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Dissipation and Residues of Rimsulfuron in Potato and Soil Under Field Conditions

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Abstract The analytical method for the residue analysis of a sulfonylurea herbicide, rimsulfuron, and its dissipation in soil and potato plants under field conditions were studied. Rimsulfuron residues were determined by Quick, Easy, Cheap, Effective, Rugged and Safe (QuEChERS) method and ultra-performance liquid chromatography coupled with tandem mass spectrometry (UPLC-MS/MS). Mean recoveries ranged from 74.6 % to 106.2 % with relative standard deviations (RSDs) of 2.0 %–13.8 % at three different spiking levels for each different matrix. The limits of detection (LOD) of rimsulfuron were ranged from 0.3 to 1.4 μg/kg, while the limits of quantification (LOQ) ranged from 0.9 to 4.3 μg/kg in different matrixes. The dissipation dynamics of rimsulfuron in the field trials in Shandong and Zhejiang Province were investigated. The half-lives in potato seedlings were 4.1 days in Shandong and 4.3 days in Zhejiang, both with a dissipation rate of 90 % about 7 days after application. The half-lives in soil were 6.0 days in Shandong and 6.6 days in Zhejiang, and with a dissipation rate of 90 % over 28 days. The terminal residues in potato and soil were not detectable. The fact that all the terminal residues were below the maximum residue level (0.1 mg/kg) set by Japan and 0.05 mg/kg set by EU. Hence it was safe for the use of this pesticide and the results also could give a reference for maximum residue limits setting of rimsulfuron in potato in China.

Keywords Rimsulfuron · Potato · Residues · Dissipation

Rimsulfuron [*N*-((4,6-dimethoxy-2-pyrimidinyl)aminocarbonyl)-3-(ethylsulfonyl)-2-pyridine-sulfonamide], is a member of the sulfonylurea family herbicide that was produced in the middle 1980s by DuPont corporation. It became commercially available in Europe in 1991, in the USA in 1994 and in China in 1997. Because of its some characters, such as low-dosage, high efficiency, low toxin and its particular function, rimsulfuron is applied at large against species of annual and perennial broadleaf weeds and grass in the cultivation of corn, potatoes and tomatoes.

Potato (*Solanum tuberosum*) is an important crop in China, which was cultivated throughout the country, and the cultivated area and the production of potato in China ranks first in the world. It is rich in sugar, vitamin, mineral elements and protein, which helps to enhance the capability of resistance to disease. However, potato suffers yield losses due to weed infestation during growth. Rimsulfuron was used to protect potato from weed, and it can increase the yields of potatoes (Haidar et al. 2005; Lu et al. 2011). In Denmark, rimsulfuron is now the most used herbicide for potato crops, 78 % of the crop area was treated with rimsulfuron in 2008; and in the USA, rimsulfuron is among the four most used herbicides for potato crops, 27 % of the crop area was treated with rimsulfuron in 2005 (Annette et al. 2010).

Literatures for rimsulfuron were mostly focused on the investigation about its environmental behavior, such as hydrolysis, photolysis, adsorption and so on (Laura et al.

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1999; Jean and Andre 1999; Vischetti et al. 2000). And a few papers reported the extraction methods, analytical methods, and dissipation of rimsulfuron in corn (Huang et al. 2002), soil (Cheryl et al. 2002; Dani et al. 2010) and surface water (Polati et al. 2006), in which these methods are the large quantities of solvent utilized, the multiple operation steps needed and also the lack of sufficient selectivity. The QuEChERS method minimized the number of sample-preparation steps and provided good recoveries for a large number of pesticides (Li et al. 2010; Wang et al. 2011; Liu et al. 2011). To our knowledge, the analytical method of residues of rimsulfuron in potato has not been published, and no one has studied the dissipation and ultimate residue of rimsulfuron in potato under field conditions.

The objective of this present study was to find out the residues, kinetics and dissipation pattern of rimsulfuron 25 % WDG formulation in the potato crops and the field soil after application, and thereby provide an evaluation for scientific, safe use of rimsulfuron.

Materials and Methods

The rimsulfuron standards (99.1 % purity) and formulations (25 % WDG) were obtained from DuPont Company of America. HPLC grade methanol was purchased from Sigma-Aldrich (Steinheim, Germany), Ultra-pure water was obtained from a Milli-Q system (Bedford, MA, USA). Analytical grade acetonitrile and NaCl for pesticide residue analysis were purchased from Beihua Fine-Chemicals Co. (Beijing, China). Analytical grade $MgSO_4$ was purchased from Sinopharm Chemical Reagent Co. Ltd (Beijing, China). C18, GCB and 0.22 μm nylon syringe filters were purchased from Agela Technologies Inc. (Tengda, Tianjin, PRC).

