



Behavior of sprayed tricyclazole in rice paddy lysimeters

Thai Khanh Phong^a, Dang Thi Tuyet Nhung^a, Kenichi Yamazaki^b, Kazuhiro Takagi^c, Hirozumi Watanabe^{a,*}

^a Tokyo University of Agriculture and Technology, 3-5-8, Saiwaicho, Fuchu, Tokyo 183-8509, Japan

^b Tokyo University of Agriculture, 1-1-1 Sakuragaoka, Setagaya, Tokyo 156-8502, Japan

^c National Institute for Agro-Environmental Sciences, 3-1-1 Kannondai, Tsukuba, Ibaraki 305-8604, Japan

ARTICLE INFO

Article history:

Received 30 September 2008

Received in revised form 23 October 2008

Accepted 26 October 2008

Available online 4 December 2008

Keywords:

Photolysis

Hydrolysis

Lysimeter

Half-life

Wash-off

ABSTRACT

The behavior of sprayed tricyclazole in rice paddy lysimeters was studied. Tricyclazole residues were measured from rice leaves and paddy water after tricyclazole spraying in paddy lysimeters. The rate of photolysis and hydrolysis of tricyclazole on the surface of rice leaves was also determined in a laboratory experiment. Tricyclazole was extracted from leaf and water samples and determined by liquid chromatography with UV or mass spectrometry. The hydrolysis half-lives of tricyclazole on rice leaves were 11.9 and 5.1 d for the formulated product and standard, respectively. The photolysis half-lives were longer, 16.4 d for the formulated product and 20.9 d for the standard. In the paddy lysimeter, tricyclazole dissipation on leaves involved either biphasic first-order kinetics or single-phase first-order kinetics, depending on the rainfall pattern. Half-lives of tricyclazole on lysimeter rice leaves were from 3.0 to 5.7 d. The dissipation of tricyclazole in paddy water followed single-phase first-order kinetics with half-lives ranging from 2.1 to 5.0 d.

© 2008 Elsevier Ltd. All rights reserved.

1. Introduction

The potential of rice pesticides to contaminate open waters is of great concern to environmentalists. In Japan, many studies have pointed out that pesticide runoff from paddy fields is responsible for the contamination of rivers (Tanabe et al., 2001; Ebise and Inoue, 2002; Sudo et al., 2002; Nakano et al., 2004). While most of the detected pesticides belong to the herbicide group, the presence of other pesticide groups such as fungicide or insecticide indicates that their potential risk cannot be neglected (Tanabe et al., 2001; Ebise and Inoue, 2002; Sudo et al., 2002).

Tricyclazole (5-methyl-1,2,4-triazolo[3,4-b]benzothiazole) is a common systemic fungicide used to control rice blast, especially in Asian countries. Because foliage application of tricyclazole is the most effective cure against rice blast (Shiba and Nagata, 1981), most of the tricyclazole is applied by spraying on the rice foliage. Tricyclazole is a medium-soluble pesticide (water solubility: 1600 mg L⁻¹) so it may easily be washed from rice leaves by rainwater. While tricyclazole toxicity for mammals is low, its toxicity for aquatic organisms is considerable. The LC₅₀ (96 h) are 7.3 and 13.5 mg L⁻¹ for rainbow trout and goldfish fingerlings, respectively. For Daphnia, the LC₅₀ (48 h) is >20 mg L⁻¹ (Tomlin, 2003). The WHO classified tricyclazole as a moderately hazardous pesticide (WHO, 2005). The potential environmental risk of tricyclazole is consid-

ered significant because it is relatively stable in water–soil systems (Padovani et al., 2006).

