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Dissipation and Residue Determination of Fluoroglycofen-Ethyl in Soybean and Soil by UPLC-MS–MS

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Abstract A rapid, highly selective, and sensitive method was developed for detecting fluoroglycofen-ethyl in soybean seed, plant, and soil using UPLC-MS–MS. The detection limits of fluoroglycofen-ethyl in soybean seed, plant, and soil were 0.5, 1, and 1 μg kg^{-1}, respectively. Recoveries ranged from 83.4 % to 99.2 %, in which intra-day RSDs were from 1.3 % to 6.7 % and inter-day RSDs were from 1.9 % to 7.0%. In the dissipation study, the half-lives of fluoroglycofen-ethyl were 34.8 (Shanxi) and 48.5 h (Heilongjiang) in soil and 43.3 h in soybean plant in both locations. The residues of fluoroglycofen-ethyl in all samples were below LODs 30 days before and during harvest.

Keywords Fluoroglycofen-ethyl · Dissipation · Soybean · Soil

In China, fluoroglycofen-ethyl is used to control weeds in soybean fields. However, fluoroglycofen-ethyl is a hazard to human health according to a rat chronic toxicity and oncogenicity study (Anonymous 1992), and could contaminate the environment seriously (Key et al. 1997). Soybean seeds are used for cooking and oil production, whereas soybean plants are used as fodder to raise animals (Kale et al. 2009). Therefore, determining the fluoroglycofen-ethyl residues in crops and soil is important to ensure safety of food, fodder in animal farming, environment, and rotated crops after harvest.

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To date, only a few studies have conducted residue analysis in grains, and soil samples (Chen et al. 2007; Pang et al. 2006; Wang et al. 2007; Wu et al. 2006). In previous studies, HPLC–UV, GC-ECD, and GC–MS have been employed. To the best of our knowledge, this is the first study on residue determination of fluoroglycofen-ethyl in soybean and soil by ultra-performance liquid chromatography-tandem mass (UPLC-MS–MS). The aims of the present study were as follows: first, to develop a UPLC-ESI–MS–MS approach for the analysis of fluoroglycofen-ethyl in soybean seed, plant, and soil with shorter analyzing time, high sensitivity, selectivity, and precision; second, to apply the explored method in field testing samples to provide scientific evidence for both environmental monitoring and fate investigation of the target compound.

Materials and Methods

Fluoroglycofen-ethyl standard (purity = 97.5 %) and its commercial formulation (10 % emulsifiable concentrates) were obtained from Qingdao Hansen Biologic Science Co., Ltd. (Shandong, China). LC-grade methanol was purchased from Fisher (Thermo Fisher Scientific Inc., USA). Analytical-grade acetone, acetonitrile, n-hexane, ethyl acetate, petroleum ether, ammonia, and sodium chloride were obtained from Beijing Chemical Co. (Beijing, China). Purified water was purchased from Wahaha Co. (Hangzhou, China). The absorbents were graphitized carbon black (GCB, 100–200 mesh, Jilin Chemical Industry Co., China) and C18 (100 mesh, Agela Co., China). The GCB (500 mg) with 6 ml-capacity cartridges and the mixture absorbent SPE (300 mg GCB and 500 mg C18) were made in our laboratory.

Chromatographic analysis of fluoroglycofen-ethyl was conducted on Waters ACQUITY UPLC system (Milford, MA, USA). Chromatographic separation was performed using a Fortis C18 1.7 μm analytical column (50 × 2.1 mm, Fortis Technologies, Ltd., Great Britain). Gradient UPLC elution was performed with 0.003 % aqueous ammonia/methanol solution (A) and 0.003 % aqueous ammonia in pure water solution (v/v, B). The target compound was separated with an elution gradient at a flow rate of 0.2 mL min^{-1}, starting with a 1 min focusing step. Meanwhile, the composition of the gradient elute was held at 85 % mobile phase A. The separation step was carried out by increasing the proportion of eluant A from 85 % to 90 % in 2 min. The column was then re-equilibrated by 85 % eluant A for 2 min. Separation and stabilization were achieved in 5 min. The column was kept at 40°C and the injection volume was 2 μL. A linear ion trap mass spectrometer LTQ XL (Thermo-Fisher, USA) equipped with an electrospray ionization source was used to detect fluoroglycofen-ethyl. The nebulizer gas was 99.999 % nitrogen and the collision gas was 99.999 % helium. Tandem MS detection was conducted in positive ion mode. The ion monitoring conditions were as follows: spray voltage, 4.0 kV; sheath gas flow rate, 30 arb; aux gas flow rate, 10 arb; capillary voltage 45 V with 350°C. Selected reaction monitoring (SRM) was used, and the precursor ion was m/z 464 $[M\text{-}H + NH_4]^+$. Under collision energy 20, its product ions m/z344 and m/z 346 were used to monitor fluoroglycofen-ethyl and the most intense ion (m/z344) was used for quantification. The scan time was 30 ms. Under these conditions, the retention time of fluoroglycofen-ethyl was about 1.70 min.

