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Environmental Fate of SYP-1924 Residues in Rice Field

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Abstract SYP-1924 is a new kind of herbicide developed by Shenyang Sciencreat Chemicals. This study has been carried out to investigate the environmental fate of SYP-1924 in rice-field system. An analytical method utilizing high-performance liquid chromatography (HPLC) with ultraviolet (UV) detection was described for the determination of new kind of herbicide SYP-1924 in rice, rice straw, soil and water. The dissipation of SYP-1924 in soil, water and rice straw was determined using the proposed method. The results showed that dissipation of SYP-1924 in rice straw and water were found to be very faster with half-life time shorter than 1.5 days. The half-life value of SYP-1924 was observed to be 4.5 days in soil. The ultimate residues of SYP-1924 in rice were found to be below the limits of the detection at level of recommended and 1.5 times recommended dosage with an interval date of 70 days.

Keywords SYP-1924 · Herbicide · Environmental fate · Rice

SYP-1924 (Chinese name: Kui Cao Xi), Ethyl 2-(2-(4-(6-chloroquinoxalin-2-yloxy) phenoxy) propanoyloxy)-3-methylbut-3-enoate (Fig. 1), is a new kind of herbicide discovered by Shenyang Sciencreat Chemicals Co. Ltd (Zhang and Li 2007; Zhang and Han 2008) possessing potential activity against grass weeds in rice field. SYP-1924 has Kow log $P = 3.86$, and was easily dissolved in organic solvent such as acetone, methanol. The commercial formulation of SYP-1924 is 10% emulsion in water (EW), which could be used for the controlling gramineous weeds such as barnyard, grass crab grass and goose grass. The extensive use of herbicide has led to the pollution of the soil and water, and accumulation of herbicide in the plants (Jiries et al. 2002; Yu and Zhou 2005). It is important to make ensure that the residues of SYP-1924 on rice do not pose any hazard to human beings. Therefore, it is necessary to study the environmental fate of SYP-1924 in rice field system in order to understand dissipation rates of SYP-1924.

The purpose of this study was to develop a simple method for the determination of SYP-1924 in rice, and to study the environmental fate of SYP-1924 in rice field. Finally we want to provide an evaluation for the scientific and safety use of SYP-1924 in rice field thorough this study.

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Materials and Methods

SYP-1924 standard (purity >99%) was obtained from Shenyang Sciencreat Chemicals Co. Ltd. (Shenyang, China). Methanol and acetonitrile were HPLC grade. Dichloromethane, ethyl acetate, petroleum ether and anhydrous sodium sulfate were analytical grade (Beijing Chemical Reagent Company, Beijing, China). Purified water was produced from a MilliQ water purification system. (Millipore, Billerica, MA, USA). Florisil (60–100 mesh) was purchased from J&K chemical (Beijing, China). Florisil was heated at 650°C for 4 h prior to use. The other reagents were used as received.

Field experiments were carried out in Shangzhuang Farm which is located at Hiadian District, Beijing, China. The field experiments were performed in three plots each

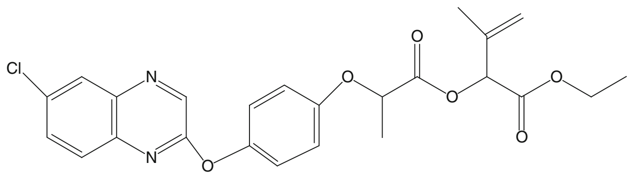

Fig. 1 Chemical structure of SYP-1924

with an area of 30 m^2. Each plot was separated by irrigation channels. To investigate the dissipation of SYP-1924 in rice straw, SYP-1924 10% EW was sprayed to the rice at doses 56.25 g a. i./ha. About 0, 0.5, 1, 3, 5, 7, 12, 21 and 30 days after application of SYP-1924, representative rice straw samples were collected randomly from the field plot. Meanwhile, 3 field plots without planting rice were used to study the dissipation of SYP-1924 in soil and water at the doses 562.5 g a. i./ha. During the experimental period, the water depths of the filed plot were kept in the range from 10 to 15 cm. Water and soil samples were taken after 0, 2, 4, 6, 8, 10, 24, 36 h and 1, 2, 3, 5, 7, 10, 14, 21, 30 days, respectively. In order to study the ultimate residues of SYP-1924 in rice and soil, field experiments were carried out to spray SYP-1924 at two levels, a lower level of 37.25 g a. i./ha (recommended dosage) and a higher level of 55.875 g a. i./ha (1.5 times of the recommended dosage), respectively. Representative rice and soil samples were collected from each treatment plots.

