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Dissipation kinetics and residues of florasulam and tribenuron-methyl in wheat ecosystem

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HIGHLIGHTS

- A method was developed to detect of florasulam and tribenuron-methyl in wheat.
- The half-lives of florasulam were 2.76–10.83 d under field conditions.
- The half-lives of tribenuron-methyl were 1.27–5.37 d under field conditions.
- Terminal residues of florasulam and tribenuron-methyl were below LOQs in all matrixes.

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ABSTRACT

The dissipation kinetics and residual levels of florasulam and tribenuron-methyl in wheat field ecosystem were determined using a quick, easy, cheap, efficient, rugged and safe method (QuEChERS) with rapid resolution liquid chromatography tandem mass spectrometry (RRLC-MS/MS). The average recoveries of florasulam and tribenuron-methyl at three spiking levels in wheat plant, soil, wheat straw and wheat grain ranged from 72.8% to 99.2% with relative standard deviations (RSDs) were less than 10.1% and 82.5% to 103.8% with RSDs were less than 9.4%, respectively. The limits of quantification (LOQs) of florasulam and tribenuron-methyl for wheat plant, wheat straw, wheat grain and soil were 0.01, 0.01, 0.005, 0.005 mg kg^{-1}, respectively. The field trials results showed that the half-lives of florasulam were 2.76–10.83 d. Half-lives for tribenuron-methyl were found to be 1.27–5.37 d. The terminal residues in wheat grain were much lower than maximum residue limits (MRLs) set by China (0.01 mg kg^{-1} for florasulam and 0.05 mg kg^{-1} for tribenuron-methyl), which considered to be safe for human beings. These results will contribute to establishing the scientific basis of the dosage of florasulam and tribenuron-methyl for use in wheat field ecosystems.

1. Introduction

Herbicides that target the acetolactate synthase (ALS), including five structurally diverse chemical classes: sulfonylureas, imidazolinones, triazolopyrimidines, pyrimidinylthio (or oxy)-benzoates and sulfonylamino-carbonyltriazolinones, are among the most widely used weed control chemicals since their introduction into the marketplace in the early 1980s (Zhou et al., 2007). These herbicides act by inhibiting ALS to prevent cell division and cell growth, and are widely used to control broad-leaved weeds and annual grasses in maize, soya bean, rice, cotton, peas and cereal grains (Bhattacharjee and Dureja, 1999; Jackson et al., 2000; Cui et al., 2009; Paul et al., 2009; Chen et al., 2009, 2010; Cruz-Hipolito et al., 2013).

The sulfonylureas and triazolopyrimidine sulfonanilide herbicides are frequently used as pre-emergence and/or post-emergence herbicides at low rates, typically less than 100 g active ingredient per hectare (deBoer et al., 2006; Boschin et al., 2007; Headley et al., 2010). They are low acute and chronic mammalian toxicities (Zhou et al., 2007; Boschin et al., 2007). However, due to their polar nature, fairly high water solubility, high phytotoxicity and adverse impacts to mammals, they are potential water pollutants and present environmental risks for crops, aquatic plants and microorganisms (Fletcher et al., 1993; Lepiece et al., 2000; Seguin et al., 2001; Olszyk et al., 2010). Hence, it is necessary to evaluate the dissipation kinetics of these herbicides and determine their terminal residues under the field conditions.

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75% florasulam • tribenuron-methyl water dispersible granule (75% WDG) containing 18.7% florasulam and 56.3% tribenuron-methyl is introduced on wheat against annual broad-leaved weeds by Jiangsu Agrochem. Laboratory Co., Ltd. Florasulam, N-(2,6-difluorophenyl)-8-fluoro-5-methoxy(1,2,4)triazolo(1,5-c)pyramid-dine-2-sulfonamide, is a triazolopyrimidine sulfonanilide herbicide having a pKa value of 4.54 at 23 °C. Aqueous solubility of florasulam is a strong function of pH, ranging from 84.0 mg L^{-1} at pH 5 to 94.2 g L^{-1} at pH 9. Tribenuron-methyl, methyl 2-[4-methoxy-6-methyl-1,3,5-triazin-2-yl(methyl)carb-amoylsulfamoyl]benzoate, is a sulfonylurea herbicide having a pKa value of 4.7. Aqueous solubility of tribenuron-methyl increases with increase of pH, ranging from 50.0 mg L^{-1} at pH 5 to 18.3 g L^{-1} at pH 9. The chemical structures of florasulam and tribenuron-methyl are showed in Fig. 1.

Intensive studies have focused on residue of florasulam in soy milk (Hernández-Borges et al., 2005a), soil (Hernández-Borges et al., 2005b), water (Hernández-Borges et al., 2005c), fruits and vegetables (Lehotay et al., 2005), barley (Díez et al., 2006), wheat (Li et al., 2013), or tribenuron-methyl in soil (Bernal et al., 1997; Menne et al., 1999; Ye et al., 2006; Zhang et al., 2011), water (D'Ascenzo et al., 1998; Polati et al., 2006), agricultural products (Akiyama et al., 2009) and fruits (Seebunrueng et al., 2013). However, to our knowledge there is no published data simultaneously reported the dissipation and terminal residues of florasulam and tribenuron-methyl in wheat and soil.

