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Residues and dissipation kinetics of triazole fungicides difenoconazole and propiconazole in wheat and soil in Chinese fields

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ABSTRACT

An analytical method for simultaneously determining the residues of difenoconazole and propiconazole in wheat straw, wheat grain and soil was developed. Mean recoveries and relative standard deviations in all samples ranged 86.2–101.3% and 3.1–12.1% for propiconazole and difenoconazole. The half-lives of difenoconazole and propiconazole were 3.6–5.5 days and 5.1–6.9 days in wheat straws, and 4.9–5.8 days and 6.1–8.4 days in soil, respectively. The residues in wheat grain were found to be <0.01 mg/kg, based on the application rate (135 g a.i./ha) and the pre-harvest interval (PHI = 28 days) recommended by the manufacturer. The results suggest that the use of difenoconazole and propiconazole on wheat is considered to be safe under the Good Agricultural Practices (GAP) in the Chinese fields, and the main factors for pesticide residue in crops are application times, rates and pre-harvest intervals.

1. Introduction

The triazole fungicides, difenoconazole (CAS No. 119446-68-3) and propiconazole (CAS No. 60207-90-1), active ingredients of various commercial fungicides, belong to the 14 α-demethylation inhibitors (DMIs) (Bai & Liu, 1987; Chen, Moore, & Nesnow, 2008; Gopinath, Radhakrishnan, & Jayaraja, 2006). The triazole fungicides are agrochemicals used worldwide in the agricultural industry due to their wide spectrum of actions (Kim, Beaudette, Shim, Trevors, & Suh, 2002). These fungicides are typically applied directly on plants (Colson, Platz, & Usher, 2003; Kim, Shim, & Suh, 2003; Li et al., 2013). They have both protective and curative activities and are extensively used for control of diseases of cereals, grapevines, banana and peanut (Munkvold, Dixon, Shriver, & Martinson, 2001), and also for the control of anthracnose of strawberry (Smith & Black, 1991).

Wheat is a staple food for a large section of the population in many countries and is one of the most important staple foods for humans worldwide (Fantke, Charles, de Alencastro, Friedrich, & Jolliet, 2011; Guler, Cakmak, Dagli, Aktumsek, & Ozparlak, 2010). With a production of 680 million tons in 2009 wheat contributes with approximately 30% to the world's average crop consumption (FAOSTAT., 2011). Furthermore, wheat is grown on more arable land than any other commercial crops (Curtis, Rajaram, & Macpherson, 2002) with an ever increasing demand due to a continuously growing global population. Since expansion of arable land is limited, cropping intensity and crop yield must be increased (FAO, 2003). It's widely cultivated in the Northeast region and the Northern region in China. Agrochemicals have been extensively used to control the disease and increase the yields. For example, the mixture of difenoconazole and propiconazole is used to control wheat fungi disease sharp eyespot (*Rhizoctonia cerealis*) potentially damaging high crop yield levels and wheat quality in many countries. In the literature, the dissipation behaviour of a single fungicide, either difenoconazole or propiconazole, was widely studied. Wang and coworkers determined the difenoconazole residues in Chinese cabbage and soil (Wang, Yong, Qin, Gong, & Ji, 2008), and recently in rice, paddy soil and paddy water (Wang, Wu, & Zhang, 2012); and the study on propiconazole in tomatoes (Panovska, Kavrakovski, & Bauer, 2000) and boronia extract (Groenewoud, Davies, & Menary, 1995) was also reported. For the use of the mixture of difenoconazole with another triazole pesticide penconazole, Rueegg and Siegfried reported the residues of difenoconazole and penconazole on apple leaves and grass and soil

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in an apple orchard in north-eastern Switzerland (Rueegg & Siegfried, 1996). Methods for determination the residues of difenoconazole and propiconazole in agro-products or environmental samples (including soil, water, etc.) were developed using HPLC-UV (Pinto et al., 2012), GC-ECD (Thom, Ottow, & Genckiser, 1997; Wang et al., 2008), GC-FID (Panovska et al., 2000), and LC–MS/MS (Carpinteiro, Ramil, Rodríguez, & Cela, 2010; Kong et al., 2012). However, little work on simultaneous determination on the residues of the pre-mixed difenoconazole and propiconazole was found in the literature, especially on cereals such as wheat.

