production scan of triflumezopyrim. The selected reaction monitoring of the precursor−product ion transition was m/z 279 for the quantitative ion transition of triflumezopyrim.

Mobile solvent systems consisting of methanol−water, acetonitrile−water, and acetonitrile−0.5% formic acid for separating the triflumezopyrim standard were examined. The results indicated that the separation effects of triflumezopyrim achieved the highest sensitivity by using gradient elution under the conditions of 2.3.5. In MRM positive mode, the chromatographic separation of triflumezopyrim was achieved by using isocratic elution with a retention time of 6.16 min.

3.2. Linear Range and Detection Limit of the Detection Method. The standard curve was drawn with the mass concentration of triflumezopyrim as the x-axis and the peak area as the y-axis. The results showed that there was a good linear relationship between the mass concentration and the corresponding peak area in a range of 0.02−12.5 mg·L^{-1} with an r of 0.998. The minimum detection limit was 0.003 mg·kg^{-1}.

3.3. Optimization of Extraction of Triflumezopyrim in Water. Triflumezopyrim was extracted from water samples by liquid−liquid extraction. The extraction efficiency of triflumezopyrim from water samples was contrasted by three different extraction solvents (ethyl acetate, dichloromethane, and dichloromethane:ethyl acetate =1:1 mixed solution). As shown in Table 1, the average recoveries of triflumezopyrim were 90.8% (dichloromethane:ethyl acetate = 1:1), 88.8% (dichloromethane), and 62.9% (ethyl acetate). Consequently, the mixed solution was used as the extraction solvent for the water samples.

3.4. Optimization of the Cleanup Procedure of Triflumezopyrim in Soil and Rice. The mixed adsorbents PSA and C$_{18}$ were used to study the effect of different additions (at total masses of 50, 100, 150, and 200 mg) on the impurity removal efficiency of the target substance in the sample under the condition of $m_{(PSA)}$:$m_{(C18)}$ = 1:1. As shown in Table 2, the results showed that the removal efficiency of impurities increased with an increase in adsorbent dosage. On the contrary, the average recovery decreased with an increase in adsorbent dosage. Taking into account, 100 mg of adsorbent $m_{(PSA)}$:$m_{(C18)}$ = 1:1 was selected to purify samples in this experiment.

Table 1. Comparison of Three Solvent Extraction Efficiencies from Water

solvent	average recoveries (%)	standard deviation (%)	relative standard deviation (%)
ethyl acetate	62.9	7.17	11.4
dichloromethane	88.8	17.6	19.8
ethyl acetate:dichloromethane = 1:1	90.8	5.99	6.59

Table 2. Comparison of the Recovery Rates of Triflumezopyrim in Soil and Rice by Different Dosages of Adsorbents

samples	adsorbent dosage (mg)	average recoveries (%)	standard deviation (%)	relative standard deviation (%)
soil	50	103	10.8	10.4
	100	96.2	7.53	7.83
	150	77.7	4.79	6.16
	200	70.6	5.88	8.32
rice	50	106	7.50	7.04
	100	101	5.19	5.13
	150	84.0	7.54	8.97
	200	73.2	5.31	7.25

3.5. Recoveries of Triflumezopyrim in Water, Soil, and Rice. The average recoveries of triflumezopyrim were in a range of 87.3−104% and the relative standard deviation (RSD) was in a range of 1.02−10.2% (Table 3). The results of determination met the requirements of residue detection.[21]

3.6. Insecticidal Activity of Triflumezopyrim. Some studies determined the distribution of pesticides in plants by calculating the mortality of pests at different sites of plants.[22,23]

Table 3. Recoveries of Triflumezopyrim in Water, Soil, Rice Root, and Rice Leaf

samples	fortified concentration (mg·kg^{-1})	average recoveries (%)	standard deviation (%)	relative standard deviation (%)
water	1.00	95.2	0.970	1.02
	0.50	90.3	5.16	5.71
	0.05	94.0	8.00	8.51
soil	1.00	96.8	5.14	5.31
	0.50	102	2.10	2.05
	0.05	99.3	1.26	1.27
rice root	1.00	94.1	9.48	10.1
	0.50	91.4	9.32	10.2
	0.05	104	1.57	1.51
rice leaf	1.00	87.3	5.98	6.85
	0.50	99.4	7.44	7.48
	0.05	98.5	3.54	3.59

