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Dissipation of fuphenthiourea residues in rice and field ecosystem after seed soaking application

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ABSTRACT

An analytical method with SPE or matrix solid-phase dispersion clean-up procedure on PSA followed by HPLC-DAD was established for determination of fuphenthiourea residues in rice, water and soil. At three concentration levels (0.05, 0.5 and 5 mg kg^{-1}), recoveries were in the range of 61.2–82.7%, with a RSD less than 13%. The LOQ of this method was 0.005, 0.02 and 0.01 mg kg^{-1} for the water, soil and rice samples, respectively. Fuphenthiourea was applied in supervised field trials at GAP conditions during rice seeding. It was found that under field conditions, the dissipation half-lives of fuphenthiourea were 0.8 d in the water and 24.8 d in the soil. At harvest, no detectable residues (< LOD) were found in the various samples.

1. Introduction

Fuphenthiourea is a novel plant growth regulator used in rice seeding (5-(2-chlorophenyl)-N-(2-(2nitrobenzoyl) hydrazinecarbonothioyl) furan-2-carboxamide; Fig. 1). This compound can improve crop leaf photosynthetic capacity, restrict water transpiration rate, improve use efficiency and enhance plant resistance to drought stress when applied at the proper concentration. It has a low vapor pressure less than 10^{-5} Pa (20 °C), and is insoluble in water, slightly soluble in alcohol and aromatic hydrocarbons and is soluble in acetonitrile and N-dimethylformamide (DMF). Fuphenthiourea is stable under normal temperatures and acid-based environment.

Until now, little was known about the determination method of fuphenthiourea in rice, nor was the residue dissipation of this compound measured under supervised field trials. An analytical detection method was developed by application of liquid chromatography coupled with UV (Garcinuño et al., 2004; Kazos et al., 2007) and mass spectrometry (Sottani et al., 2003; Lindh et al., 2008; Jones et al., 2010).

This study deals with solid-phase extraction (SPE) and matrix solid-phase dispersion (MSPD) procedures followed by HPLC-DAD method to determine the fuphenthiourea residue and residue dynamics. The supervised field trials were conducted to monitor the dissipation rates and the final residue levels of fuphenthiourea in the rice and the ecosystem.

2. Experiment

2.1. Chemicals and solutions

The analytical standards of fuphenthiourea (98.0%) and the commercial formulations (10% EC) were provided from Wanquan Pesticide Factory (Hebei, China). Acetonitrile and methanol of HPLC grade were procured from Fisher Chemicals (FairLawn, NJ, USA). HPLC-grade water was prepared by a Milli-Q water purification system (Millipore, USA). Acetone (99.5%), formic acid (88%), acetic acid (99.5%), hydrochloric acid (36–38%), phosphoric acid (85%), ammonium acetate (98%), magnesium sulfate (98%) and sodium chloride (99.5%) of analytical grade were purchased from Sinopharm Chemical Reagent (Beijing, China). SPE columns were from Sepuco (C_{18}, 100 and 500 mg) and primary secondary amine (PSA) sorbent was purchased from Varian, Inc.

Fuphenthiourea stock standard solutions of 100 mg l^{-1} were prepared in acetonitrile and stored at -20 °C. Working standard solutions were prepared by dilution of the corresponding stock standard solution with acetonitrile and stored at -20 °C.

2.2. Field trial study

Field trials were conducted in Beijing and Changsha (Hunan Province, China) according to “the Guideline for Pesticide Residue Field Experiment” issued by the Institute of the Control of Agrochemicals, Ministry and Agriculture, the People’s Republic of China.

2.2.1. Residue dynamics experiments

Laboratory simulated dissipation experiments in water were performed in a plastic barrel at an application dosage level of

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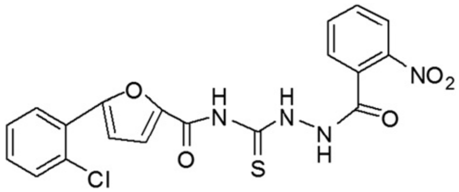

Fig. 1. The chemical structure of fuphenthiourea.

40 l ha^{-1} without light in the lab. Representative water samples were collected in the plastic bottles at different depth of water randomly, filtered through a 12-cm Buchner funnel and blended together at 0 (2 h after application), 1, 3, 5, 7, 14, 21, 30, 45 and 70 d after spraying.

Monitoring of fuphenthiourea residue in water and soil was conducted by spraying the commercial formulations on a blank pool and field at high application dosage level of 10 and 5 l a.i. ha^{-1}, respectively, in Beijing. Representative soil samples were randomly collected by a soil auger to a depth of 10 cm from the surface removing stones and other unwanted materials at 0 (2 h after application), 1, 3, 5, 7, 14, 21, 30, 45 and 70 d after spraying. Representative water samples were collected in plastic bottles at different depths randomly, filtered through a 12-cm Buchner funnel and blended together at 0 (2 h after application), 1, 2, 3, 4 and 5 d after spraying.

All these samples were stored at -20 °C until analyzed.

2.2.2. Final residue experiments

Triplicate plots and a control plot were set at each experiment field, which were separated by irrigation channels. The area of each plot was 30 m^2.

