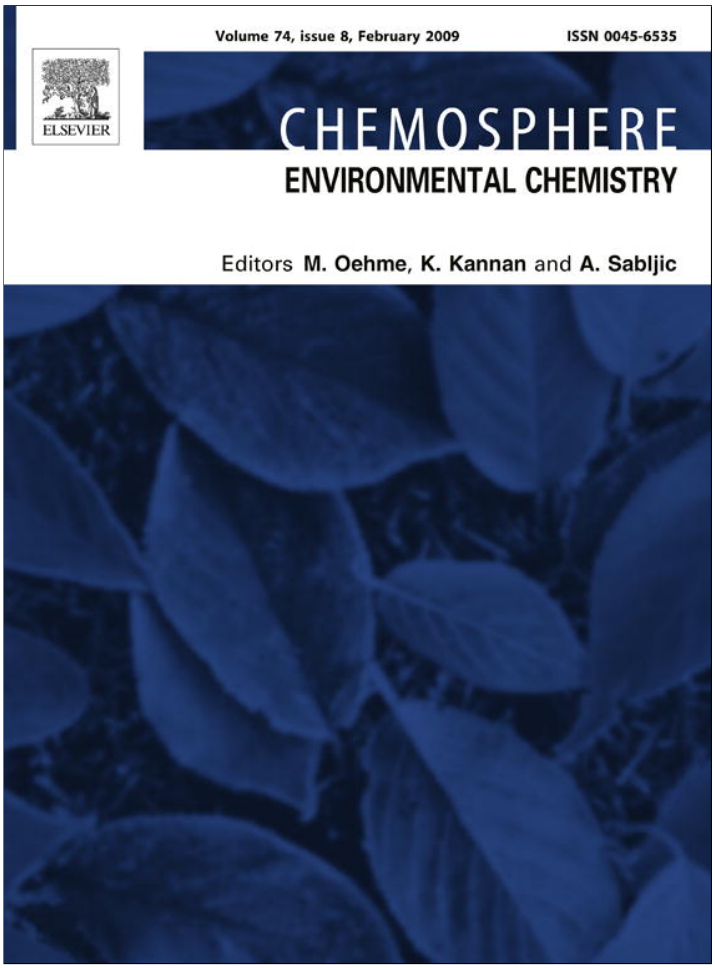
Provided for non-commercial research and education use.
Not for reproduction, distribution or commercial use.



This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

http://www.elsevier.com/copyright

Author's personal copy

Chemosphere 74 (2009) 1085–1089

Contents lists available at ScienceDirect

Chemosphere

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

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 LC_{50} (96 h) are 7.3 and 13.5 mg L^{-1} for rainbow trout and goldfish fingerlings, respectively. For Daphnia, the LC_{50} (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 considered 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).

0045-6535/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.chemosphere.2008.10.050

Author's personal copy

(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 m^2 (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 ± 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

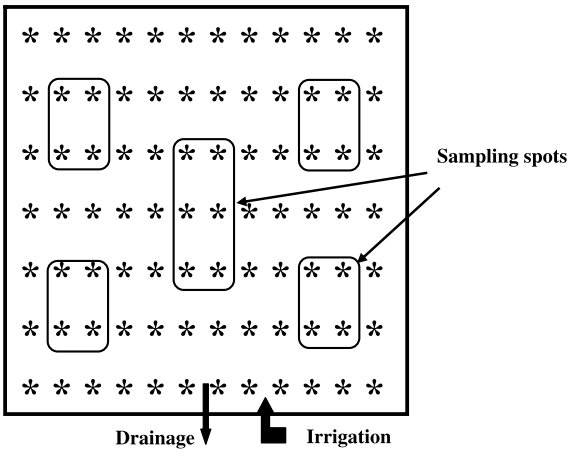


Fig. 1. Layout of the lysimeters.

Author's personal copy

Table 1
First order rate constants and half-lives for the degradation of tricyclazole on leaf surface.