This method generally combined bioassay and pesticide systemic studies to determine the distribution of pesticides in plants by observing the death of pests or the inhibition of pathogenic microorganisms.[22,23] Through two application methods, we could observe the insecticidal activities of triflumezopyrim against *N. lugens* and its LC_{50} value in Table 4. According to our insecticidal activity tests, without direct contact with insecticide, both application methods showed a good insecticidal effect on *N. lugens* at 0.5 $mg \cdot L^{-1}$. Thus, triflumezopyrim was supposed to be transferred to various parts of the rice plant against *N. lugens*. The mortality of *N. lugens* increased during the test period, indicating that triflumezopyrim had formed accumulation in the rice plants. Comparing these two methods, we found that the mortality of *N. lugens* under hydroponic treatment was higher than that under rice dipping treatment, which means that triflumezopyrim could have better acropetal direction and accumulation in rice.

Table 4. Insecticidal Activity of Triflumezopyrim on *N. lugens* with Two Application Methods[a]

treatment	time (h)	regression equation	regression equation (*R*)	LC_{50} ($mg \cdot L^{-1}$)
hydroponic treatment	24	$y = 1.41 + 2.59x$	0.936	0.286
	48	$y = 2.16 + 2.83x$	0.923	0.172
	72	$y = 4.12 + 4.13x$	0.938	0.101
rice dipping treatment	24	$y = 0.412 + 1.52x$	0.973	0.535
	48	$y = 0.565 + 1.78x$	0.984	0.484
	72	$y = 1.16 + 2.12x$	0.954	0.285

[a] The formula for calculating adjusted mortality of *N. lugens* is as follows: $P = (P_t - P_c)/(1 - P_c) \times 100\%$, where P is the adjusted mortality (%), P_t is the mortality of the experimental group (%), and P_c is the mortality of the no-treatment control group (%).

3.7. Distribution of Triflumezopyrim in Rice.

3.7.1. Distribution of Triflumezopyrim in Rice through Hydroponic Treatment. The initial concentrations of triflumezopyrim in rice with hydroponic treatment were 2.5 and 5 $mg \cdot L^{-1}$. Both groups showed that the triflumezopyrim could be detected in the four parts of rice. As shown in Figure 2, the contents of triflumezopyrim in roots were significantly increased (from 0.421 to 0.927 $mg \cdot kg^{-1}$ and from 0.818 to 1.42 $mg \cdot kg^{-1}$); meanwhile, the root concentration factor (RCF) values of two treatments were 0.175−0.463 and 0.168−0.303 within 72 h, which means that triflumezopyrim could be absorbed by roots. The concentration in upper leaves had increased within 72 h in both groups. The total content of triflumezopyrim in the 5 $mg \cdot L^{-1}$ treatment group was higher than that in the 2.5 $mg \cdot L^{-1}$ treatment group. Although both groups indicated that the contents of triflumezopyrim in roots were higher than those in other parts, the total content of upper leaves was higher than that of roots. The balance between uptake and metabolism may provide an explanation for this phenomenon.[24] The transmission of pesticides in plants mainly depends on transpiration flow,[25] and the content of triflumezopyrim in the third leaf was higher than that in the first or second leaf (Figure 2) within 72 h, which means that triflumezopyrim had acropetal direction in rice.

3.7.2. Distribution of Triflumezopyrim in Rice through Foliar Treatment. The application concentrations of triflumezopyrim for foliar treatment were 2.5 and 5 $mg \cdot L^{-1}$. The triflumezopyrim was not detected in the first leaf and second leaf at 24 h in the 2.5 $mg \cdot L^{-1}$ treatment group. Twenty-four, forty-eight, and seventy-two hours after treatment, the contents of triflumezopyrim in the third leaf were 1.22−1.48 and 1.40−2.25 $mg \cdot kg^{-1}$. It had a good ability to be absorbed by plant leaves. The content of triflumezopyrim in rice mostly accumulated in the treatment leaves. However, the first leaf and second leaf had less triflumezopyrim. The total content of triflumezopyrim in the rice in the 5 $mg \cdot L^{-1}$ treatment group was higher than that in the 2.5 $mg \cdot L^{-1}$ treatment group, and the content of triflumezopyrim in the third leaf was far higher than that in the first or second leaf (Figure 3). After treatment with triflumezopyrim at two groups, triflumezopyrim was not detected in the roots and rhizosphere soil within 72 h.

