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Behavior of Butachlor and Pyrazosulfuron-ethyl in Paddy Water Using Micro Paddy Lysimeters under Different Temperature Conditions in Spring and Summer

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Abstract The behavior of butachlor and pyrazosulfuron-ethyl in paddy water was investigated using micro paddy lysimeters with prescribed hydrological conditions under ambient temperature in spring and summer for simulating two rice crop seasons. Although they were not significantly different, the dissipation of both herbicides in paddy water in the summer experiment was faster than in the spring experiment. The half-lives (DT_{50}) in paddy water for spring and summer experiments were 3.2 and 2.5 days for butachlor, and 3.1 and 1.6 days for pyrazosulfuron-ethyl, respectively.

Keywords Temperature · Butachlor · Pyrazosulfuron-ethyl · Micro paddy lysimeter

Butachlor (N-butoxymethyl-2-chloro-2,6-diethylacetanilide) and pyrazosulfuron-ethyl (ethyl 5-(N-(4,6-dimethoxypyrimidin-2-ylcarbamoyl)sulfamoyl)-1-methyl-1H-pyrazole-4-carboxylate) are pre-emergence herbicides which have been widely used in Asia to control weeds in rice paddy fields (Chen and Chen 1979; Iwafune et al. 2010; Xu et al. 2008). Appreciable pesticide runoff from rice paddies associated with inappropriate water management and significant rainfall is likely to contaminate nearby watersheds and aquatic ecosystems (Watanabe et al. 2007; Inao and Kitamura 1999). As a result, butachlor and pyrazosulfuron-ethyl herbicides were detected in a river near rice paddies during an herbicide application period (Iwafune et al. 2010). The behavior of pesticides in the paddy field environment is usually complex and influenced by many factors, such as temperature, pH, solar radiation, microbial activities, soil properties and agricultural practice (Chen and Chen 1979; Samanta et al. 1999; Sarmah and Sabadie 2002; Vulliet et al. 2004; Zheng et al. 2008). In many Asian tropical regions such as Taiwan, China, India and Vietnam, rice is cultivated twice a year, first in the spring and secondly in the summer. Herbicides applied during the two rice crop seasons may have different fates and transport characteristics depending on environmental conditions such as the temperature variation (Chen and Chen 1979; Samanta et al. 1999; Sarmah and Sabadie 2002; Vulliet et al. 2004; Zheng et al. 2008; Xu et al. 2008).

The influence of temperature on pesticide fate during the two rice crop seasons in the actual paddy field is difficult to assess due to combined effects of multiple factors including water level, precipitation, percolation, and seepage rates (Watanabe et al. 2006, 2007). Moreover, field experiments are usually expensive and labor intensive; hence alternative methods to assist in the investigation of pesticide fate in rice paddies are required. In order to reduce the uncertainty associated with the factors noted above, and clarify the response from temperature, a lysimeter experiment may serve as an alternative. In Japan, outdoor lysimeters were used to develop mitigation techniques controlling the runoff of pesticides from paddy fields (Watanabe et al. 2008). A micro paddy lysimeter (MPL) has proven to be a useful tool to investigate the fate and transport of pesticides in the rice paddy environment (Nhung et al. 2009; Thuyet et al. 2010, 2012). Precise control of hydrological conditions in the MPL experiment enables a simplification of environmental scenarios while studying pesticide behavior in actual paddy fields (Nhung et al. 2009; Thuyet et al. 2010, 2012). In addition, MPL experiments are economical and are not labor

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intensive (Thuyet et al. 2012). Consequently, the aims of this study were to evaluate the environmental behavior of two herbicides, butachlor and pyrazosulfuron-ethyl, using a MPL with prescribed hydrological conditions under ambient temperatures in spring and summer for simulating two rice crop seasons, and to clarify the effects of temperature variation on the behavior of these herbicides during the different seasons.