The final residue experiments were performed with a dosage level of 100 mg l^{-1} (the recommended level from label use) and a higher dosage level of 200 mg l^{-1}. The treatment was conducted by soaking rice seeds for 48 h with the two application levels before seeding. Representative water samples were collected immediately after the last irrigation while representative soil and rice samples were collected at harvest. Rice grains were ground to 40-mesh with a cereal grinder (Tianjin Taisite Instrument Co., Ltd., China).

All samples were stored at -20 °C until analyzed.

2.3. Instrumentation and apparatus

A Waters Liquid Chromatography 717 plus Autosampler with a 2996 Photodiode Array Detector operated at 320 nm was used to analyze the fuphenthiourea. Separations were achieved in 600 controller separation system with a Develosil ODS-5 column (150 mm × 4.6 mm, 5 μm) which was maintained at 25 °C. The mobile phase was acetonitrile:0.2% aqueous formic acid (60:40, v/v) with a total flow of 1 ml min^{-1} and the injection volume was 20 μL. The analyses were carried out under isocratic conditions. Data acquisition and analysis were performed with the Empower Software package, Version 6.20. 100.1362, supplied by Waters. The retention time of fuphenthiourea was 7.5 min.

Centrifugation was performed in two different instruments: an Anke TDL-40B centrifuge equipped with a bucket rotor (4 × 100 ml) (Shanghai, China) and a Sigma 3K15 microcentrifuge equipped with angular rotor (24 × 2.0 ml) (BMH Instruments Co., Ltd., China), a MTN-2800D Pressure Blowing Concentrator (Tianjin Autoscience Instrument Co., Ltd.), and a QL-901 Vortex (Kylin-bell Lab Instruments Co., Ltd., Jiangsu, China) were used for preparing the samples. Samples were stored in a Meiling BCD-245W Refrigerator Freezer (Beijing, China).

2.4. Sample preparation

Rice, soil and water samples were taken from fields and stored at -20 °C until analysis. Blank samples were used for validation studies and matrix-matched standard calibrations. Samples for recovery studies were spiked with a corresponding volume of the working solution and left for 30 min before the extraction.

2.4.1. Water

100 ml of paddy water samples having 5 ml 0.5 mol l^{-1} hydrochloric acid added were passed through a C_{18} (100 mg) cartridges which were preconditioned with 4 ml methanol followed by 4 ml water. After the water samples were filtered through the cartridges under vacuum, the cartridges were washed with 4 ml purified water. Analyte was eluted by 2 ml acetonitrile:0.2% aqueous formic acid (80:20, v/v) and made to a constant volume of 2 ml for HPLC analysis.

2.4.2. Soil

The characteristic of the soil for dissipation experiments in Beijing was silt loam at pH 7.23. Soil samples were dried at ambient temperature and screened through 40-mesh sieves. A portion (10 g) of homogenized soil sample was weighed into a 50 ml centrifuge tube and then extracted with 20 and 15 ml acetonitrile:0.1 mol l^{-1} aqueous phosphoric acid (80:20, v/v) subsequently followed by vortexing for 5 min vigorously. The two parts of extract were blended together after centrifugation (3800 rpm, 5 min). An aliquot (10 ml) of the extract added with 10 ml purified water was loaded on C18 (500 mg) cartridge which was preconditioned with 5 ml acetonitrile and 5 ml water subsequently under vacuum. The cartridges were washed with 3 ml 20% aqueous acetonitrile and the analyte was eluted by 4 × 1 ml acetonitrile:water (80:20, v/v). Sodium chloride (0.5 g) was added into elutant resulting in two separated phases by the salting-out process. The upper layer was transferred into a graduate tube and concentrated into 0.5 ml under nitrogen purge. The concentration was filtered through 0.45 μm membrane for HPLC analysis.

2.4.3. Rice

A portion (10 g) of ground rice grains was weighed into a 50 ml centrifuge tube, and then 5 ml 0.1 mol l^{-1} aqueous phosphoric acid and 10 ml acetonitrile were added, followed by vortexing for 5 min and centrifuging at 3800 rpm for 5 min subsequently. The upper layer was poured into a tube containing 0.5 g sodium chloride and then shaked vigorously. The extract (3 ml) was transferred into another graduated tube and concentrated to 1 ml under nitrogen purge. The concentrated extract was transferred into a 2 ml mircocentrifuge tube and purified by matrix solid-phase dispersion method. 150 mg anhydrous magnesium sulfate and 100 mg primary secondary amine (PSA) added into the tube with the exact was vortexed for 1 min again before centrifugation (6000 rpm, 5 min). The upper layer was filtered through 0.45 μm membrane for HPLC analysis.

2.5. Statistical analysis

The dissipation kinetics of fuphenthiourea in water, soil and rice were determined by plotting the residue concentration against time and the maximum squares of correlation coefficients found were used to determine the equations of best fit curves. For all the samples studied, exponential relationships were found to apply, corresponding to the first order rate equation. Confirmation of the first order kinetics was further made graphically from linearity of the plots of ln C against time. The rate equation was calculated from the equation of $C_t = C_0 e^{-kt}$, where C_t represents the concentration of the pesticide residue at time t, C_0 represents the initial concentration and k is the rate constant in days^{-1}. The half-life ($t_{1/2}$) was determined from the k value for each experiment, being $t_{1/2} = \ln 2/k$.