3.7.3. Translocation of Triflumezopyrim in Rice. TF was used to evaluate the level of chemical transfer in the plants by the transfer of chemical substances from roots to stems or leaves. $TF_{\text{hydroponic}} = C_{\text{leaf}}/C_{\text{root}}$ (hydroponic treatment) and $TF_{\text{foliage}} = C_{\text{root}}/C_{\text{leaf}}$ (foliar treatment) were used to evaluate the transfer of triflumezopyrim in rice.[26] Compared with the foliar treatment group, the triflumezopyrim transmission distance in the hydroponic treatment group was further and the transmission efficiency was higher (Figures 4 and 5). The TF values of the two treatment groups are shown in Tables 5 and 6. In the hydroponic treatment group, the $TF_{\text{third leaf}}$ value was greater than the $TF_{\text{first leaf}}$ or $TF_{\text{second leaf.}}$ In the foliar treatment group, the $TF_{\text{second leaf}}$ value was greater than the $TF_{\text{first leaf}}$. However, the TF_{foliage} value of the foliar treatment group was lower than that of the hydroponic treatment group. In contrast, the triflumezopyrim had better upward transportation in rice. Ge et al.[27] proposed that the direction of

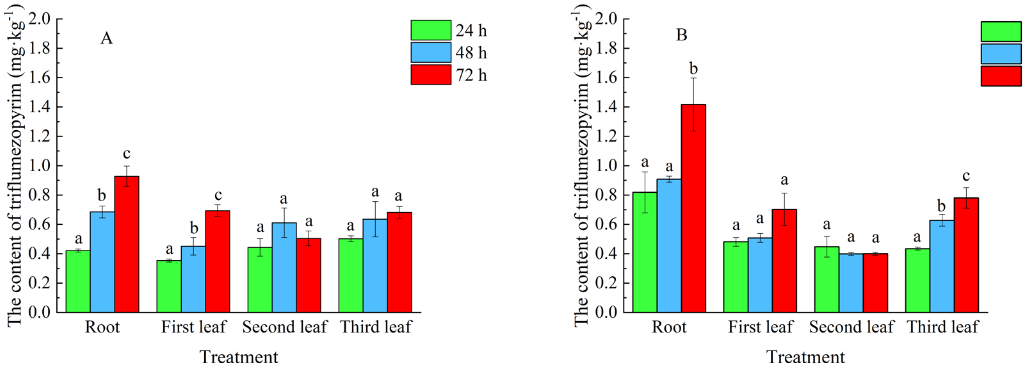

Figure 2. Contents of triflumezopyrim in different parts of rice treated with hydroponic treatment. A and B correspond to 2.5 and 5 mg·L−1, respectively. Values are means ± SE (n = 3). Means with the same letter are not significantly different (Fisher's test, p ≤ 0.05).

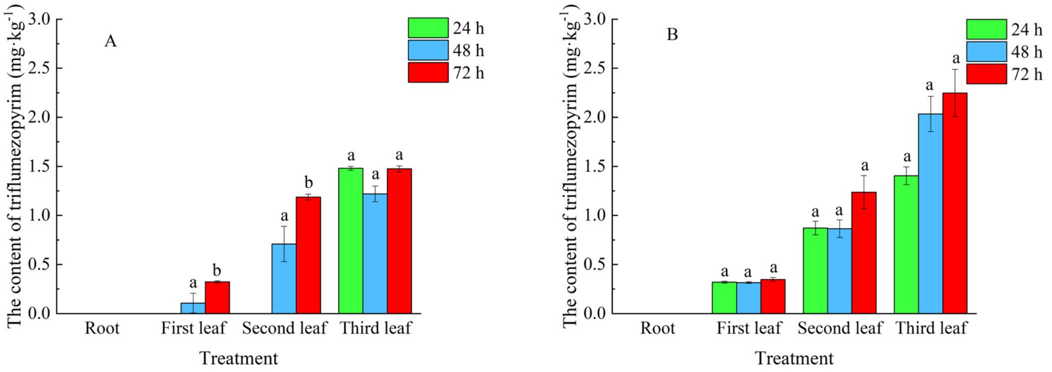

Figure 3. Contents of triflumezopyrim in different parts of rice treated with foliar treatment. A and B correspond to 2.5 and 5 mg·L−1, respectively. In both treatments, triflumezopyrim was not detected in the roots, and it was not detected in the first leaf of group A at 24 h. Values are means ± SE (n = 3). Means with the same letter are not significantly different (Fisher's test, $p \leq 0.05$).