This study aims at: (1) to develop a simple, fast and efficient analytical method to simultaneously determine the difenoconazole and propiconazole residues in wheat straw, wheat grain and soil using LC–MS/MS; (2) to evaluate the dissipation kinetics of difenoconazole and propiconazole in wheat straw and soil; and (3) to assess the safe use of the pre-mixed difenoconazole and propiconazole based their residues in wheat grain in comparison to the maximum residues limits (MRLs) issued by various governments and international authorities.

2. Materials and methods

2.1. Materials and equipment

2.1.1. Equipment

HPLC-MS/MS analysis was performed on a 1200SL HPLC system equipped with an Agilent G6410A triple quadrupole mass spectrometer (Agilent Technologies, Santa Clara, CA, USA). The LC–MS/MS system was controlled by MassHunter software. The analytical column was an Agilent ZORBAX SB-C18 (2.1 × 150 mm, 5 μm). Other equipment included an IKA high-speed homogenizer (T-18; IKA Werke, Staufen, Germany), a shaker (PYB, China Academy of Science Wuhan Science Equipment Factory, Wuhan, China), and a centrifuge (Beckman Coulter, Avanti J-30I, Brea, CA, USA), a nitrogen evaporator (N-EVAP 112; Organomation Associates, Inc., Berlin, MA, USA).

2.1.2. Chemicals

Analytical standards, difenoconazole (97%, w/w) and propiconazole (98%, w/w) were purchased from Sigma–Aldrich (Shanghai, China). A pre-prepared formulation of emulsifiable concentrate containing 15% of difenoconazole and 15% of propiconazole was obtained from Jiangsu Dongbao Pesticide & Chemical Co. Ltd. (Jiangsu, China). Acetone, *n*-hexane and methanol were purchased from Merck (Darmstadt, German). Purified water was prepared by a Milli-Q (Millipore, Bedford, MA) water purification system. All other solvents and reagents used in the present study were of HPLC grade or analytical grade.

2.1.3. Preparation of standard solutions

A stock standard solution containing both difenoconazole and propiconazole was prepared by weighing the analytical standards (difenoconazole and propiconazole) and dissolving them in methanol. Working standard solutions (0.01, 0.02, 0.1, 1, 2 and 5 mg/L) were prepared by diluting the stock solution or a working solution using methanol; and the other set of working standard solutions were matrix standards, prepared by diluting the stock solution or a working matrix standard using the extract of a clean control. Both solvent and matrix standards were analysed in the same analytical batch. All standard solutions were maintained in amber bottles at 4 °C.

2.2. Field trials

A multi-location field study was conducted in wheat fields in three different provinces in China from 2012 to 2013, i.e., Site 1 in East China (Nanjing City, Jiangsu Province), Site 2 in Northeast China (Changchun City, Jilin Province) and Site 3 in North China (Shijiazhuang City, Hebei Province). These three provinces are located in different monsoonal climates and thus reflect various climatic and environmental conditions in China.

The study was conducted according to "Standard Operating Procedures on Pesticide Registration Residue Field Trials" issued by the Institute for the Control of Agrochemicals, Ministry of Agriculture, PR China (ICAMA, Institute for the Control of Agrochemicals, Ministry of Agriculture, P. R. China, 2007). The study included the dissipation kinetics experiments and residue determination. The details about field experiments of the three trials are listed in Table 1.

As can be seen in Table 1, per ICAMA's SOPs (ICAMA, 2007), each trial consisted of totally fourteen (14) different treatment numbers, including one (1) control, twelve (12) treated for residue

Table 1
Details about the field trials of residues and degradations of difenoconazole and propiconazole in wheat and soils in three experimental sites in China.

Treatment number[a]	Sample type	Application rate (g a.i./ha)	Number of Application[b] (times)	PHI[c] (day)	Sampling object[d] (crop fraction, water, or soil)
I	Treated samples			14	Grain,
II	(for residue study, only)		2[e]	21	straw,
III		135[e]		28[d]	soil
IV				14	
V			3	21	
VI				28	
VII				14	
VIII			2	21	
IX		202.5		28	
X				14	
XI			3	21	
XII				28	
XIII	Treated samples (for decline study)	135	1	0 (2 h), 1, 3, 5, 7, 14, 21 and 28	Straw, soil
XIV	Control	/	/	0 (2 h), 28	Grain, straw, soil

[a] Plot area of each treatment number of 30 m^2.
[b] Intervals between applications was 10 days.
[c] Pre-harvest intervals (PHI).
[d] Treated samples in triplicate.
[e] Manufacturer recommended maximum application rate (135 g a.i./ha); manufacturer recommended maximum number of times of application (2 times, interval of 7 days); and manufacturer recommended pre-harvest interval (PHI = 28 days).