Ecotoxicology and Environmental Safety 86 (2012) 111–115

Contents lists available at SciVerse ScienceDirect

Ecotoxicology and Environmental Safety

journal homepage: www.elsevier.com/locate/ecoenv

Dissipation of difenoconazole in rice, paddy soil, and paddy water under field conditions

K. Wang, J.X. Wu, H.Y. Zhang *

College of Science, China Agricultural University, Beijing 100193, PR China

ARTICLE INFO

Article history:
Received 15 March 2012
Received in revised form
10 August 2012
Accepted 29 August 2012
Available online 10 October 2012

Keywords:
Difenoconazole
Dissipation
Water
Soil
Rice
GC–MS
Fungicide

ABSTRACT

An analytical method for determining the residue of a broad-spectrum fungicide, difenoconazole, in soil and rice crop matrices is described. Mean recoveries and relative standard deviation (RSD) in paddy soil, water, rice plant, rice hull, and husked rice matrices at three spiking levels ranged 71.8–115.8% and 1.6–7.8%, respectively. The half-life of difenoconazole was determined at three different field sites in Guangxi, Hubei, and Zhejiang provinces in China via a dissipation experiment, in which a 30% aqueous suspension concentrate of difenoconazole and propiconazole (15% difenoconazole, 15% propiconazole) was applied at high dosages. The half-lives of difenoconazole in water, rice plant, and soil in Guangxi were 0.30, 2.59 and 23.26 days, 2.50, 1.77 and 2.82 days in Hubei, and 2.71, 1.39 and 6.61 days in Zhejiang, respectively. Difenoconazole concentrations in soil, rice hull, and husked rice samples were below the detection limit at pre-harvest intervals of 30, 40 and 50 days after fungicide application. The concentration in straw at pre-harvest intervals of 30, 40 and 50 days in the three experimental locations ranged from 0.037 mg kg^{-1} and 2.53 mg kg^{-1}.

1. Introduction

Rice consumption has increased worldwide over recent decades, especially in Asia, as it has become one of the most common foods (Nguyen et al., 2008; Pareja et al., 2011). In China, rice is the main food and accounts for about 23% of planting area worldwide and more than 30% of total production, ranking first in the world (Zhang et al., 2011).

Pesticides are routinely used in integrated farm management programs to reduce possible losses. Fungicides belong to this group of high production agrochemicals and were mainly used for treating gray rot, downy and powdery mildew, and oidium (Carpinteiro et al., 2010). Pesticides undergo transformations in the environment when applied to crops. These persistent agrochemicals often cause health hazards to non-target organisms, including animals and humans.

Difenoconazole is a broad-spectrum triazole fungicide (Wang et al., 2008). As a systemic sterol demethylation inhibitor (DMI), difenoconazole interferes with mycelia growth and inhibits the germination of pathogens by spores, thus ultimately inhibiting fungal growth (Reuveni and Sheglov, 2002; Hamada et al., 2011). Difenoconazole has been extensively used in a wide range of crops in many countries due to its ability to control various fungal diseases. It is also one of the most important and widely-used pesticides for disease control in rice (Kong et al., 2012). Therefore, it is important to determine the dissipation behavior of difenoconazole in edible raw food and in the environment.

Previous studies have investigated the dissipation behavior of difenoconazole in apples, grapes and soil (Thom et al., 1997; Banerjee et al., 2008). Rice is an original and special product of China, and no studies have investigated the dissipation behavior of difenoconazole in rice. The present study was performed in open rice fields in Guangxi, Hubei and Zhejiang provinces in 2010. The aims of this work were to establish a simple, fast, and efficient analytical method to detect difenoconazole residues in rice and soil and to evaluate the dissipation behavior of difenoconazole in rice plant, water, and soil.

2. Material and methods

2.1. Chemical material

Difenoconazole stock standard solutions of 100 mg L^{-1} in acetone were supplied by the Institute of Environmental Monitoring of China Agriculture Ministry and stored at −20 °C. A working standard solution was prepared by dilution with acetonitrile and stored at −20 °C. Difenoconazole and propiconazole (30% aqueous suspension concentrate (SC); 15% difenoconazole, 15% propiconazole) was supplied by Antai Chemical Industry Company Limited, Guangxi Province. Acetonitrile of HPLC-grade was purchased from Fisher Chemicals (FairLawn, NJ, USA). HPLC-grade water was

* Corresponding author. fax: +8610 62733620.
E-mail address: hongyan@cau.edu.cn (H.Y. Zhang).

0147-6513/$ - see front matter © 2012 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.ecoenv.2012.08.026

prepared by a Milli-Q water purification system (Millipore, USA). Sodium chloride (99.5%) of analytical grade was purchased from Sinopharm Chemical Reagent (Beijing, China). Primary secondary amine (PSA) sorbent was purchased from Varian, Inc.

2.2. Field experiment

Field experiments were performed in Guangxi, Hubei and Zhejiang provinces in 2010 according to "The Guideline for Pesticide Residue Field Experiments" issued by the Institute of the Control of Agrochemicals, Ministry and Agriculture, the People's Republic of China. These three provinces are located in different monsoonal climates and thus reflect various climatic and environmental conditions in China.