Materials and Methods

A MPL was installed according to the procedure described in previous studies (Thuyet et al. 2010, 2012). Briefly, triplicate stainless steel MPL chambers of 50 × 35 × 30 cm (length × width × height), were filled with 3 soil layers: a glass bead layer (1 cm), a hardpan layer (2 cm), and a plow layer (14 cm) from bottom to top, respectively. A sheet of glass fiber filter paper (GF/A, What-man) was used to separate the glass bead and hardpan layer. The MPL layers were independently prepared during the experiment setup. Soil was collected from a rice paddy plot at the university farm of Tokyo University of Agriculture and Technology (TUAT), Japan. The soil was classified as light clay and the organic carbon content was 3.96 % (Watanabe et al. 2007). Three MPLs were placed under outdoor conditions in an experimental field at TUAT in spring and summer for simulating the two rice crop seasons. The side walls of MPLs were covered by urethane foam insulation and were buried under the soil to prevent significant heat transport from ambient air (Fig. 1). A transparent plastic roof was used to cover MPLs when natural rainfall occurred. Although the model region for double cropping of paddy rice in this study was Taichung, Taiwan, MPL experiments were conducted in Japan from May 13 to June 2 in 2011 for the spring crop season and from August 18 to September 7 in 2009 for the summer crop season. These seasons are referred to as S1 and S2, respectively. MPLs were prepared 1 week before herbicide application.

Physico-chemical properties of the two herbicides studied are shown in Table 1. Granular formulations of commercial products of Masetto® for butachlor (10 % w/w) and Akuto® for pyrazosulfuron-ethyl (0.3 % w/w) were purchased from Kumiai Chemical Industry, Tokyo, Japan. Both application rates were 10 kg/ha as recommended by the product labels.

In the experiments, the daily depth of water was maintained at 4 cm in the MPLs. The percolation rate of MPL was adjusted to be 0.5 cm/day. Evapotranspiration (ET) from MPL was estimated by a small evaporation pan (20 × 15 × 12 cm) set up near the MPL. Input and output of water in the MPL were monitored during the experimental period. Temperatures for surface water and 1 cm soil depth were recorded every hour during the experiment using temperature sensors connected to data loggers (UIZ 3633; UIZIN, Tokyo, Japan). The hourly air temperature was downloaded from the local weather station in Fuchu city, Tokyo, Japan. The pH in paddy water was measured by pH meter (D-23; HORIBA, Kyoto, Japan). Water samples were collected for each MPL at 0, 1, 3, 7, 14 and 21 days after herbicide application (DAHA). Composite water samples were made by collecting water samples from 5 spots. Herbicide concentrations in the samples were analyzed within 1 day after sampling.

Acetonitrile, acetone, acetic acid, phosphoric acid, and methanol were of analytical grade. Analytical grade standards (98 % purity) of both herbicides were obtained from Wako (Osaka, Japan). Deionized water (Millipore, Billerica, MA, USA), 1.2-μm glass fiber filters and 0.2-μm syringe filters (Whatman, Maidstone, UK), and a solid-phase cartridge (ENVI C18 Superclean, 500 mg/6 mL, Supelco, MI, USA) were used for chemical analysis. Prior to extraction, water samples were filtered through glass fiber filters (GF/B, Whatman). Water samples for pyrazosulfuron-ethyl analysis were adjusted to pH = 2.5 by phosphoric acid before extraction. The solid-phase cartridges were pre-activated

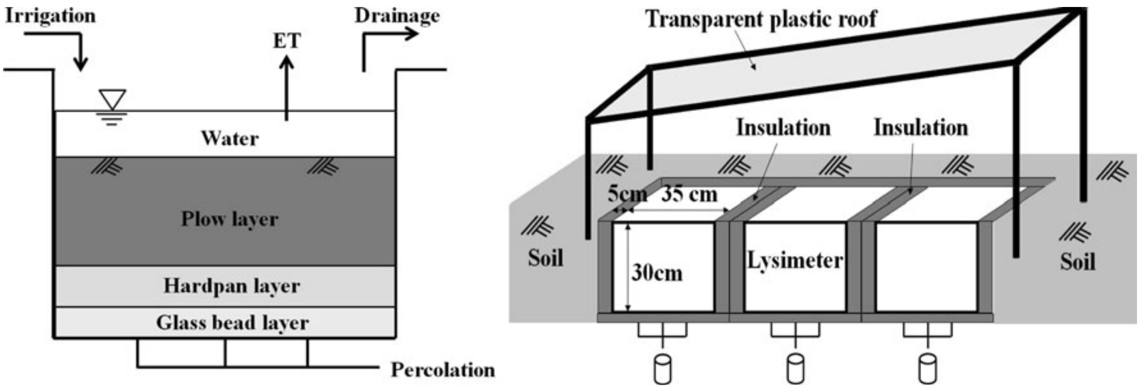

Fig. 1 Design and installation of MPL

Table 1 Physico-chemical properties of the two herbicides studied (IUPAC 2012)