	Rate constant (d^{-1})		Half-life (d)		
	Hydrolysis	Photolysis	Hydrolysis	Photolysis	Overall
Product	0.0582	0.0422	11.9	16.4	6.9
Standard	0.1371	0.0331	5.1	20.9	4.1

LC-DAD analysis. The detection limit was 10 $\mu g L^{-1}$ and the recovery ($n = 3$) was 76.1 ± 3.5%.

Due to the limited sample mass, leaf samples from the photolysis experiment were also cut into pieces but were soaked in 20 mL acetonitrile. The mixture was shaken for 10 min and left to stay still for 2 h. A 2 mL aliquot of the acetonitrile extract was filtered into a vial for LC–MS analysis. The detection limit was 0.5 $\mu g L^{-1}$ and the recovery ($n = 3$) was 98.2 ± 5.3%.

3. Results and discussion

3.1. Hydrolysis and photolysis of tricyclazole on rice leaves

In general, there was an obvious difference in the rates between tricyclazole in the product and those in standard solution (Table 1). This difference is probably because the acetonitrile solvent in the standard solution has assisted tricyclazole in penetrating into the leaf cells. As a consequence, more tricyclazole would be hydrolyzed inside the cell and less tricyclazole could absorb sunlight to initiate the photolysis process. Acetonitrile also has low quantum efficiency (Vulliet et al., 2001) i.e., it is less effective in receiving sunlight energy for chemical reaction.

The rate of hydrolysis of sprayed tricyclazole on the rice leaf was faster than that of photolysis (Table 1). For the overall degradation of sprayed tricyclazole on rice leaf, hydrolysis seems to play a major role as compared with its photolysis. It is also reported that tricyclazole is relatively stable under UV light (Tomlin, 2003). Therefore, hydrolysis is expected to have greater effect on tricyclazole behavior in the water compartment of the lysimeter.

3.2. Lysimeter experiment

3.2.1. Dissipation of tricyclazole on the foliage of lysimeter

The leaf coverage of the lysimeter was not full in both 2006 and 2007 (Table 2), which resulted in a large portion of the spray not being intercepted by the foliage. The value of leaf coverage was slightly different ($p < 0.05$) between the two lysimeters in both years. At 10 wk after transplanting, more than 20% of the area of paddy water surface was exposed to direct spray drift. Results reported by Wauchope and Street (1987) indicated that full coverage may increase the interception of tricyclazole, but the leaf coverage values may vary, depending on the timing of fungicide treatment. However, leaf coverage values other than the full coverage may be useful for risk assessment or model validation purposes.

The concentrations of tricyclazole in the spray solutions used in 2006 and 2007 were somewhat different (Table 2), probably due to the preparation process. Between the two years, errors during the preparation of the spray solution such as mixing and taking small amount of the emulsion formulation seemed to result in concentration variation (24%). The difference in concentration of the spray solutions have resulted in a difference in the actual application rate and the initial concentration of tricyclazole between the 2 years.

Tricyclazole dissipated rapidly on the surface of rice leaves (Fig. 2), especially following an early rainfall event. In 2006, a rainfall of 20.5 mm, which occurred at 16 h after spraying, reduced 72% and 53% of the concentration of tricyclazole in rice leaves in lysimeters 1 and 3, respectively. In 2007, a rainfall of only 2 mm at 1 DAS also caused a reduction of 37% in tricyclazole concentration in both lysimeters 1 and 3. The larger and windier rainfall may be the reason for the variation in the 2006 reduction data. The amount of tricyclazole loss through wash-off in this study was comparable with that reported by Cohen and Steinmetz (1986) for several pesticides that were applied to model surface and then subjected to simulated rainfalls (2.5, 25, and 38 mm). This behavior is similar to the behavior of other pesticides reported in the literature where most of the wash-off loss occurred early in the wash-off event (Willis et al., 1992, 1994; Hunsche et al., 2007). Hunsche et al. (2007) reported that up to 90% of mancozeb was washed off from apple seedlings after 5 mm of simulated rainfall. However, in a separate study with simulated rainfall, Phong et al. (2008) found that less than 25% of deposited tricyclazole was washed from rice foliage with drying time from 24 to 72 h.