Rice straw, rice hull and rice: A 10 g aliquot of sample was placed in the homogenizer cup with the addition of 50 mL acetonitrile. The mixture was macerated at 18,000 rpm for 3 min in a high-speed disperser (ULTRA-TURRAX, T 25D model, IKA, Germany). For the soil samples, a 10 g aliquot of soil samples was placed in the conical flask with adding 50 mL acetonitrile. The samples were shaken for 1 h. The homogenate was transferred into a 100 mL centrifuge tube. The centrifuge tube was shaken by hand for 30 s after addition of 10 g NaCl and the extracts was centrifuged at 4,000 rpm for 3 min. A 20 mL aliquot of acetonitrile was evaporated to dryness on a vacuum rotary evaporator (Buchi R-114, Germany). The residue was dissolved in 5 mL petroleum ether for the following clean-up.

A glass column was packed with a plug of glass wool and about 2–3 cm layer of anhydrous sodium sulfate at the bottom. Then 5 g Florisil sorbent was added to the column, then another 2–3 cm layer of anhydrous sodium sulfate was added to the above sorbent. The column was conditioned with 20 mL petroleum ether. Then 5 mL petroleum ether of the reconstituted residue was preloaded to the column, followed by 25 mL petroleum ether. The petroleum ether friction was discarded, and 20 mL petroleum ether/ethyl acetate (80:20, v/v) was added to the column for the elution of SYP-1924. The solution was evaporated to dryness in a water bath at 50°C, the residue was dissolved in 1 mL methanol for the HPLC analysis.

A 100 mL aliquot of water sample was transferred to a 250-mL separatory funnel, with the addition of a 25 mL aliquot of petroleum ether. After shaking for 30 s, the aqueous and organic layers were allowed to separate for 5 min. The petroleum ether layer was collected in a 100-mL boiling flask. The liquid–liquid extraction procedure was repeated twice with two additional 25 mL aliquots petroleum ether, combing the three extracts in the same flask. The solution was evaporated to dryness with the vacuum rotary evaporator and dissolved in 1 mL methanol for the further instrument analysis.

A Shimadzu model LC-10ATvp HPLC with a Shimadzu SPD-10ATvp UV–VIS detector was used in the chromatographic analysis (Tokyo Japan). A Inertsil ODS C18 column (250 × 4.6 mm) was used as the separation column with the mobile phase consisting of methanol and water (90:10, v/v). The flow rate was 1 mL/min, and the injection volume was 20 μL.

The dissipation dynamics of the herbicide in the rice filed were determined by plotting residue concentration against different interval time (days or hours) after application. Since the first-order model has been used to interpret pesticide degradation process, we want to use this model for the study of SYP-1924 in the environment. The dissipation rate equation was calculated from the following first order rate $C_t = C_0 e^{-kt}$ where C_t represents the concentration of the pesticide residue at time t, C_0 represents the initial deposits and k is the rate constant in days^{-1} or hours^{-1}. The half-life time was calculated from the following equation $t_{0.5} = \ln 2/k$.