Parameters	Butachlor	Pyrazosulfuron-ethyl
Molecular formula	$C_{17}H_{26}ClNO_2$	$C_{14}H_{18}N_6O_7S$
Molecular mass	311.9 g/mol	414.29 g/mol
Vapor pressure (25°C)	0.24 mPa	0.0147 mPa
Octanol/water partition coefficient (logP)	4.5	3.16
Water solubility (20°C)	20 mg/L	14.5 mg/L
Soil sorption coefficient (Koc) mL/g	700	154
Henry's law constant at 20°C (dimensionless)	1.54×10^{-6}	1.72×10^{-7}

with 5 mL of acetonitrile, followed by 5 mL of distilled water. An appropriate volume of water sample was then loaded into the cartridge at a flow rate of 4 mL/min aspirated by a peristaltic pump (Tokyo Rikakikai, Tokyo, Japan), then herbicides were eluted from the cartridges with 6 mL of acetonitrile at a rate of 1 mL/min. The eluate was evaporated down to 1 mL by a gentle stream of nitrogen. The samples were filtered through syringe filters and kept at 4°C for high performance liquid chromatography (HPLC) analysis. The HPLC system (Shimadzu, Kyoto, Japan) consisted of a separations module and a diode array detector. The separations module was equipped with a Shimadzu C-18 column (150 × 4.6 mm I.D., 4.6 μm particle size), which was kept at 40°C during the analytical operation. The pump was set in isocratic mode at a flow rate of 1 mL/min with the mobile phase of acetonitrile: 0.01 % acetic acid (30:70; and 50:50, v/v) for butachlor and pyrazosulfuron-ethyl, respectively. Detection wavelengths of 215 nm and 242 nm were selected for measurements of butachlor and pyrazosulfuron-ethyl, respectively. Sample injection volume was 20 μL (Ayano et al. 2004; Doan et al. 2009; Sabik et al. 2000).

Results and Discussion

The monitoring periods in Tokyo, Japan, were determined by comparing the mean temperatures of two crop seasons in Taiwan. In Taiwan, the first rice crop season usually extends from February to July and second rice crop season is from August to December. The herbicide application and concurrent period when paddy water has the highest herbicide concentrations is generally in February and August in Taiwan. Therefore, daily mean temperatures in February in Taichung, Taiwan and May in Fuchu, Tokyo and those in August in Taiwan and Tokyo from 10 years (1999–2008) of meteorological data were compared. The daily average temperatures in Taiwan were 17.8 ± 1.0 for February and 28.4 ± 1.1°C for August, and the corresponding values in Japan were 18.3 ± 0.7 for May and 26.8 ± 0.9°C for August, respectively. The temperature ranges for simulating pesticide fates during the first and second rice crop seasons appeared to be adequate for S1 in May and for S2 in August in Tokyo.

During the experiment, the mean values of air temperature in Fuchu city, Tokyo, and the monitored mean temperatures of surface water and soil at 1 cm depth were 17.9, 18.7 and 18.7°C for S1 and 24.6, 24.8 and 24.8°C for S2, respectively. The pH of paddy water was slightly alkaline and ranged from 8.0 to 9.2 for S1 and from 7.5 to 10.2 for S2, respectively. The pH values were in agreement with previous studies. The daily average pH in MPL was about 8.3 (Nhung et al. 2009) and the measured pH fluctuated between 7.7 and 10.7 with the average pH of 9.8 ± 0.8 (Thuyet et al. 2012).