Table 2
Leaf coverage, concentration of spray solution, application rate, and rainfall amount during the monitoring periods in 2006 and 2007.

			2006	2007
Leaf coverage	Lysimeter 1	%	70.0	80.0
	Lysimeter 3	%	73.0	73.5
Concentration of spray solution		$mg L^{-1}$	420	320
Actual application rate		$g ha^{-1}$	210	160
Total rainfall amount		mm	64.5	66.0
No. of rainfall events			5	8

Although the total rainfall amount during the monitoring period was similar between 2006 and 2007 (Table 2), the distribution of the rainfall event and rainfall depth have resulted in a difference in the half-lives of tricyclazole between the 2 years. The dissipation of tricyclazole on the foliage depended not only on the

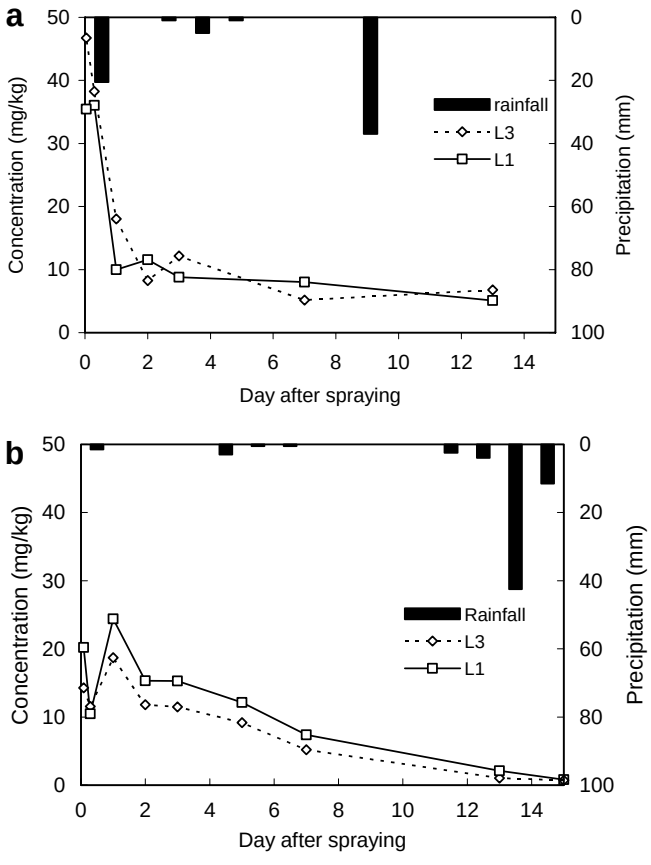


Fig. 2. Dissipation of tricyclazole on rice leaves in (a) 2006 and (b) 2007.

Author's personal copy

properties of tricyclazole but also on the rainfall pattern. Therefore, the concentration of tricyclazole on the leaves fluctuated according to rainfall amount. In 2006, the dissipation of tricyclazole in rice tissue fit the biphasic first-order kinetics better. This kinetics reflects the occurrence of two distinct dissipation phases and biphasic data can be treated as two separate linear regressions. In many cases, a biphasic curve may reflect the existence of both a readily available pool of material and a less available pool of material, the existence of multiple compartments (e.g., surface of leaf, interior of leaf), multiple isomers, and/or transformation processes with different rates (Whitmyre et al., 2004). The half-lives in the first phase of 2 d in 2006 were short (1 and 0.8 d for lysimeter 1 and lysimeter 3, respectively) due to a sharp drop in concentration by appreciable wash-off events. Meanwhile, the half-lives in the second phase (2−13 DAS) were remarkably longer than the laboratory data obtained from the hydrolysis–photolysis experiment (10.6 and 17.7 d for lysimeter 1 and lysimeter 3, respectively). This was probably because most of the tricyclazole readily available for wash-off and degradation were already washed away by the first rainfall event. A similar fate of other foliage spray pesticides was reported by Antonious et al. (1998).

