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Dissipation and Residues of Flutriafol in Wheat and Soil Under Field Conditions

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Abstract A simple, sensitive method for the analysis of flutriafol in wheat and soil was developed using high performance liquid chromatography tandem mass spectrometry (HPLC–MS/MS). The dissipation dynamics and ultimate residue of flutriafol in wheat and soil were detected using the established method. The half-lives of flutriafol in wheat plant were 4.09 days (Hebei) and 1.54 days (Hubei), while in soil were 6.25 days (Hebei) and 3.16 days (Hubei), respectively. The final residues of flutriafol were below 0.5 mg/kg (MRL of EU) in wheat grain 28 days after the treatment.

Keywords Flutriafol · Wheat · Soil · Dissipation · Residues

Flutriafol [(RS)-2,4′-difluoro-α-(1H-1,2,4-triazol-1-ylmethyl) benzhydryl alcohol] is a triazole fungicide, which has a broad fungicide activeness and is a strong systemic pesticide. It is widely used to prevent and cure the straw, panicle disease and soil-spread diseases of cereal crops (mainly contains wheat, barley, rye, corn), such as powdery mildew, rust, smut, leaf spot, etc. Flutriafol is low toxic to fish under the permitted dose. Although it is a low-level toxic pesticide, flutriafol could carry some risk to the environment and living creatures.

To ensure the food safety for consumers and to regulate international trade and legislation, some countries have established maximum residue limits (MRLs) for flutriafol in some commodities. EU has established the MRL of flutriafol in cereals (including wheat) as 0.5 mg/kg. In Japan and Italy, the MRLs in wheat were set at 0.02 and 0.1 mg/kg, respectively. In China, the MRL in wheat was suggested to be 0.5 mg/kg.

Although the residue analysis of flutriafol have been reported in some materials, the literatures were mostly about the multi-residue determination of flutriafol, such as in natural water (Antonia et al. 2008), wine (Jiang et al. 2009), infant foods and weaning foods (Sharma et al. 2005). A HPLC–MS/MS method was carried out for determination of seven triazole fungicide including flutriafol residues in vegetables (Huang et al. 2011).

Yu et al. (2010) developed a method to determine residue of flutriafol in wheat and soil by GC, but the pre-treatment was complicated. The samples were extracted with acetonitrile, cleaned-up through Florisil SPE small column, and the analysis was then performed on GC-FTD detection. Until now, no literature was reported on the dissipation and ultimate residue of flutriafol in wheat ecosystem.

In this study, a simple and rapid method for residue analysis of flutriafol in wheat and soil by HPLC–MS/MS was developed. Using this method, we investigated the dissipation dynamics and ultimate residue of flutriafol in wheat and soil under the field conditions, and thereby provided an evaluation for scientific and safely use of flutriafol on wheat crops.

Materials and Methods

The flutriafol (250 g/L SC) was obtained from Jiangsu Agrochem Laboratory (Jiangsu, China). High-performance liquid chromatography (HPLC)-grade methanol and acetonitrile was supplied by Fisher Scientific (US). Ultrapure

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water was obtained from Aquapro Ultrapure Water System (Chongqing, China). Analytical-grade sodium chloride was purchased from Beijing Reagent Company (Beijing, China).

All analyses were conducted with an Agilent 6410 B Triple Quad HPLC–MS/MS. The spectral acquisition was done in the positive electron spray ionization, and multiple reactions monitoring (MRM) was utilized for flutriafol. There were two parent-daughter ion pairs: m/z 302.1/123.1, 302.1/70.1. The collision energy was 22 and 15 eV, respectively. Nitrogen was used as the dry air. The gas temperature was 350°C and the gas flow rate was 8.0 L min^{-1}. The nebulizer was 35.0 psi, the fragmentors were 220 V. A reverse-phase Zorbax C_{18} column (50 mm × 2.1 mm × 3.5 μm particle size) was used and maintained at 30°C. The mobile phase consisted of acetonitrile/acid water (0.1 % formic acid) (70/30 by volume), with a flow rate of 0.3 mL min^{-1}. The injection volume was 5 μL. The retention time (R_t) of flutriafol was 0.74 min.

In this study, field trials including the dissipation experiments and the final residue experiments were carried out at two provinces: Hebei (in the north of China) and Hubei (in the south of China), in 2011. Each treatment consisted of three replicate plots with an area of 30 m^2 for each plot, and the plots were separated by irrigation channels.

To investigate the dissipation of flutriafol in soil and wheat plant, flutriafol 250 g/L SC was sprayed on the wheat field when the wheat turned green. In order to reach the detection limits of the residue analysis method, the applied dose was set as 90 g a.i.ha^{-1}, which was three times of the recommended dosage level. Representative wheat plant and soil samples were randomly collected at 2 h, 1, 3, 5, 7, 14, 21, 30, 45 and 60 days after spraying. The collected wheat plant samples were comminuted with a grinder (IKA, German). All collected samples were stored in a freezer at −20°C for further analysis.