Chromatographic separation was carried out on a Waters Acquity UPLC binary solvent manager, an Acquity UPLC manager, and an Acuity cartridge heater equipped with a Waters Acquity UPLC BEH Shield RP18 column (100 × 2.1 mm, 1.7 μm particle size; Milford, MA, USA). This column is packed with a C18 reverse-phase bound to an ethylene-bridged hybrid (BEH) substrate. The mobile phases, which were composed of ultrapure water as mobile phase A and methanol as mobile phase B, were pumped at a flow rate of 0.3 mL/min. The gradient elution was: 0–2.0 min, 90 %–10 % A; 2.0–2.5 min, 10 % A; 2.5–2.6 min, 10 %–90 %; then held at 90 % A for 2.4 min. Separation and stabilization were achieved in 5.0 min. The column was kept at 45°C and the temperature in the autosampler was set at 5°C, the injection volume was 3 μL. Analysis of rimsulfuron was conducted on a triple-quadrupole mass spectrometer (TQD, Waters Crop.) using the multiple reaction monitoring (MRM) mode and positive ESI+ mode. The nebulizer gas was 99.95 % nitrogen, and the collision was 99.999 % argon with a pressure of 2×10^{-3} mbar in the T-wave cell. The conditions were typically as follows: the capillary voltage was set at 3.0 kV, and the cone voltage was 25 V; the source temperature and desolvation temperature were held at 120 and 350°C, respectively; The cone and desolvation gas were set at a flow of 50 and 500 L/h respectively; 432 (m/z) was selected as the precursor ion, and its quantitative and qualitative product ions were 182 (m/z) and 325 (m/z), respectively; when the collision energies were 18 and 15 V, respectively. For UPLC analysis, Masslynx NT v.4.1 (Waters) software was used to process quantitative data obtained from the calibration standards and samples. Under the described conditions, the retention time of rimsulfuron was approximately 1.74 min.

In the field trials, including the dissipation experiments and the terminal residue experiments, were carried out both in Shandong and Zhejiang Province, China in 2011, according to the Guidelines for Pesticide Residue Field Trials (NY/T 788-2004), issued by the Ministry of Agriculture, the People's Republic of China. Different treatments and control plot were 30 m^2 and the buffer zone was set up between plots. Each treatment was with three replicates. The application of rimsulfuron 25 % WDG was in the dosage of 2.25 g (a.i.)/ha (one and half times of the recommended dosage) with one time spray. Representative potato seedlings and soil samples were collected in 2 h, 1, 3, 7, 14, 21 and 28 days after spraying. The terminal residue experiments were carried out with a dosage level 1.5 g (a.i.)/ha and a higher dosage level 2.25 g (a.i.)/ha, respectively. Potato seedlings and soil samples were collected on harvest days after the application of rimsulfuron 25 % WDG. Soil samples were collected from different depths ranging from 0 to 10 cm with a stainless steel soil tube drill. Little stones and other unwanted materials were removed. Seedlings samples without roots were collected, cutted and immediately put into polyethylene bags. All of the sub-samples were kept in a deep-frozen (−20°C) environment until analyzed. Residue concentration and half-life of rimsulfuron were calculated by the first-order kinetics equations, $Ct = C_0 e^{-kt}$ and $t_{1/2} = \ln 2/k$, respectively. The variables are defined as follows: Ct denotes the concentration of the pesticide residue at time (t), C_0 denotes the initial concentration, k is the rate constant, and $t_{1/2}$ is the half-life.

About 10 g soil samples and 10 g potato samples (potato and potato seedlings) were put in a 50 mL centrifuge tube and 10 mL acetonitrile was added. The tubes were vortexed for 4 min and allowed to stand for 15 min at room temperature. Then 4 g anhydrous magnesium sulfate ($MgSO_4$) and 2 g NaCl were added. The tubes were capped and immediately vortexed vigorously for 1 min and then centrifuged for 5 min at RCF 2,077*g*. Then, 1.5 mL of the upper layer (acetonitrile) was transferred into a 2.0 mL dispersive-SPE micro-centrifuge tube containing 50 mg C18 (for potato seedlings samples, 50 mg GCB) and 150 mg anhydrous $MgSO_4$. And the tubes were well capped and vortexed for 1 min. The tubes were then centrifuged for 5 min at RCF 2,077*g*. Then, they were filtered through 0.22 mm Nylon syringe filters for UPLC-MS/MS analysis.