Meanwhile, the single first-order kinetics fit well the 2007 data, except for the early fluctuation. The half-lives of tricyclazole in the two lysimeters were 3.1 and 3.0 d for lysimeter 1 and lysimeter 3, respectively, which were shorter than the laboratory data because of the presence of rainfall events during the monitoring period. However, the calculated half-lives of tricyclazole in the first 2 d after spraying were also shorter than the overall rate due to the effect of early rainfall on the dissipation of sprayed pesticides.

The half-lives of tricyclazole over the two monitoring periods were comparable with previously reported data. Ishiguro et al. (1992) reported that tricyclazole half-lives ranged from 2.1 d to 7.3 d, depending on leaf position and rainfall pattern. It means that tricyclazole behavior on rice leaves may vary, depending on the type and condition of foliage. Chaves et al. (2007) also reported a significant variation in half-life value of chlorothalonil in different types of foliage.

3.2.2. Dissipation of tricyclazole in lysimeter water

Fig. 3 shows the changes in concentrations of tricyclazole in the paddy water of the studied lysimeters in the 2 years as well as the runoff water collected at the drainage gate in the first runoff event in 2006. In general, the trend of tricyclazole dissipation in the two monitoring periods was similar. Immediately after spraying, more than 50 $\mu g L^{-1}$ of tricyclazole was detected in the paddy water as the spray drift deposited into the water compartment. The tricyclazole concentration seemed to decrease because the product diffused and equilibrated with the soil compartment. The initial concentrations of tricyclazole in paddy water were different between lysimeters partly due to the difference in water level and leaf coverage. In addition, the initial concentrations were also different between the 2 years because of the difference in application mass.

During the monitoring periods, the concentration of tricyclazole in paddy water peaked at the first rainfall event a few hours after spraying, followed by the smooth decline of tricyclazole concentrations in both 2006 and 2007. The importance of the rainfall timing to the pesticide wash-off from rice foliage and subsequent transport into paddy water was illustrated in the figures. The sharp drop in concentration on the leaf and the sharp increase in concentration on paddy water coincided with the first rainfall events in both lysimeters. Early rainfalls tend to wash most of the pesticides available on leaf surface (Willis et al., 1992, 1994; Hunsche et al., 2007), and in the paddy field case, load them into the water compartment. These remarkable amounts of pesticides may increase the pesticide concentration in paddy water. Meanwhile, the wash-off amount during the second rainfall event was reported to be much smaller than the first one (Phong et al., 2008). Therefore, the wash-off amounts of latter rainfall events were probably not sufficient to increase the concentration of tricyclazole in paddy water.

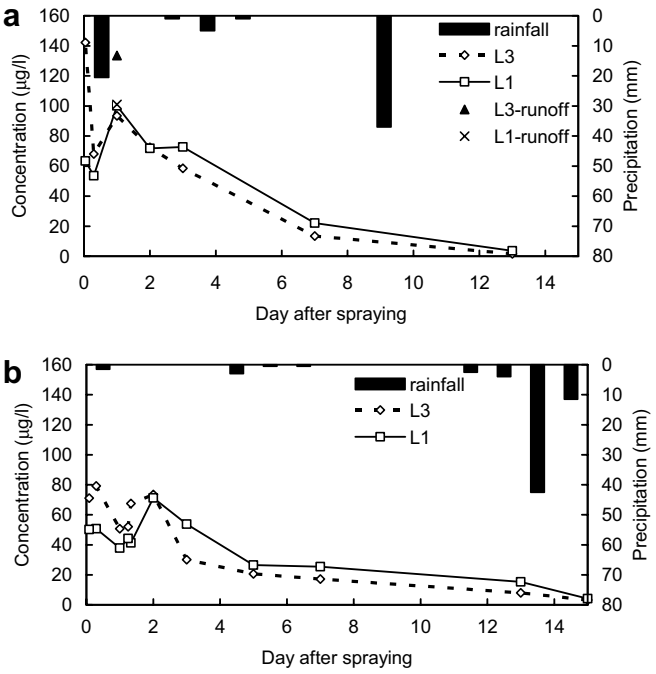


Fig. 3. Dissipation of tricyclazole in paddy water in (a) 2006 and (b) 2007.