The ultimate residue experiment was performed at a low dosage level of 30 g a.i. ha^{-1} (the recommended dosage), as well as at a high dosage level of 45 g a.i.ha^{-1} (1.5 times of the recommended dosage), respectively. When the wheat turned green, the high and low dosage treatments both were sprayed once and twice. The treatment interval was 7 days. During the harvest time the sample of wheat grain, straw and soil were randomly collected on the interval of 28, 35, 45 days after the last spraying for residue studies.

Homogeneous samples (2 g soil, 2 g wheat straw, 2 g wheat grain) were separately put into 50 mL centrifuge tube and 10 mL methanol (20 mL for the wheat straw) was added. The centrifuge tube was placed on a mechanical shaker and shaken for 30 min. Then the mixture was centrifuged at 3,800 rpm for 5 min. After the extracts were centrifuged, the supernatant (1 mL) was filtered with a 0.22 μm poly-propylene filter to an auto sampler vial for the HPLC–MS/MS analysis.

Homogeneous sample of the wheat plant (2 g) was put into a 50 mL centrifuge tube. Acetonitrile (20 mL) and water (10 mL) was added. The centrifuge tube was placed on a mechanical shaker and shaken for 30 min. After that, sodium chloride (5 g) was added and then vortexed for 1 min on a vortexer (QL-901, Haimen Qilinbeier Instrument Co., Ltd., Jiangsu Province, China). The following steps (centrifuge and analysis) were the same as the steps described above for the soil.

Results and Discussion

There was a positive linear relationship ($y = 1008577\ x - 2{,}994.6$, $R^2 = 0.9977$) between the peak area (y) of flutriafol and its concentration (x) in the range 0.001–1.00 mg/L. The fortified study was carried out at levels of 0.05, 0.10 and 0.50 mg/kg to determine the recovery levels and precision of the analytical method. The results were listed in Table 1. The average recoveries of flutriafol were 70.60 %–103.41 % with the relative standard deviation of 1.3 %–11.3 %. At a signal-to-noise ratio of 3, the limit of detection of the method was 0.001 mg/kg for soil, 0.01 mg/kg for wheat plant and wheat straw, 0.005 mg/kg for wheat grain, respectively. Similarly, the limit of quantification was 0.005 mg/kg for soil, 0.05 mg/kg for wheat plant and wheat straw, 0.025 mg/kg for wheat grain at a signal-to-noise ratio of 10. The recovery and precision results were acceptable according to the residues analysis quality control guide.

Table 1 Fortified recoveries of flutirafol in wheat and soil samples

Samples	Added (mg/kg)	Average recovery (%)	SD (%)	RSD (%)
Soil	0.5	95.93	7.82	7.85
	0.1	103.87	5.47	5.41
	0.05	77.92	2.60	2.49
Wheat grain	0.5	89.75	6.51	6.40
	0.1	76.95	6.48	6.52
	0.05	100.71	2.10	2.75
Wheat plant	0.5	82.45	3.02	2.76
	0.1	80.87	4.08	3.84
	0.05	76.45	1.36	1.35
Wheat straw	0.5	94.02	8.22	8.56
	0.1	73.59	2.09	2.81
	0.05	82.23	5.14	5.95

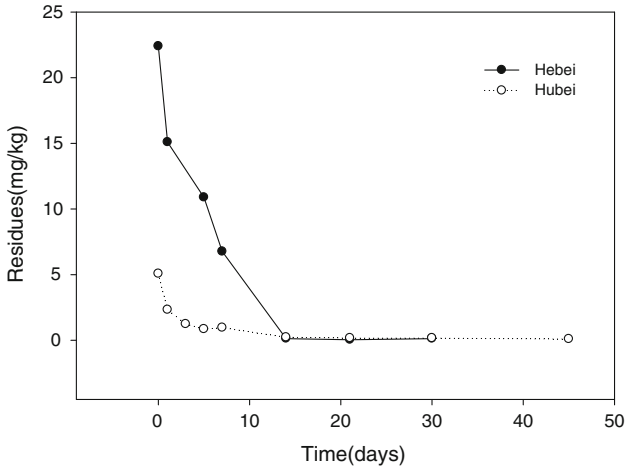

Fig. 1 Dissipation of flutriafol in wheat plant

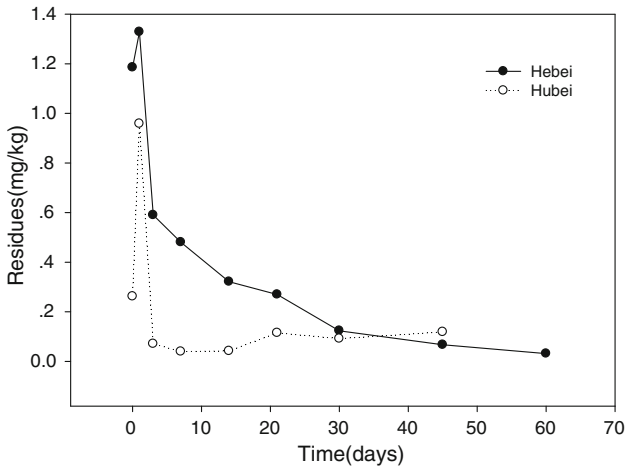

Fig. 2 Dissipation of flutriafol in soil

The dissipation results of flutriafol in wheat plant were shown in Fig. 1. The initial residues in wheat plant were 4.72 and 20.95 mg/kg at the two locations. The dissipation dynamics of flutriafol could be described by the following first-order rate equation: $C = 20.9466e^{-0.1696x}$ (Hebei), $C = 4.7157e^{-0.4507x}$ (Hubei), respectively. The obvious deference between the initial residues may result from multiple reasons, such as planting density, growing conditions and weather condition (temperature, rainfall, wind speed etc.). The half-lives calculated from regression equation were found to be 4.09 days (Hebei) and 1.54 days (Hubei).