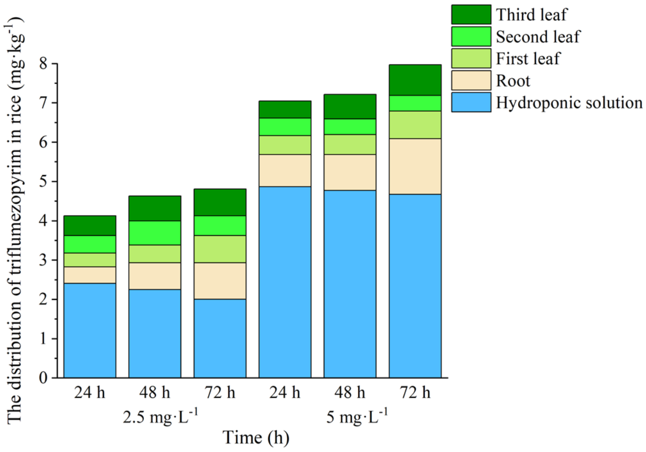

Figure 4. Distribution of triflumezopyrim in rice with hydroponic treatment.

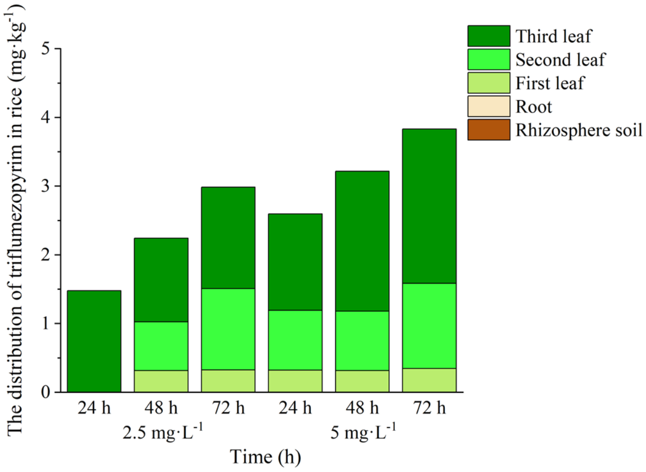

Figure 5. Distribution of triflumezopyrim in rice with foliar treatment. Triflumezopyrim was not detected in the root and rhizosphere soil.

translocation of compounds in the plants was related to the log K_{ow} value by measuring the concentration of triflumezopyrim in *n*-octanol and water in an equilibrium state. The triflumezopyrim (log K_{ow} = 1.24)[28] could transmit upward through xylem very well when the log K_{ow} < 1.8.[29] Thus, triflumezopyrim could be absorbed effectively and had better acropetal direction translocation ability in rice; however, it was not easy to transmit to the lower leaves through foliar treatment.

4. DISCUSSION

A method for the determination of triflumezopyrim in water, soil, and rice was established by liquid−liquid extraction and QuEChERS sample pretreatment. The complex composition of the soil and rice matrix not only interfered with the extraction efficiency of the target compound but also interfered with the determination of the target compound and had a serious impact on the column efficiency. Zhang et al.[20,30] proposed that in the pretreatment of the QuEChERS sample, acetonitrile, methanol, acetone, and ethyl acetate were used as extraction solvents. In contrast, acetonitrile was found to have high extraction efficiency and little interference under our experimental conditions.

C_{18} has a good adsorption for nonpolar components, so it can effectively remove nonpolar impurities in the sample.[31,32] Wang et al.[33] found out that PSA can effectively remove various organic acids, pigments, carbohydrates, and fatty acids in the sample by comparing the use of various adsorbents. Georgakopoulos et al.[34] and Herrmann and Poulsen[35] believe that C_{18} was suitable for the purification of some low-fat samples, including cereals and vegetables at a certain dosage. Therefore, referring to the purification method of Li,[36] we mixed adsorbents PSA and C_{18} at different additions to study the difference.