The QuEChERS method is well known for its applicability in simultaneous analysis of a large number of pesticides in a variety of food matrices (Abd-Alrahman, 2014). The method has undergone various modifications and enhancements, which were designed to improve recovery for specific types of pesticides or types of food, over the years since its first introduction (Wilkowska and Biziuk, 2011). There are two official methods available: AOAC Official Method 2007.01 and European Committee for Standardization Standard Method EN 15662 (Lehotay et al., 2010).

The aim of this paper is to establish a simple QuEChERS preparation approach coupled with highly selective RRLC-MS/MS for the simultaneous determination of florasulam and tribenuron-methyl in wheat grain, wheat plant, wheat straw and soil. Meanwhile, the dissipation kinetics of florasulam and tribenuron-methyl in wheat plant, soil and the residue in wheat straw, wheat grain and soil were investigated in the open wheat fields in Beijing and Shandong province in 2013. The results obtained would help to provide basic information for developing regulations to guard safe use of florasulam and tribenuron-methyl in weeds control in wheat field ecosystem.

2. Materials and methods

2.1. Chemicals and agents

Florasulam standard (98.5% purity) and 75% WDG were supplied by Jiangsu Agrochem. Laboratory Co., Ltd (Changzhou, China). Tribenuron-methyl standard of 1000 mg L^{-1} in acetonitrile was purchased from Agricultural Environmental Protection Institution of Tianjin (Tianjin, China). HPLC-grade acetonitrile and formic acid were bought from Thermo Fisher Co., Ltd. (MA, USA). HPLC-grade water was prepared using a Millipore Milli-Q reagent water system (MA, USA). Primary secondary amine (PSA, 40–60 μm), graphitized carbon black (GCB, 40–60 μm) and syringe filter (polytetrafluoroethylene, PTEF, 0.22 μm) were obtained from Tianjin Bonna-Agela Technologies (Tianjin, China). Anhydrous magnesium sulphate ($MgSO_4$), sodium chloride (NaCl), acetic acid and acetonitrile of analytical grade were purchased from Beijing Chemical Reagents Company (Beijing, China).

2.2. Field trials

The field trials, including the dissipation and residues experiments, were carried out at two different locations, Laiyang (120.99°E, 36.97°N, east of China, semi-humid continental monsoon climate), Shandong province and Beijing (116.46°E, 39.92°N, north of China, warm and semi-humid continental monsoon climate) from April to July 2013. The experiments were designed according to NY/T 788-2004 (Guideline on Pesticide Residue Trials) issued by Ministry of Agriculture, P. R. China. There were 5 treatments including 4 formulation treatments and 1 control treatment in the field experiments. Each experimental plot was 30 m^2 and each treatment was carried out in triplicates. A buffer zone was used to separate the plots of different treatments.

During the experimental period in 2013, the number of rain fall events in Laiyang and Beijing was 15 and 23, respectively, and the average temperature was 21 and 23 °C, respectively. The characteristic properties of the soil used in the fields at the two sites were as follows: Laiyang, clay loam, organic matter 3.89%, cation exchange capacity (CEC) 16.7 cmol kg^{-1}, pH 7.32; Beijing, sandy brown soil, organic matter 2.70%, pH 6.73, CEC 29.7 cmol kg^{-1}.

To investigate the dissipation of florasulam and tribenuron-methyl in wheat plant and soil, 75% WDG was dissolved in water and sprayed at a dose of 84.38 g active ingredient per hectare (g a.i. ha^{-1}, 1.5 times of the recommended high dosage) on the surface of wheat plant and the bare soil with no plants. The untreated plots were sprayed with water as control. Representative wheat plant and soil samples were collected from three replicate plots on 2 h, 1, 3, 5, 7, 14, 21 and 28 d after spraying. 2 kg plant samples were collected randomly from each plot. About 1 kg soil samples were randomly sampled to a depth of 0–10 cm in each plot using a soil sampling drill (i.d. 40 mm × height 30 cm) at 10 different spots. Both plant and soil samples were stored in a freezer at −20 °C until analyzed.

The terminal residue experiments were carried out with a dosage level 56.25 g a.i. ha^{-1} (recommended high dosage) and a higher dosage level 84.38 g a.i. ha^{-1} (1.5 times of the recommended high dosage). The representative wheat straw (1 kg), wheat grain (2 kg), and soil (1 kg) samples were randomly collected at the harvest time. The samples were stored in a deep freezer at −20 °C for further analysis.

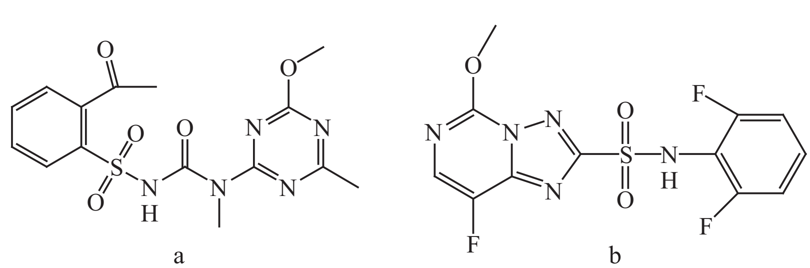

Fig. 1. Chemical structures of tribenuron-methyl (a) and florasulam (b).