Results and Discussion

The recovery test was carried out to evaluate the proposed analytical method for the study on the environmental behavior of SYP-1924 in rice field. SYP-1924 was fortified to the untreatment rice straw, rice, soil and water samples at concentration levels 0.05, 0.20, 1.00 mg/kg (water samples fortified at 0.002, 0.010, 0.050 mg/kg) and each sample was analyzed as described procedure in sample pretreatment with three replicate. The results were shown in Table 1. The average recoveries determined for SYP-1924 in all the concentration levels were found to be >75%. The precision of the method expressed as relative standard deviations (RSD) ranged from 1.4 to 9.0%. The limit of detection (LOD) calculated as a sample concentration ($S/N = 3$) for rice straw, rice hull, rice was 0.02 mg/kg. The LOD for soil and water was 0.01 mg/kg and 0.001 mg/kg, respectively. The recovery and precision

Table 1 Recovery data of SYP-1924 in different samples

Sample type	Added (mg/kg)	Recovery (%)			Average recovery (%)	Precision (RSD) (%)
		1	2	3		
Water	0.002	95.1	94.7	92.5	94.1 ± 1.4	1.4
	0.01	97.8	92.4	93.4	96.5 ± 2.9	3
	0.05	93.4	91.7	98.9	94.7 ± 3.8	4
Soil	0.05	82.6	83.7	76.4	80.9 ± 3.9	4.9
	0.2	81.5	78.9	91.5	84.0 ± 6.7	7.9
	1	89.8	81.4	92.8	88.0 ± 5.9	6.7
Rice straw	0.05	74.5	81.4	78.9	78.3 ± 3.5	4.5
	0.2	84.6	75.6	73.4	77.9 ± 5.9	7.6
	1	89.7	82.6	77.5	83.2 ± 6.1	7.4
Rice hull	0.05	91.1	91.1	78.4	84.7 ± 7.3	8.4
	0.2	86.9	81	93.4	87.1 ± 6.2	7.1
	1	98.8	91.4	87.6	92.6 ± 5.7	6.2
Rice	0.05	71.9	85.4	78.6	78.6 ± 6.8	8.6
	0.2	72.9	75.5	79.3	79.4 ± 3.2	4.2
	1	76.1	84.3	80.6	80.3 ± 4.1	5.1

results were acceptable according to Residues Analysis Quality Control Guide.

The dissipation data of SYP-1924 in rice straw was shown in Fig. 2. As shown in Fig. 2, SYP-1924 residue rapidly degraded in rice straw after treatment. The initial deposits of SYP-1924 in straw in 2007 and 2008 were 1.1 and 1.7 mg/kg, respectively. The amount of SYP-1924 residue was below the LOD of the analytical method after 7 days, and the dissipation dynamics of SYP-1924 can be interpreted by the following first-order model $C = 0.5809e^{-0.49t}$ and $C = 1.1807e^{-0.4117t}$, respectively. The half-life time of SYP-1924 in rice straw was 1.41 and 1.14 days, respectively.

In order to study the dissipation of SYP-1924 in water and paddy soil, another experiment was performed in a blank soil with 10 times of recommended doses. The results were shown in Figs. 3 and 4. The initial concentration of SYP-1924 in water was 0.98 and 1.1 mg/kg, respectively, and it