The water balance for the two experiments is shown in Table 2. The percolation and ET output in S1 and S2 were similar. The percolation outputs between S1 and S2 were not significantly different (*t* test, two tail, *p* value = 0.223). The drainage amounts between S1 and S2 were different because of excessive water loss during S2 experiment. Consequently, the difference in total input or output between S1 and S2 were about 22 percent relative to the mean. However, the contribution of herbicide losses from drainage was small and the difference in water balance between S1 and S2 did not affect herbicide mass balance as discussed later.

Concentrations of the herbicides over 21 days are shown in Fig. 2. Concentrations were the highest at 1 day after herbicide application (DAHA), and decreased exponentially afterwards. The average butachlor concentrations were 356.9 ± 33.8 and 211.1 ± 18.6 μg/L for S1 and S2, respectively. The herbicide concentrations during 0 DAHA in this study were not monitored however the herbicide concentrations in paddy water between 0 and 1 DAHA were reported to vary greatly (Nhung et al. 2009; Thuyet et al. 2012). The variation became small after 1 DAHA.

Table 2 Water balance in the MPL for S1 and S2 experiments

		S1	S2
Input (cm)	Irrigation	22.8 (±0.5)	28.5 (±0.1)
	Percolation	9.6 (±0.6)	8.8 (±0.5)
Output (cm)	Drainage	7.0 (±0.2)	11.9 (±0.6)
	ET[a]	6.0 (N/A)	7.8 (N/A)
	Total	22.6	28.5

The value in parentheses is the standard deviation of the mean

N/A not available

[a] Measured evaporation from a pan placed next to MPLs

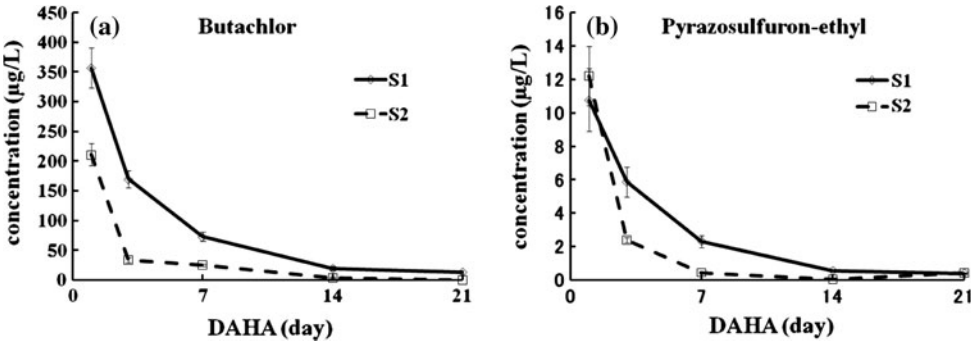

Fig. 2 Concentrations of butachlor (**a**) and pyrazosulfuron-ethyl (**b**) in paddy water in S1 and S2 experiments. Error bars represent the standard deviation

The discrepancy of butachlor concentrations at 1 DAHA between S1 and S2 could result from possible initial degradation processes such as photodegradation, biodegradation and volatilization process in paddy water (Chen and Chen 1978, 1979). However, the butachlor loss by volatilization in this study seems to be minor as discussed later. The concentrations of butachlor in S2 were lower than those in S1, and the dissipation of butachlor until 7 DAHA was faster in S2 than that of S1 (Fig. 2a). Higher ambient temperature condition during S2 experiment in August probably increased the dissipation rate as compared to that in S1 in May. Chen and Chen (1978, 1979) reported that degradation and dissipation of butachlor were faster in the second rice crop season which starts in August in Taiwan, and that photodecomposition, volatilization and microbial degradation were the major pathways of dissipation of the herbicide from paddy fields in the second rice crop season.

Average pyrazosulfuron-ethyl concentrations were 10.8 ± 1.9 and 12.2 ± 1.8 μg/L for S1 and S2, respectively. The concentration of pyrazosulfuron-ethyl in S2 at 1 DAHA was higher than that in S1 experiment, and the dissipation of pyrazosulfuron-ethyl was faster in the S2 experiment (Fig. 2b). The dissipation of pyrazosulfuron-ethyl has been reported to be influenced by pH, being slower at neutral pH than at acidic and basic pH (Sarmah and Sabadie 2002; Zheng et al. 2008). However, the average pH between S1 and S2 in this study, was not statistically different during monitoring (*t* test, two tail, *p* value = 0.160). The reason for the fast dissipation in S2 is probably that hydrolysis of these herbicides consistently increased with increasing temperature at a fixed pH. A 10°C increase in temperature was reported to increase the average rate of pyrazosulfuron-ethyl hydrolysis by 2.4 times at pH 3 and 4.5 times at pH 9 (Zheng et al. 2008).