During rainfall events, runoff of paddy water occurred only at one time (1 DAS in 2006) because, at that moment, the water level was already high as a result of previous large rainfalls. The concentrations of tricyclazole in runoff water were equal or higher than that in lysimeter water, being 101.0 and 133.6 $\mu g L^{-1}$ for lysimeters 1 and 3, respectively. This is reasonable since the wash-off water from rice foliage at this earlier stage containing high concentration of tricyclazole reached the surface of the water compartment before being mixed up with the water of the lysimeter. The concentrations of tricyclazole in runoff water were high compared with the data of a previous study. Padovani et al. (2006) reported that the maximum concentrations of tricyclazole measured at the outlet of paddy farms in Italy at 2 DAS was less than 15.6 $\mu g L^{-1}$ with a greater application rate.

Tricyclazole dissipation in the water compartment of the two lysimeters followed the first-order kinetics in both 2006 and 2007, although there was a difference in rainfall pattern. However, the dissipation curves in 2006 fit this kinetics better as they had higher correlation values (R^2) than those in 2007. The half-lives of tricyclazole in paddy water in 2006 were 3.0 and 2.1 d for lysimeter 1 and lysimeter 3, respectively. The corresponding data in 2007 were 5.0 and 3.5 d. The half-life values in 2006 were shorter than those in 2007 probably because of the runoff event in 2006, which resulted in losses of tricyclazole in both lysimeters. Also the vigorous growth of algae in the studied lysimeters in 2007 may reduce the effect of photolysis on tricyclazole in paddy water. The half-lives of tricyclazole in lysimeter 1 were longer than those in lysimeter 3 in both monitoring periods, even though the environmental conditions of the two lysimeters were similar. This variation may be due to errors in sampling and chemical analysis.

4. Conclusion

Dissipation of tricyclazole on rice leaves was determined under laboratory condition. The overall half-lives of tricyclazole

Author's personal copy

degradation on rice leaves were 6.9 and 4.1 d for formulated product and standard, respectively. The hydrolysis process plays a more important role than photolysis in the overall dissipation of tricyclazole on the leaves.

Concentrations of tricyclazole were also measured on rice leaves and water of two lysimeters for 13 d (in 2006) and 15 d (in 2007) after fungicide application. Tricyclazole was detected in all post-application samples. Early rainfalls after spraying washed a considerable amount of tricyclazole from the rice leaves, which made the dissipation process either as a biphasic first-order kinetics (in 2006) or a simple first-order kinetics (in 2007). A large rainfall event also induced runoff containing high concentration of tricyclazole from lysimeters. Meanwhile, the dissipation of tricyclazole in paddy water followed simple first-order kinetics with half-lives ranging from 2.1 to 5.0 d.

Acknowledgment

We would like to acknowledge Kumiai Chemical Industry (Japan) for supplying the BEAMzol product.

References

Antonious, G.F., Byers, M.E., Snyder, J.C., 1998. Residues and fate of endosulfan on field-grown pepper and tomato. Pestic. Sci. 54, 61–67.

Chaves, A., Shea, D., Cope, W.G., 2007. Environmental fate of chlorothalonil in a Costa Rican banana plantation. Chemosphere 69, 1166–1174.

Cohen, M.L., Steinmetz, W.D., 1986. Foliar wash-off of pesticides by rainfall. Environ. Sci. Technol. 20, 521–523.

Ebise, S., Inoue, T., 2002. Runoff characteristics of pesticides from paddy fields and reduction of risk to the aquatic environment. Water Sci. Technol. 45, 127–131.

Hunsche, M., Damerow, L., Schmitz-Eiberger, M., Noga, G., 2007. Mancozeb wash-off from apple seedlings by simulated rainfall as affected by drying time of fungicide deposit and rain characteristics. Crop Prot. 26, 768–774.