Uptake and translocation characteristics of pesticides in the plants are important factors affecting the application methods and activities. Systemic pesticides can be absorbed in plants by their stems, leaves, and roots, and then they can effectively prevent and control harmful organisms when the concentration of the pesticide reaches the effective dose in plants. In this study, the insecticidal activities of triflumezopyrim against *N. lugens* under two application methods were both very high at 0.5 mg·L^{-1} within 72 h. Thus, we supposed that triflumezopyrim could be transferred to various parts of the rice plant, forming accumulation against *N. lugens*. Therefore, we chose two application concentations of 2.5 and 5 mg·L^{-1} for systemic research within 72 h. Uptake and translocation characteristics of the pesticide in the plants can effectively improve the utilization rate of the pesticide as well as affect their toxicological behaviors, such as the accumulation site, pesticide lasting validity period, metabolic process, and degradation dynamics. Although there was no significant difference between the two concentrations in this research at

Table 5. Transfer Factors of Triflumezopyrim in Rice Treated with Hydroponic Treatment

	$TF_{first\ leaf}$		$TF_{second\ leaf}$		$TF_{third\ leaf}$	
treatment time (h)	2.5 mg L^{-1}	5 mg L^{-1}	2.5 mg L^{-1}	5 mg L^{-1}	2.5 mg L^{-1}	5 mg L^{-1}
24	0.840	0.588	1.05	0.574	1.19	0.531
48	0.658	0.560	0.892	0.439	0.928	0.692
72	0.748	0.496	0.544	0.283	0.735	0.551
$TF_{average}$	0.749	0.548	0.829	0.423	0.952	0.591

Table 6. Transfer Factors of Triflumezopyrim in Rice Treated with Foliar Treatment

	TF_{root}		$TF_{first\ leaf}$		$TF_{second\ leaf}$	
treatment time (h)	2.5 mg L^{-1}	5 mg L^{-1}	2.5 mg L^{-1}	5 mg L^{-1}	2.5 mg L^{-1}	5 mg L^{-1}
24	0	0	0	0.228	0	0.621
48	0	0	0.258	0.155	0.582	0.426
72	0	0	0.220	0.155	0.804	0.550
$TF_{average}$	0	0	0.159	0.179	0.462	0.532

low doses, we found that triflumezopyrim could be absorbed and translocated in rice plants, so from the view of pesticide utilization, such research was meaningful.

In hydroponic treatment, triflumezopyrim could be absorbed effectively by the rice roots and transported to the upper leaves of rice. In the Kleier model, the effect of log K_{ow} on the downward transport of exogenous compounds in the plants was considered, and the log K_{ow} is optimal for the phloem movement in a range of 1−3.[37] However, in the foliar treatment group, although triflumezopyrim was detected in the lower leaves, triflumezopyrim was not detected in root samples in the short term. Zebrowski et al. found that the systemicity of xenobiotics was related to the physical and chemical properties of the agent, the growth period of plants, or other conditions.[25] In addition, the concentrations of the two treatment groups were similar, and thus there was no significant difference between the two results. The systemicity of pesticides mainly depended on their physical and chemical properties.[38] The movement of active ingredients from the site of application to the biochemical target could be significantly influenced by the uptake of pesticides in the plants. Many approaches have been used to enhance the uptake of pesticides in the plants during both the discovery phase and the field use.[39,40] Therefore, our next work will improve their systemic conductivity through formulation processing. Triflumezopyrim was not easily transmitted to the lower leaves but mostly concentrated on the treated leaves. Rice planthoppers mainly damaged the leaf sheath part of the stem base; attention should be paid to spray sites to avoid waste. Triflumezopyrim was not detected in rhizosphere soil, indicating that triflumezopyrim was relatively safe for the environment. In this study, the uptake ability of triflumezopyrim in the rice plant and evaluation methods of pesticide translocation were discussed to provide scientific guidance for the application and preparation of pesticides as well as the foundation for pesticide safety evaluation.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jafc.9b07868.

Test method for judging the systemicity of triflumezopyrim by testing the insecticidal activity of different sites in rice plants (PDF)

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Notes

The authors declare no competing financial interest.

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