Figure 3 shows the pesticide mass balance in water at 1, 3, 7, 14 and 21 DAHA as percentages of the pesticide mass in paddy water at the first day (%MFD) in S1 and S2. The two major dissipation pathways in the paddy water were identified to be degradation and losses through percolation and drainage as reported by Takagi et al. (2012). The total mass of degraded butachlor at 3 DAHA in S2 (65.7 %MFD) was higher than that in S1 (38.8 %MFD), and the corresponding values for pyrazosulfuron-ethyl were 59.4 and 32.0 %MFD for S2 and S1, respectively. At the end of the monitoring period, both herbicides in the S1 and S2 had entirely dissipated through degradation, percolation and drainage. The amount of drainage and percolation relative to total water output was 74 % for S1 and 73 % for S2 (Table 2). However, the cumulative mass loss of herbicides by drainage and percolation in S1 and S2 at 21 DAHA were 27.1 and 34.8 %MFD for butachlor, 27.0 and 34.2 %MFD for pyrazosulfuron-ethyl, respectively (Fig. 3). Comparing to the total of cumulative herbicide losses though drainage and percolation, the cumulative herbicide losses by degradation in S1 and S2 at the end of the monitoring period were 2.5 and 1.9 times higher for butachlor and 2.5 and 1.8 times higher for pyrazosulfuron-ethyl, respectively (Fig. 3). Therefore, degradation is considered to be the major dissipation pathway for herbicides in paddy water. The difference of temperatures in the S1 and S2 could result in the difference degradation rates of both herbicides, as discussed in the next section.

Linear regression analyses were used to determine half-lives (DT_{50}) using first-order kinetics for the first 14 DAHA. The DT_{50}s for butachlor were 3.2 and 2.5 days for the S1 and S2 seasons, respectively (Table 3). Chen and Chen (1979) reported the half-lives for butachlor to be 5.5 and 0.8 days in the first and second rice crop seasons, respectively, in Taiwan. Degradation of butachlor was more rapid in the S2, which may have resulted from the increased temperature during S2. Due to its vapor pressure (0.24 mPa), butachlor might be significantly volatile especially during high temperature. In laboratory tests carried out by Chen and Chen (1979), the volatilization of butachlor from aqueous solution was significantly influenced by temperature. The loss of butachlor over 2 days by volatilization from a 0.05 M $CaCl_2$ solution was 4.5 % at 21.5°C, and 30 % at 40°C (Chen and Chen 1979). In this experiment, the monitored mean temperatures of surface water in the spring and summer crop seasons were 18.7 and 24.8°C. According to the report by Chen and Chen (1979), the volatilization loss of butachlor seems to be minor and the difference between S1 and S2 maybe small. However detailed laboratory studies are