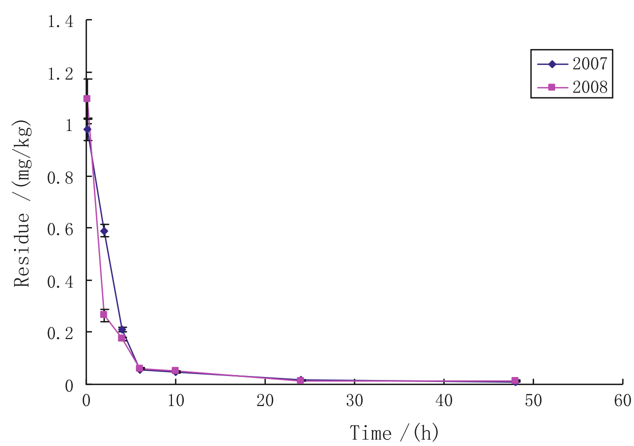

Fig. 3 Dissipation of SYP-1924 in water

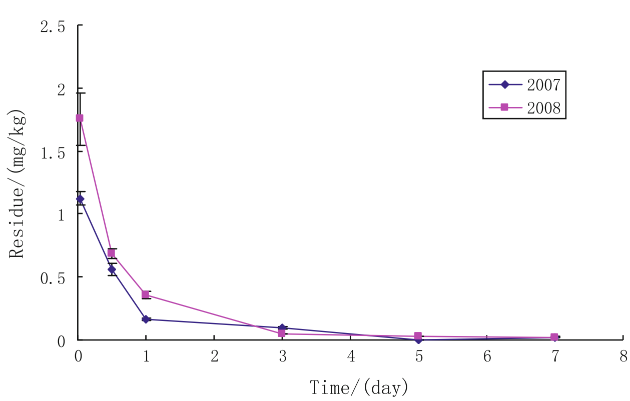

Fig. 2 Dissipation of SYP-1924 in rice straw

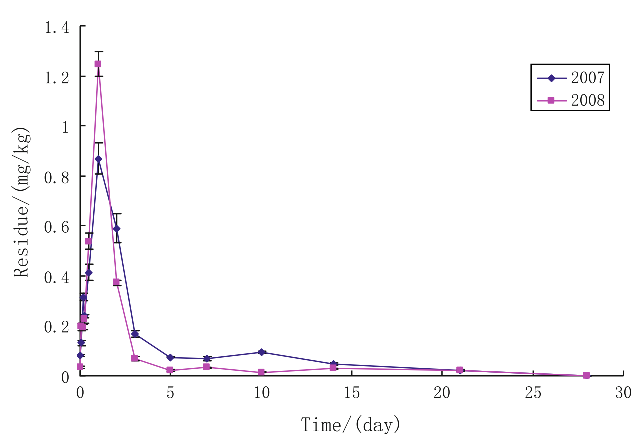

Fig. 4 Dissipation of SYP-1924 in soil

Table 2 Ultimate residues of SYP-1924 in rice, rice hull and soil

Year	Doses	PHI (days)	Concentration (mg/kg)		
			Rice	Rice hull	Soil
2007	37.5 g a. i./ha.	70	ND	ND	ND
	56.25 g a. i./ha.	70	ND	ND	ND
	Ck		ND	ND	ND
2008	37.5 g a. i./ha.	70	ND	ND	ND
	56.25 g a. i./ha.	70	0.0273 ± 0.0028	0.0475 ± 0.0036	0.0320 ± 0.003
	Ck		ND	ND	ND

degraded more than 98% after 14 h. The dissipation dynamics of SYP-1924 could also be described by the equation ($C = 0.3023e^{-0.0881t}$ $C = 0.2373e^{-0.074t}$) with a half-life time 7.9 and 9.4 h, respectively. The short half-life time of SYP-1924 in water may be attributed to the fact that SYP-1924 was easily adsorbed by soil because its Kow log P is 3.86. The dissipation dynamic of SYP-1924 in soil appeared to follow a pseudo-first-order kinetic process. The initial concentration of SYP-1924 in soil was 0.0511 and 0.0344 mg/kg, respectively. Then a sharp increase of SYP-1924 residues in soil was occurred within the first day. The maximum concentration of SYP-1924 in soil was 0.87 and 1.24 mg/kg after 24 h which means this compound could be rapidly transferred form water to soil. The SYP-1924 residue in soil became undetectable after 28 d treatment. The half-lives of SYP-1924 in soil were 4.51 and 4.48 days in 2007 and 2008, respectively. Compared with half-life in rice straw, degradation of SYP-1924 was faster in rice straw than in soil.

The ultimate residue data of SYP-1924 in soil and rice in 2007 and 2008 was listed in Table 2. As shown in Table 2, the residue concentrations in most of the samples were found to be undetectable at level of recommended and 1.5-fold recommended levels after 70 days herbicide application. There were no available maximum residue limits established by WHO/FAO or other governmental agencies for the SYP-1924 in crops. Because of its lower toxicity to non-target species and very short half-life time, SYP-1924 could be considered as safety to human being and environment after its application in the rice field.

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