Ishiguro, K., Takechi, S., Hashimoto, A., 1992. Behavior of tricyclazole residue on rice leaves and its efficacy for rice leaf blast control in the field. Ann. Phytopath. Soc. Japan 58, 259–266.

Krieger, M.S., Cook, W.L., Kennard, L.M., 2000. Extraction of tricyclazole from soil and sediment with subcritical water. J. Agr. Food Chem. 48, 2178–2183.

Miao, Z., Padovani, L., Riparbelli, C., Ritter, Amy M., Trevisan, M., Capri, E., 2003. Prediction of the environmental concentration of pesticide in paddy field and surrounding surface water bodies. Paddy Water Environ. 1, 121–132.

Nakano, Y., Miyazaki, A., Yoshida, T., Ono, K., Inoue, T., 2004. A study on pesticide runoff from paddy fields to a river in rural region-1: field survey of pesticide runoff in the Kozakura River, Japan. Water Res. 38, 3017–3022.

Phong, T.K., Nhung, D.T.T., Yamazaki, K., Takagi, K., Watanabe, H., 2008. Simulated rainfall removal of tricyclazole sprayed on rice foliage. Bull. Environ. Contam. Toxicol. 80, 438–442.

Padovani, L., Capri, E., Padovani, C., Puglisi, E., Trevisan, M., 2006. Monitoring tricyclazole residues in rice paddy watersheds. Chemosphere 62, 303–314.

Shiba, Y., Nagata, T., 1981. The mode of action of tricyclazole in controlling rice blast. Ann. Phytopath. Soc. Japan 47, 662–667, (in Japanese with English abstract).

Sudo, M., Kunimatsu, T., Okubo, T., 2002. Concentration and loading of pesticide residues in Lake Biwa basin (Japan). Water Res. 36, 315–329.

Tanabe, A., Mitobe, H., Kawata, K., Yasuhara, A., Shibamoto, T., 2001. Seasonal and spatial studies on pesticide residues in surface waters of the Shinano river in Japan. J. Agr. Food Chem. 49, 3847–3852.

Tomlin, C., 2003. The Pesticide Manual, 13th ed. British Crop Protection Council, Farnham, UK.

Vulliet, E., Emmelin, C., Scrano, L., Bufo, S.A., Chovelon, J.M., Meallier, P., Grenier-Loustalot, M.F., 2001. Photochemical degradation of acifluorfen in aqueous solution. J. Agr. Food Chem. 49, 4795–4800.

Watanabe, H., Inao, K., Vu, H.S., Phong, T.K., Ishihara, S., Takagi, K., Tournebize, J., 2008. Pesticide exposure assessment in rice paddy areas: a Japanese perspective. In: Capri, E., Karpouza, D. (Eds.), Pesticide Risk Assessment in Rice Paddies: Theory and Practice. Elsevier, Amsterdam, Netherland, pp. 167–211.

Wauchope, R.D., Street, J.E., 1987. Fate of a water-soluble herbicide spray on foliage Part 1: Spray efficiency: Measurement of initial deposition and absorption. Pestic. Sci. 19, 243–252.

Whitmyre, G.K., Ross, J.H., Lunchick, C., Volger, B., Singer, S., 2004. Biphasic dissipation kinetics for dislodgeable foliar residues in estimating postapplication occupational exposures to endosulfan. Arch. Environ. Contam. Toxicol. 46, 17–23.

WHO, 2005. The WHO recommended classification of pesticides by hazards and guideline to classification: 2004. WHO, Geneva.

Willis, G.H., McDowell, L.L., Smith, S., Southwick, L.M., 1992. Foliar washoff of oil-applied malathion and permethrin as a function of time after application. J. Agr. Food Chem. 40, 1086–1089.

Willis, G.H., McDowell, L.L., Southwick, L.M., Smith, S., 1994. Azinphosmethyl and fenvalerate washoff from cotton plants as a function of time between application and initial rainfall. Arch. Environ. Contam. Toxicol. 27, 115–120.