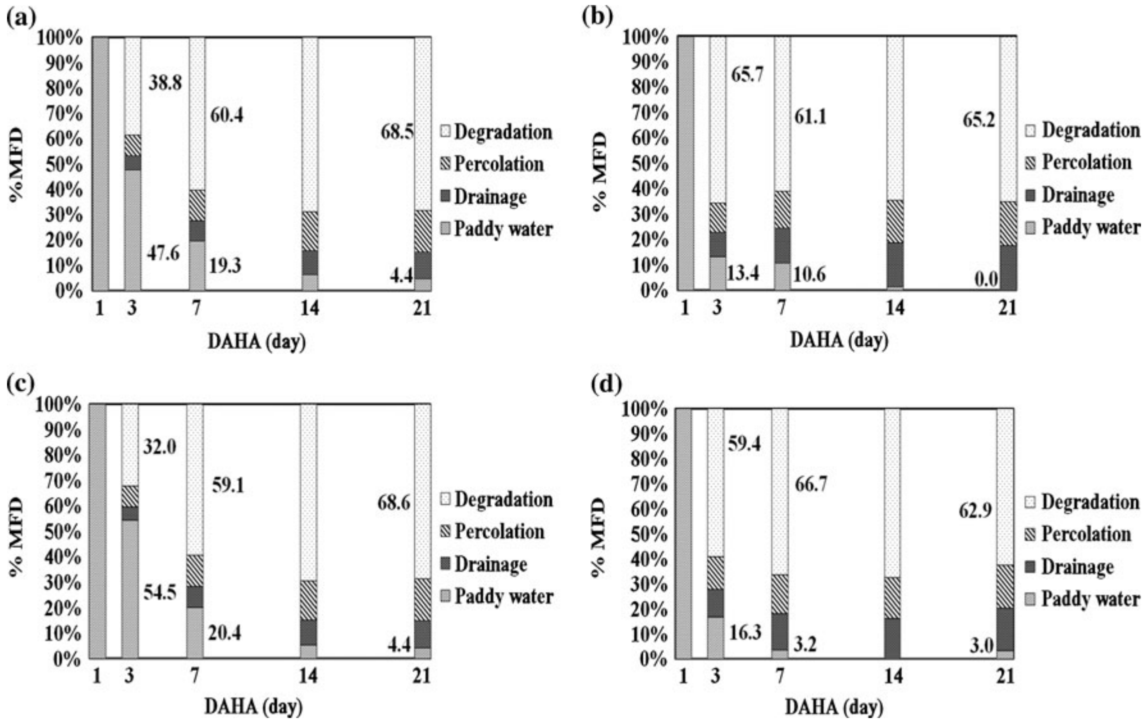

Fig. 3 Pesticide mass balance in paddy water for butachlor in S1 (**a**) and S2 (**b**) and pyrazosulfuron-ethyl in S1 (**c**) and S2 (**d**) as percentages of the pesticide mass in paddy water at first day (%MFD). Upper and lower numbers indicate the percentage of butachlor and pyrazosulfuron-ethyl lost by degradation and the percentage remaining in the paddy water, respectively

needed for clarifying the effect of volatilization on the environmental fate of butachlor. For pyrazosulfuron-ethyl, the DT_{50}s were 3.1 and 1.6 days for S1 and S2, respectively (Table 3). Pyrazosulfuron-ethyl in S2 also dissipated faster than in S1. Hydrolysis of sulfonylurea herbicides similar to pyrazosulfuron-ethyl showed a marked effect by temperature on degradation rate and half-life. The average decrease in DT_{50} for each 5°C increase in temperature was 1.3-fold, 1.6-fold, 2.1-fold and 2.4-fold for thifensulfuron-methyl, primisulfuron-methyl, prosulfuron, and rimsulfuron, respectively (Dinelli et al. 1997).

Table 3 DT_{50} (days) for butachlor and pyrazosulfuron-ethyl in paddy water for S1 and S2 experiments

	Butachlor		Pyrazosulfuron-ethyl	
Water	S1	S2	S1	S2
R^2	0.986	0.899	0.995	0.975
DT_{50} (day)	3.2	2.5	3.1	1.6
DT_{50}^{a} (95 confidence intervals)	(2.3–5.1)	(1.4–3.4)	(2.6–3.9)	(1.1–3.2)

R^2 is the coefficient of determination

[a] Lower and upper 95% confidence intervals are provided in parentheses

In summary, the MPL has provided a useful tool for the measurement of herbicide loss due to various environmental factors. The herbicides butachlor and pyrazosulfuron-ethyl were found to dissipate from rice paddy water faster during the summer than the spring crop season. The major dissipation pathway for both herbicides in the paddy water was through degradation. The behavior of these two herbicides appeared to exhibit different contributions of degradation processes based on temperature. However, further investigation on degradation processes in paddy water as well as in soil will help to clarify the mechanisms that determine the fate of these herbicides in paddy environment.