The experimental fields were located in Shanxi and Heilongjiang provinces. In each location, the trial field was divided into 30 m^2 blocks for the control. The dissipation dynamics experiment was conducted from May 2008 to October 2008. The soybean plant (experiment plots) and bald soil (experiment plots) were both sprayed with a 10 % (w/w) emulsifiable concentrates of fluoroglycofen-ethyl at a dosage of 85.22 g active ingredient/hectare (1.5 times the manufacturer's commended dosage). Both soil samples and soybean plant samples were collected at 0 h, 4 h, 8 h, 24 h, 36 h, 2 d, 3 d, 5 d, 7 d, and 10 d after spraying. To investigate the risk of fluoroglycofen-ethyl to food, forage plant, and rotated crops for the succeeding year, the samples of soybean seed, plant, and soil were collected 30 days before and during harvest. Soil samples were collected from 0 to 15 cm depth of topsoil. Blank samples were collected from the control plot without spraying pesticide. All samples were kept at −20°C in a refrigerator until analysis. All the calculations for the analyses of the field samples were based on dry weight.

Soybean Seed

A 3 g sample was extracted using 15 mL acetonitrile by Vortex shaker for 1 min and by ultrasonic extraction for 15 min in sequence. The extract was centrifuged at 4,000 r min^{-1} for 10 min. The supernatant was transferred into a round flask and the residue was re-extracted by 15 mL acetonitrile. Then, the supernatant was combined in the above flask, concentrated to nearly 1 mL by the rotary evaporator at 40°C, followed by drying with nitrogen gas flux and dissolution with 6 mL acetonitrile. The supernatant was then centrifuged at 4,000 r min^{-1} for 10 min. Up to 4 mL extract solution was loaded on the mixture SPE cartridge, which was preconditioned with 4 mL acetonitrile before use. Fluoroglycofen-ethyl was eluted with 15 mL acetonitrile, concentrated by the rotary evaporator at 40°C, dried with nitrogen gas flux, and then dissolved in 2 mL methanol. Finally, the sample was filtered by a 0.2 μm PVDF syringe filter, followed by chromatographic injection. The soybean plant and soil samples were also treated with 0.2 μm PVDF syringe filter before injection.

Soybean Plant

A 5 g sample was extracted using 30 mL acetonitrile by Vortex shaker for 1 min and ultrasonic extracted for 10 min at room temperature. Approximately 4 g sodium chloride was added into the extraction, followed by another round of Vortex shaking for 1 min. Centrifugation followed, which lasted for 4,000 r min^{-1} for 10 min. The supernatant was then transferred into a graduated cylinder. The residue was re-extracted by 20 mL acetonitrile, and the extraction was centrifuged and collected in the same graduated cylinder. The volume was adjusted to 50 mL with acetonitrile, and 25 mL was concentrated to nearly 1 mL by the rotary evaporator at 40°C. Drying with nitrogen gas flux, dissolution with 3 mL n-hexane, and loading on a GCB cartridge (500 mg, 6 mL) preconditioned with 3 mL acetone and 3 mL n-hexane before use followed. Fluoroglycofen-ethyl was eluted with 9 mL acetone/n-hexane (1/2, v/v) and concentrated by the rotary evaporator at 40°C, dried with nitrogen gas flux, and then dissolved in 5 mL methanol.

Soil

Up to 10 g soil was extracted using 40 mL acetone/ethyl acetate (1/2, v/v) following Lingyun Wu et al. (2006). Up to 20 mL extraction solution was concentrated to nearly 1 mL and loaded on SPE of GCB cartridge, which was preconditioned with 6 mL petroleum ether/ethyl acetate (3/2, v/v) before use. Fluoroglycofen-ethyl was eluted with 8 mL petroleum ether/ethyl acetate (3/2, v/v) and

concentrated to nearly 5 mL by the rotary evaporator at 40°C, followed by drying with nitrogen gas flux and dissolution with 5 mL methanol.