The designs of the residue and dissipation field experiments are shown in Table 1. There were 15 treatments, including 14 difenoconazole and propiconazole 30% SC treatments, and 1 control treatment. Each experiment plot was 30 m^2 and each treatment was assessed with three replicate plots. No pesticide was used during the entire period of rice growth in the control treatment. A buffer area of 30 m^2 was used to separate the plots of different treatments.

To investigate the dissipation dynamics of difenoconazole in rice plants, difenoconazole and propiconazole 30% SC were dissolved in 750 Lwater and applied using a JACTO-HD400 internal pump backpack sprayer at an active ingredient dose of 135 g a. i. ha^{-1} (1.5-fold higher of the recommended high dosage) on the rice plant. To determine dissipation in paddy water and soil, difenoconazole was applied evenly on the surface waters in the open field with 4–6 cm water depth. The water depth remained at 4–6 cm during the dissipation experiment. Water samples were collected randomly using a 500 ml cup and then mixed in a barrel. Subsamples of paddy water (500 ml) were stored in a plastic bottle at −20 °C until analyzed. Fungicides were sprayed at the rice heading stage. Representative rice plant, paddy water, and paddy soil samples were collected randomly at several time points in each plot at 2 h (calculated as the original concentration), and 1, 2, 3, 5, 7, 14, 21, 30 45 days after spraying.

For the residue experiment, the difenoconazole and propiconazole 30% SC solution was applied at a low dosage of 90 g a. i. ha^{-1} (recommended high dosage) and a high dosage of 135 g a. i. ha^{-1} (1.5-fold higher of the recommended high dosage) for two and three times with pre-harvest interval 30, 40 and 50 days, respectively.

2.3. Sampling and storage

The rice, rice straw, and paddy soils were sampled at pre-harvest intervals of 30, 40 and 50 days after the last fungicide application for residue experiments. Dissipation samples were collected randomly from each plot at different time intervals i.e., 0 day (2 h after application), 1, 2, 3, 5, 7, 14, 21, 30, 45 days after fungicide application. Soil samples were collected randomly from each plot using a soil auger to a depth of 10 cm from the surface. Little stones, roots, stems and other unwanted materials were removed.

Water samples were collected in the plastic bottles randomly from each plot and filtered through a Buchner funnel. The pH of the water collected from Guangxi, Hubei and Zhejiang were 6.3, 6.7 and 6.6, respectively. Plant samples with roots were collected and washed. Soil, straw, and rice samples were collected for terminal residue analysis at the time of harvest. Rice was air-dried at room temperature and shelled into rice hull and husked rice. Husked rice was ground to powder. All samples were placed in a deep freezer at −18 °C and analyzed within 2 months.

2.4. Analytical procedure

2.4.1. Preparation of water sample

A portion (10 ml) of paddy water was transferred into a 50 ml centrifuge tube and 20 ml acetonitrile and 3.0 g sodium chloride were added. The solution was vortexed for 2 min and subsequently centrifuged at RCF 3802 × g for 5 min. The supernatant acetonitrile layer (10 ml) was transferred into a 100 ml round bottom flask and vacuum evaporated to dryness. The residue was then dissolved with 1 ml acetonitrile and then transferred into a 2 ml centrifuge tube containing 50 mg primary secondary amine (PSA) and then vortexed for 1 min. The extract was centrifuged at RCF 9168 × g for 5 min and then filtered through a 0.22 μm membrane filter (PTFE) into an autosampler vial and analyzed by GC–MS without further cleanup.

2.4.2. Preparation of soil sample

A portion (10.0 g) of homogenized soil sample was weighed into a 50 ml centrifuge tube and then 20 ml acetonitrile, 5 ml

Table 1
Design of the residue and dissipation experiments for difenoconazole in rice and soil.

Treatments		Dosage of application (g a.i ha^{-1})	Number of applications	Experiments	Time of sampling (days)
Serial number	Area (m^2)				
1	30 × 3	90	2	Residue	30
2	30 × 3	90	2	Residue	40
3	30 × 3	90	2	Residue	50
4	30 × 3	90	3	Residue	30
5	30 × 3	90	3	Residue	40
6	30 × 3	90	3	Residue	50
7	30 × 3	135	2	Residue	30
8	30 × 3	135	2	Residue	40
9	30 × 3	135	2	Residue	50
10	30 × 3	135	3	Residue	30
11	30 × 3	135	3	Residue	40
12	30 × 3	135	3	Residue	50
13	30 × 3	135	1	Dissipation in rice straw	2 h, 1 d, 2 d, 3 d, 5 d, 7 d, 14 d, 21 d, 30 d, 45 d
14	30 × 3	135	1	Dissipation in water and paddy	2 h, 1 d, 2 d, 3 d, 5 d, 7 d, 14 d, 21 d, 30 d, 45 d
15	30 × 3	0	-	Control	Sampled at the beginning, middle and the end of the experiment