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References

Ayano E, Hi Kanazawa, Ando M, Nishimura T (2004) Determination and quantitation of sulfonylurea and urea herbicides in water samples using liquid chromatography with electrospray ionization mass spectrometric detection. Anal Chim Acta 507:211–218

Chen YL, Chen CC (1978) Photodecomposition of a herbicide, butachlor. J Pestic Sci 3:143–148

Chen YL, Chen JS (1979) Degradation and dissipation of herbicide butachlor in paddy fields. J Pestic Sci 4:432–438

Dinelli G, Vicari A, Bonetti A, Catizone P (1997) Hydrolytic dissipation of four sulfonylurea herbicides. J Agric Food Chem 45:1940–1945

Doan NH, Thuyet DQ, Ok J, Watanabe H (2009) Development of a method for determination of butachlor and pyrazosulfuron-ethyl in water using HPLC. P Int Symp Environ Iss 81–87

Inao K, Kitamura Y (1999) Pesticide paddy field model (PADDY) for predicting pesticide concentrations in water and soil in paddy fields. J Pestic Sci 55:38–46

IUPAC (2012) The global network for information and properties on agrochemicals. Available via http://sitem.herts.ac.uk/aeru/iupac. Accessed 8 June 2012

Iwafune T, Inao K, Horio T, Iwasaki N, Yokoyama A, Nagai T (2010) Behavior of paddy pesticides and major metabolites in the Sakura River, Ibaraki, Japan. J Pestic Sci 35(2):114–123

Nhung DTT, Phong TK, Watanabe H, Iwafune T, Thuyet DQ (2009) Simulating the dissipation of two herbicides using micro paddy lysimeters. Chemosphere 77:1393–1399

Sabik H, Jeannot R, Rondeau B (2000) Multiresidue methods using solid-phase extraction techniques for monitoring priority pesticides, including triazines and degradation products, in ground and surface waters. J Chromatogr A 885:217–236

Samanta S, Kole RK, Chowdnury A (1999) Photodegradation of metsulfuron-methyl in aqueous solution. Chemosphere 39(6): 873–879

Sarmah AK, Sabadie J (2002) Hydrolysis of sulfonylurea herbicides in soils and aqueous solutions: a review. J Agric Food Chem 50:6253–6265

Takagi K, Fajardo FF, Ishizaka M, Phong TK, Watanabe H, Boulange J (2012) Fate and transport of bensulfuron-methyl and imazosulfuron in paddy fields: experiment and model simulation. Paddy Water Environ 10:139–151

Thuyet DQ, Hien TQ, Watanabe H, Saito H, Phong TK, Nishimura T (2010) Micro paddy lysimeter for monitoring solute transport in paddy environment. Paddy Water Environ 8:235–245

Thuyet DQ, Watanabe H, Takagi K, Yamazaki K, Nhung DTT (2012) Behavior of nursery-box-applied imidacloprid in micro paddy lysimeter. J Pestic Sci 37:20–27

Vulliet E, Emmelin C, Chovelon JM (2004) Influence of pH and irradiation wavelength on the photochemical degradation of sulfonylureas. J Photochem Photobiol A Chem 163:69–75

Watanabe H, Nguyen MHT, Komany S, Vu HS, Phong TK, Asami Y, Tournebize J (2006) Applicability of ELISA in pesticide monitoring to control runoff of bensulfuron-methyl and simetryn from paddy fields. J Pestic Sci 31:123–129

Watanabe H, Nguyen MHT, Souphasay K, Vu SH, Phong TK, Tournebize J, Ishihara S (2007) Effect of water management practice on pesticide behavior in paddy water. Agric Water Manag 88:132–140

Watanabe H, Inao K, Vu SH, Phong TK, Ishihara S, Takagi K, Tournebize J (2008) Chapter 8: pesticide exposure assessment in rice paddy areas: a Japanese perspective. Pesticide risk assessment in rice paddies, Theory and Practice

Xu J, Li X, Xu Y, Qiu L, Pan C (2008) Biodegradation of pyrazosulfuron-ethyl by three strains of bacteria isolated from contaminated soils. Chemosphere 74:682–687

Zheng W, Yates SR, Papiernik SK (2008) Transformation kinetics and mechanism of the sulfonylurea herbicides pyrazosulfuron-ethyl and halosulfuron-methyl in aqueous solutions. J Agric Food Chem 56:7367–7372