Results and Discussion

Quantitation was conducted using calibration curves. The calibration curves was studied by external matrix-matched standards at five concentrations of 0.01, 0.05, 0.1, 0.5, 1.0 mg/kg for different matrices. The response function was found to be linear with a good coefficient of determination (R^2) higher than 0.99 in all kinds of matrix standards solutions for rimsulfuron. The recovery, accuracy and the precision studies were evaluated by extraction and analysis of five replicates at three different spike levels (0.01, 0.05, 0.1 mg/kg) for soil, potato and potato seedling samples. The recoveries for rimsulfuron in soil were varied from 74.6 % to 85.5 % with RSD from 2.9 % to 11.4 %. The limits of detection and quantification (LOD and LOQ), defined as the lowest concentration that the analytical process can reliably differentiate from background levels, were estimated for spiked samples (0.01 mg/kg) based on an S/N of 3:1 and 10:1. The results are shown in Table 1.

Table 2 showed the dissipation of rimsulfuron in potato seedlings and soil under field conditions. The initial concentrations in the Shandong and Zhejiang potato seedlings samples were 4.16 and 0.99 mg/kg, respectively. The decline in rimsulfuron concentration was gradual and continuous after application. Concentrations were reduced by more than 90 % 7 days after application both in Shandong and in Zhejiang. And initial concentrations in soil were 0.27 and 0.05 mg/kg in Shandong and in Zhejiang with half-lives of 6.0 and 6.6 days, respectively. The dissipation rate was slower than in potato seedlings, with declining 82.2 % and 81.5 % after 14 days in Shandong and in Zhejiang, respectively.

When rimsulfuron (25 % WDG) was applied at a dosage level 1.5 g (a.i.)/ha and a higher dosage level 2.25 g (a.i.)/ha, terminal residues in potato and soil were evaluated during the harvest time from the treated plots in 2011. The terminal residue data were not detectable. The results showed that concentration of rimsulfuron in potato and soil were both below the LOQ.

In the classical QuEChERS method, PSA and anhydrous $MgSO_4$ were adding in extract and then vortex usually. So we selected the PSA to try to achieve simple clean-up, but the recovery rate rimsulfuron was undesirable (<50 %). The reason may be that PSA has a stronger absorbent ability, resulting in the poor recovery of rimsulfuron. Finally, after a series of attempts, we chose 50 mg of C18 instead of PSA for simple purification and the results were all acceptable. For potato seedlings samples, in order to effectively remove pigment, additionally added 50 mg of GCB. By using dispersive-SPE clean-up, it saves time and solvent compared with the traditional SPE approach.

To conclude, a rapid and sensitive method was developed for analysis of rimsulfuron in potato and soil using UPLC-MS/MS. Based on it, the dissipation and terminal

Table 1 The average recoveries, LODs and LOQs of rimsulfuron in potato and soil samples (n = 5)

Sample type	Added (mg/kg)	Average recovery (%)	RSD (%)	LOD (μg/kg)	LOQ (μg/kg)
Soil	0.01	83.6	2.9	0.3	0.9
	0.05	74.6	3.2		
	0.1	85.5	11.4		
Potato	0.01	86.8	13.8	0.5	1.6
	0.05	101.3	2.1		
	0.1	101.4	2.0		
Potato seedling	0.01	78.9	9.5	1.1	3.4
	0.05	89.6	3.0		
	0.1	106.2	10.9		

Table 2 Half life and other statistical parameters for rimsulfuron dissipation in different samples under field conditions, 2011

Sample	Locality	Regression equation	Determination coefficient (R^2)	Half life $t_{1/2}$ (days)
Potato seedling	Shandong	$C = 2.028e^{-0.1692t}$	0.8559	4.1
	Zhejiang	$C = 0.7261e^{-0.1615t}$	0.8624	4.3
Soil	Shandong	$C = 0.251e^{-0.1164t}$	0.989	6.0
	Zhejiang	$C = 0.0467e^{-0.1057t}$	0.9782	6.6

residue of rimsulfuron in potato and soil of Shandong and Zhejiang Province were investigated. While the FAO/WHO has not established maximum residue limits (MRLs) in potato for rimsulfuron, EU and Japan's MRL for rimsulfuron in potato is 0.05 and 0.1 mg/kg, respectively. At the time of harvest, no residues were detectable in potato and soil. The results showed that concentration of rimsulfuron in potato and soil were both below the LOQ. The result will give a suggestion of reasonable and safe use of rimsulfuron, and can also provide reference to set MRL value in potato in China.

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