Results and Discussion

UPLC was performed using Fortis C18 (50 × 2.1 mm) column and optimized to reach minimal run time. UPLC-MS–MS chromatograms of the blank and fortified samples ensured there were no interference peaks in the region of target compound detection. Under 0.2 mL min^{-1} UPLC elution of 85 % A, the retention time of the fluoroglycofen-ethyl was slowed to 1.70 min, which allowed elution of the more polar substance before fluoroglycofen-ethyl in the extract solution to remove interference of ionization for mass spectra analysis. The peak width at the base was 0.20 min for fluoroglycofen-ethyl and scan time was set at 30 ms to ensure enough data points for fluoroglycofen-ethyl chromatographic peak. The total analysis time of fluoroglycofen-ethyl was 5 min, which is a great advantage of the present method compared with at least 18 min in the published HPLC–UV, MS–MS, or other methods (Chen et al. 2007; Pang et al. 2006; Wang et al. 2007; Wu et al. 2006).

The analysis of fluoroglycofen-ethyl was performed via SRM mode. ESI positive mode was chosen for the present study because of the higher response signals. The spray voltage, capillary voltage, and capillary temperature were optimized. The most intense ion $[M\text{-}H + NH_4]^+$ (m/z464) was used as precursor ion. Its ester was broken to form the fragments, which were a couple of isotopic ions including chlorine atom at m/z 344 and m/z346 with an intensity ratio of 3:1, which was used to identify fluoroglycofen-ethyl. Among them, the most intensive ion m/z344 was quantitative ion. For all samples, UPLC-MS–MS method provided high ability on selectivity and separation of the target compound and restricted ion fragment under SRM mode.

Oil, pigments, and many other components in soybean seed and plant interfere with fluoroglycofen-ethyl residue analysis. Compared with other organic solvents, acetonitrile can extract fluoroglycofen-ethyl from soybean seed and plant matrix, while avoiding oil extraction and other non-polar interference. GCB and C_{18} absorbents in SPE column could remove pigments and other interference from seed and soybean plant effectively. GCB could also be used in soil.

This matrix effect may affect the reproducibility and accuracy of the method positively or negatively by influencing the signal response (Di Muccio et al. 2006). Thus, investigating the matrix effect in the three matrices (soybean seed, plant, and soil) by comparing matrix-matched standard with pure solvent standard is necessary. The signal suppression enhancements (SSEs) for fluoroglycofen-ethyl in soybean seed, soybean plant, and soil were measured to estimate matrix effects (Li et al. 2011). The SSE was defined through the following equation:

$$\text{SSE}\ (\%) = \frac{\text{Slope of matrix} - \text{matched calibration curve}}{\text{Slope of standard calibration curve}} \quad (1)$$

Table 1 Calibration curves in the solvent and in the three matrices

Matrix	Range of concentration level, (μg L^{-1})	Regression equation	R^2	SSE (%)
Methanol	0.5–500	y = 0.000315 x + 3.134329	0.9996	
Soybean seed	0.5–500	y = 0.000350 x − 4.180684	0.9947	111.11
Soybean plant	0.5–500	y = 0.000390 x + 3.449311	0.9987	123.81
Soil	0.5–500	y = 0.000523 x − 0.066240	0.9999	166.03

Up to 27 samples were analyzed in 3 different matrices and solvent standards to evaluate the approach specificity from chromatograms based on the high-linearity calibration curves ($R^2 > 0.9947$) for standard solution and matrix-matched standard (Table 1). The result indicated that significant suppression was observed for fluoroglycofen-ethyl in soybean seed, soybean plant, and soil, whereas the matrix effect was very remarkable based on the two tailed t test ($P < 0.01$). In the present research, matrix-matched standards were performed to reduce the matrix effect in all three matrices.

Recoveries and RSDs of fluoroglycofen-ethyl were investigated in spiked samples at 2 levels (1 and 10 μg kg^{-1} for soybean seed, 5 and 100 μg kg^{-1} for soybean plant and soil, respectively) in 5 replicates on three different days (Table 2). The recoveries were calculated based on the matrix-matched calibration curves. The average recoveries were at acceptable ranges of 83.4 %–91.2 %, 84.1 %–87.8 %, 86.7 %–99.2 % for soybean seed, soybean plant, and soil, respectively. The intra-day RSDs (n = 5) and inter-day RSDs (n = 15) of the developed method ranged from 1.3 % to 6.7 % and from 1.9 % to 7.0 %, respectively. One-way ANOVA at 95 % confidence limits was used for further statistical analysis. No significant difference was observed among inter-day assays ($P = 0.343$).