Tricyclazole's fate in a basin scale was investigated, where high concentrations of tricyclazole were found in the water at the outlet of paddy farms (Padovani et al., 2006). Few other studies about the fate of tricyclazole in the soil system and on rice leaves are available in the literature (Ishiguro et al., 1992; Krieger et al., 2000), but no detailed information about the behavior of tricyclazole sprayed on rice plants has been reported. Meanwhile, the application of numerical models for predicting pesticide concentrations in rice paddy condition requires detailed information on pesticide behavior and water balance data. The lack of necessary information about tricyclazole resulted in a rough estimation of parameters for model application (Miao et al., 2003). Therefore, a detailed investigation on the behavior of tricyclazole under rice paddy condition may be useful for risk assessment as well as modeling purposes.

The aim of this study was to investigate the dissipation of tricyclazole on the rice leaf surface and the behavior of tricyclazole applied to rice paddy lysimeters under natural condition in a 2-year monitoring study.

2. Materials and methods

2.1. Chemicals and reagents

Tricyclazole standard (purity >99%) and LC–MS-grade acetonitrile were purchased from Wako Pure Chemical Industries

* Corresponding author. Tel./fax: +81 42 367 5889.
E-mail address: pochi@cc.tuat.ac.jp (H. Watanabe).

(Osaka, Japan). Water was produced with a MilliQ Water Purification System (Millipore, Billerica, MA, USA). Extracts and water samples were filtered through 0.2 µm disposable polyethersulfone filters (Whatman, Florham Park, NJ, USA) prior to LC injection.

2.2. LC-DAD analyses

Analyses were performed on the Waters Alliance HPLC System (Waters, Milford, MA, USA) consisting of the 2695 Separations Module and the 2996 photo diode array detector controlled by the MassLynx software from the computer. The analytical column was a Wakosil-II 5C18 AR column (4.6 mm × 150 mm, 5 µm particle size, Wako Pure Chemical Industries, Osaka, Japan), which was kept at 40 °C during the analytical run. Detection was done at 230 nm. The pump was set in isocratic mode at the rate of 1 mL min⁻¹ with the mobile phase of acetonitrile:water (20:80, v/v). Sample injection volume was 20 µL.

2.3. LC-MS analyses

The analyses were conducted with an Agilent HP-1100 chromatograph (Palo Alto, CA, USA) equipped with a Micromass ZQ 4000 mass spectrometer (Waters, Milford, MA, USA). The same column was used as in the LC-DAD analyses. Analyses were carried out using an isocratic mixture of acetonitrile–water (80:20, v/v) as the mobile phase. Ionization was performed by the electrospray ionization source (ESI) in a positive mode. The operating conditions were capillary voltage, 3500 V; desolvation gas flow rate, 450 L h⁻¹; and desolvation temperature, 450 °C. Acquisition was in a selected ion-recording mode at 190 m/z. The mass spectrometer was equipped with a MassLynx System Manager.

2.4. Determination of hydrolysis and photolysis on rice leaf

A separate experiment was conducted to determine the hydrolysis and photolysis rates of tricyclazole. Tricyclazole is not a volatile compound, its vapor pressure being 5.86×10^{-7} Pa at 20 °C (Tomlin, 2003). Therefore, volatilization of tricyclazole can be neglected and hydrolysis rates of tricyclazole can be determined by monitoring the dissipation of tricyclazole on the rice leaf in the dark. Meanwhile, it was assumed that dissipation of tricyclazole under natural sunlight was due to the combined effect of hydrolysis and photolysis. Therefore, the photolysis rate was obtained by subtracting the hydrolysis rate from the overall dissipation rate determined under natural sunlight and ambient temperature.

Rice leaves from a farm without any history of tricyclazole use were excised, cut into 9 cm segments, and then stuck in a plastic plate. Five-milliliter aliquot of tricyclazole solutions, prepared from a commercial product (320 mg L⁻¹) and pure standard (190 mg L⁻¹), was applied by micro syringe on each leaf segment. The plastic plates were then placed in glass basins with an inclination of 45°. Half of the basins were covered with quark glass and exposed under sunlight, while the other half were covered with aluminum foil and placed next to the former. Three leaf segments were taken everyday and combined to make composite samples of each test during the 5 d monitoring period. The monitoring is short because the leaves started to wilt after 5 d of exposure.