Figure 2 showed the dissipation data of flutriafol in the soil samples. The initial residues of flutriafol in soil were 0.55 and 1.21 mg/kg. The dynamics (initial from the highest point) could be described by the equation: $C = 1.2076e^{-0.1109x}$ (Hebei), $C = 0.5505e^{-0.2192x}$ (Hubei), respectively. The results showed that the dissipation speed of flutriafol in soil was a little slower than in wheat plant. More than 78 % of the initial residue dissipated after 45 days. Although at 1–2 days there was a raise and down proceed of the residue in soil, the dissipation rate of flutriafol in soil was rapidly. The half-lives of flutriafol in soil at the two locations were 6.25 days (Hebei) and 3.16 days (Hubei), respectively.

The ultimate residue data were shown in Table 2. According to the results, the residues of flutriafol in wheat grain and soil were all below 0.5 mg/kg in 28, 35 and 45 days after the treatment. Residues in wheat straw were a little higher than in wheat gain. The ultimate residue of flutriafol in wheat grain and straw in Hubei were a bit higher than in Hebei, which may due to the different climate.

From the results of final residue experiments in fields of Hebei and Hubei province in 2011, the residues of flutriafol in wheat grain were below 0.5 mg/kg 28 days after the treatment. Compared with the MRL from EU (0.5 mg/kg) and China (suggested to be 0.5 mg/kg), flutriafol (250 g/L SC) can be considered safe to be used on wheat as a good alternative to high-toxicity pesticides, and the pre-harvest interval (PHI) was suggested to be set as 28 days.

A simple, quick and reliable residue analytical method using HPLC–MS/MS for the detection and monitoring of flutriafol in wheat and soil were developed in this study. Prior to this paper, Yu et al. (2010) used acetonitrile as the solvent to extract flutriafol in wheat and soil. Both methanol and acetonitrile are frequently-used extractant. However, flutriafol has a high solubility of 69 g/L in methanol while no data in acetonitrile. Therefore, we tried to use methanol to extract flutriafol in wheat grain, straw, plant and soil. The results showed that the fortified recoveries in wheat grain, straw and soil were satisfied for the residue analysis of flutriafol. But for wheat plant, the fortified recovery was 64.3 %, which didn't meet the analytical requirements. Two methods were tried to improve this phenomenon: (a) methanol was changed to acetonitrile; (b) acetonitrile (20 mL) and water (10 mL) were used as the extractant and then sodium chloride was added. Eventually method b was confirmed to be the more suitable one. By this means, not only the flutriafol could be extracted well but also made some contribution to the purification of wheat plant samples.

In conclusion, the dissipation and final residue of flutriafol in wheat ecosystem were investigated using the established method. The results suggested that according to the MRL of EU and China, it was safe for wheat and soil environment when sprayed twice with flutriafol (250 g/L SC) at the recommended dosage, and the pre-harvest interval (PHI) should be 28 days between the last application of the formulation and the harvest of wheat. The

Table 2 Ultimate residue of flutriafol in soil, wheat grain and straw

Interval (days)	Dosage	Spray times	Residue (mg/kg)					
			Wheat grain		Wheat straw		Soil	
			Hebei	Hubei	Hebei	Hubei	Hebei	Hubei
28	Low dosage	1	ND	0.2138	0.3235	0.2998	0.099	0.0647
		2	ND	0.2972	1.0015	4.2544	0.2706	0.0267
	High dosage	1	ND	0.3243	0.668	0.4936	0.0415	0.3117
		2	0.0291	0.2986	0.7953	3.0591	0.2168	0.0263
35	Low dosage	1	ND	0.0257	0.6539	0.3406	0.0242	ND
		2	ND	0.3111	ND	3.2196	0.0815	0.0315
	High dosage	1	0.1932	0.2884	0.1536	1.0953	0.0498	0.2432
		2	ND	0.0226	0.798	5.2859	0.2494	0.0255
45	Low dosage	1	ND	0.0148	ND	0.4626	0.0906	0.2864
		2	ND	0.0235	ND	3.6587	0.0621	0.1281
	High dosage	1	ND	0.0219	0.0168	0.4942	0.0807	0.2774
		2	ND	0.0156	ND	2.3634	0.1068	0.0254

ND means not detected, below the LOD of the method

final residues and dissipation rates of flutriafol were studied to provide a quantitative evaluation for the safe use of flutriafol in wheat.

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