Based on S/N of 3, the LODs of fluoroglycofen-ethyl were 0.5, 1, and 1 μg kg^{-1} for soybean seed, plant, and soil. The LOQs, corresponding to the low fortified level in the recovery study, were 1, 5, and 5 μg kg^{-1} in soybean seed, plant, and soil, respectively. Comparing with the

Table 2 Accuracy and precision of the proposed method

Sample	Fortified level (μg kg^{-1})	Intra-day (n = 5)						Inter-day (n = 15)
		Day 1		Day 2		Day 3		
		Average recoveries (%)	RSD (%)	Average recoveries (%)	RSD (%)	Average recoveries (%)	RSD (%)	RSD (%)
Soybean seed	1	88.6	2.5	84.8	3.5	83.6	3.0	3.8
	10	91.2	1.3	83.4	2.4	87.7	3.9	4.6
Soybean plant	5	84.1	3.8	84.1	3.9	84.7	3.4	3.4
	100	87.8	1.6	86.5	2.3	86.6	1.8	1.9
Soil	5	91.6	5.9	91.7	6.6	99.2	6.1	7.0
	100	96.8	3.8	86.7	6.1	92.3	6.7	7.0

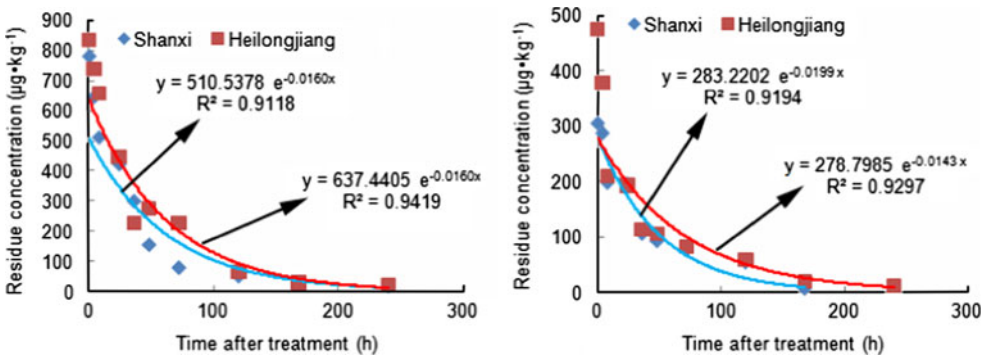

Fig. 1 Fluoroglycofen-ethyl residue dissipation in soybean plant (*left*) and in soil (*right*)

lowest LODs of fluoroglycofen-ethyl at 3 and 10 μg kg^{-1} for soybean seed and soil respectively in the published approaches (Chen et al. 2007; Pang et al. 2006; Wang et al. 2007; Wu et al. 2006), the LODs for soybean seed and soil in the present study are the most sensitive.

The concentrations of fluoroglycofen-ethyl residues investigated at approximately 150 and 180 days after spraying were all below LODs (0.5 μg kg^{-1}for soybean seed and 1 μg kg^{-1} for soybean plant and soil). The final residues of fluoroglycofen-ethyl in soybean seed indicated no risk to consumers because all residues were below the maximum residue levels (MRLs) established by China (50 μg kg^{-1}) in soybean seed (Anonymous 2010) and Germany (10 μg kg^{-1}) in all products of plant origin (Anonymous 1999). All residues represent no risk to animal farming after harvest, environment, and rotated crops because all residues in soybean plant and soil were below the LODs as well.

The dissipation behavior of fluoroglycofen-ethyl was investigated in Shanxi and Heilongjiang provinces. For soybean plant, fluoroglycofen-ethyl residue dissipated 10 days from 780.3 to 18.4 μg kg^{-1} in Shanxi province and from 833.2 to 22.8 μg kg^{-1} in Heilongjiang province, respectively, after 10 days. However, in terms of soil residue, fluoroglycofen-ethyl degraded within 10 days in the topsoil from 305.0 μg kg^{-1} to non-detected (<1 μg kg^{-1}) in Shanxi province and from 475.1 to 12.0 μg kg^{-1} in Heilongjiang province, respectively. The dynamic degradation with time of fluoroglycofen-ethyl in soybean plant and soil was described by pseudo-first-order equations. The corresponding curves showing the dissipation rate are plotted in Fig. 1.

The half-lives obtained for fluoroglycofen-ethyl in soybean plant were 43.3 h in both locations. The half-lives in soil were 34.8 h (Shanxi province) and 48.5 h (Heilongjiang province), respectively. The results indicated that fluoroglycofen-ethyl dissipated fast in both topsoil and plant in both trial field locations.

In summary, the present research developed and validated a rapid, highly selective, and sensitive UPLC-MS–MS method for quantization and identification of fluoroglycofen-ethyl in soybean seed, plant, and soil samples. The results of the dissipation and residue study revealed that fluoroglycofen-ethyl poses no harm to the environment, consumers, animal farming after harvest, and rotated crops.

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