2.5. Lysimeter experiment

2.5.1. Lysimeter

Two outdoor lysimeters, namely lysimeter 1 and lysimeter 3, 4 m² (2 m × 2 m) in size with concrete walls at the National Institute for Agro-Environmental Science were used in this experiment. A detailed description of the lysimeters can be found in Watanabe et al. (2008). Rice (*Oryza sativa* var. Nihonbare) was grown for 2

months before fungicide spraying in order to simulate the blast treatment with high leaf coverage in both lysimeters. Before spraying tricyclazole, leaf coverage was determined by analyzing digital pictures using Adobe Photoshop software. BEAMzol (Kumiai Chemical Industry, Tokyo, Japan), which contains 20% of tricyclazole in the form of an emulsion product, was diluted 500 times with water and applied according to instructions on the product label. The tricyclazole spraying was carried out on July 20, 2006 and on July 16, 2007 for each monitoring period, respectively.

2.5.2. Sample collection

Composite water samples of 500 mL from five spots (Fig. 1) in each lysimeter were taken before the spray and then at 1 h, 3 h, and 1, 2, 3, 7, and 13 d after spraying (DAS). Along with water sampling, a composite sample of five leaves was taken at each of the five spots. In the case when runoff occurred, runoff water sample was collected into a 1 l glass bottle placed at the end of the runoff pipe.

2.6. Sample extraction

2.6.1. Water

Water samples were filtered through 1.2 µm glass filters (GF/C, Whatman); the solid-phase was then extracted using a Waters Sep-Pak Plus PS-2 cartridge. Prior to use, the cartridges were initially conditioned with 5 mL of acetone, followed by 5 mL of distilled water. An appropriate volume of the water sample was loaded into the cartridge at a flow rate of 10 mL min⁻¹. The cartridges were then washed with 10 mL of distilled water. The cartridges were air-dried for 10 min before the herbicides were eluted by 6 mL of acetone at the rate of 1 mL min⁻¹. The acetone extracts were collected and evaporated to dryness by a gentle stream of nitrogen and the residue was dissolved in 1 mL of mobile phase for LC-DAD analysis. The detection limit was 5 µg L⁻¹ and the recovery ($n=3$) was $88.4 \pm 1.8\%$.

2.6.2. Leaf

The leaf samples (2 g) from the lysimeter were cut into small pieces and were placed in a cone flask with 100 mL acetone. The cone flask was capped and shaken for 10 min. The acetone solution was removed and the leaves were extracted again with 50 mL acetone. The extracts were filtered with a filter paper and then evaporated with a vacuum rotary evaporator at 55 °C until the final volume reached 5 mL. The residue was dissolved in 100 mL water and filtered into a clean flask. The aqueous extracts were subjected to solid-phase extraction, similar to that of the water sample before

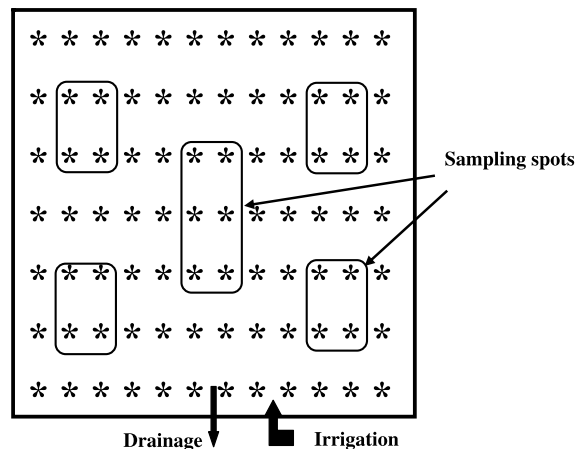


Fig. 1. Layout of the lysimeters.

Download English Version:

<https://daneshyari.com/en/article/4413267>

Download Persian Version:

<https://daneshyari.com/article/4413267>

[Daneshyari.com](https://daneshyari.com)