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Alternative Water Management for Controlling Simetryn and Thiobencarb Runoff from Paddy Fields

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Paddy fields are the main non-point sources of environmental pollution in Japan since they account for more than 50% of the agricultural land, and consequently, use about half of the domestic agricultural pesticides. Previously, a number of rice pesticides were detected in river and lake systems (Nagafuchi et al., 1994; Tanabe et al., 1996) and the impact of pesticides in surface water on fish, algae and aquatic plants has been reported (Ueji and Inao, 2001). However until recently, few management practices are recommended to Japanese farmers to prevent pesticide runoff.

Simetryn [N^2, N^4-diethyl-6-methylthio-1,3,5-triazine-2,4-diamine] and thiobencarb (S-4-chlorobenzyl diethylthiocarbamate) are the principal herbicides in Japan. However, little is known about their behavior in actual paddies in Japan especially under controlled water management.

The importance of the water management has been emphasized for controlling pesticide runoff. Holding water is a good mitigative practice for pesticide problems in rice paddies. The appropriate duration of the water holding period in Japan has been previously discussed (Ishii et al. 2004; Watanabe et al. 2006). However, information is limited to a few specific pesticides.

Meanwhile, intense monsoon rainfalls during the cultivation period make the water management more complicated. Nagafuchi et al. (1994) reported that pesticide loss from an intense rainfall after application reached 20-30%. In order to control pesticide runoff following appreciable rainfall events, the importance of an excess water storage capacity (EWSC) in paddies that is created by installing a high drainage gate to store rainfall water has been proven by Watanabe et al. (2006). Although a few centimeters of EWSC remarkably reduces herbicide runoff during significant rain events, the appropriate EWSC for practical rice production in Japan has not been documented.

Therefore, our objectives are to monitor the water balance and fate of simetryn and thiobencarb in paddy water and paddy surface soil using two different EWSCs (1 and 3 cm-depths) and to evaluate the effectiveness of the EWSC in reducing the loss of the applied herbicides by runoff during rainfall events.

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MATERIALS AND METHODS

Two paddy plots of 0.15 ha (28 × 48m) in the experimental farm of the Tokyo University of Agriculture and Technology (TUAT) in Fuchu, Tokyo were used for this study in 2004. The plots contain a light clay soil with an organic carbon content of 3.96%. Automatic irrigation systems (Rakutaro®, Nihon System Kaihatsu Co. Ltd.) were installed to keep the paddy water depth at 2 to 4 centimeters. A 7cm high (from the soil surface) drainage gate was installed in one plot (denoted as plot 1) while the other plot (denoted as plot 2) had the lower 5 cm one. We define the depth between the top of the drainage gate and paddy water level as the excess water storage depth (EWSD), and the average EWSD during the monitoring period to be the excess water storage capacity (EWSC). Consequently, these setups implied a minimum EWSC of 3 cm for plot 1 and of 1 cm for plot 2.

The volumes of the irrigation from the pipeline and precipitation were recorded. The depth of the paddy water was monitored and the volume of the surface drainage rate through a 30-cm wide rectangular drainage weir was calculated using the paddy water level data. The evapotranspiration (ET) value was obtained from a lysimeter having four growing rice plants placed in plot 1. Subsurface water loss including percolation and lateral seepage were calculated from other components of the water balance equation (Watanabe et al., 2006).

The granular herbicide KumishotSM® (Kumiai Chemical Industry, Tokyo, Japan) containing simetryn and thiobencarb was applied on June 24th, 2004. The application rates of the active ingredient were 450gha^{-1} and 1500gha^{-1} for the simetryn and thiobencarb, respectively.

A rainfall simulation was carried out to clarify the response of the two management scenarios to ordinary rainfall events. A precipitation pattern for June 2002 was then selected because it had a similar monthly total precipitation with an average of archival records, but concentrated in a short and intense rainfall pattern. A simple simulation was carried out by irrigating water directly to the center of the plots. The flow rate, water volume, time span of the simulation and field water data before and after the simulation were recorded.

Composite samples from 5 spots (four corners and the center) were taken from each plot. At each spot, a 30-cm diameter PVC ring was driven into the muddy layer, and the inner water was first sampled and then removed by an aspirator. Samples of the surface soil (0-1cm) were obtained using a stainless spoon. Sampling was carried out at 0, 1, 3, 7, 14, 22, and 35 days after the herbicide application (DAHA). All samples were kept frozen until the chemical analysis.

All standards and reagents used in this study were of analytical grade and were purchased from Wako Pure Chemical Industries (Osaka, Japan). The water samples were analyzed using the method developed by Tanabe et al. (1998). Briefly, the water was filtered through 1.2 μm glass filters (GF/C, Whatman) then solid phase extracted using a Waters Sep-Pak Plus PS-2 cartridge. Prior to use, the cartridges were washed with 5ml of acetone, followed by 5ml of distilled water. An appropriate volume of the water sample was loaded into the cartridge at the flow rate of 10ml min^{-1}. The cartridges were then washed with 10ml of distilled water. The cartridges were air-dried for 10 min before the herbicides were eluted by 6ml of acetone at the rate of 1ml min^{-1}. The acetone extracts were collected and evaporated to 1ml by a gentle stream of nitrogen.

The water samples were analyzed using an Agilent (Palo Alto, USA) 6890N gas chromatograph equipped with an Agilent 5973 MSN mass spectrometer and a fused-silica DB-5 MS capillary column (J&W Scientific, Rancho Cordova, USA). The mass spectrometer was set in the selected ion monitoring mode. The detection limits are 0.01μg l^{-1} for both herbicides and the recoveries (n=3) are 83.2 ± 3.5% and 86.6 ± 1.2% for simetryn and thiobencarb, respectively.

The soil samples were centrifuged at 12,000 rpm for 15 minutes and then ground in a ceramic mortar. The final moisture content was measured. A 20-g soil sample was weighed into a 200ml Erlenmeyer flask containing 100ml of acetone. The mixture was sonicated for 10 minutes and then shaken for 2 hours. The soil was then removed from the solution by filtering the slurry solution. The residual soil was washed twice with 20ml of acetone. All the filtrates were combined and the acetone solution was evaporated to 10ml with a rotary evaporator. The remaining solution mixed with 30ml of saline water (NaCl 10%) was extracted twice with 30ml of dichloromethane in a separatory funnel. The two dichloromethane extracts were combined and dried with 20g of anhydrous sodium sulfate. The extract was then filtered through silicone-treated filter paper (1PS, Whatman). Dichloromethane was rotor-evaporated from the filtered solution at 35°C. The residue was dissolved in 5ml of acetone using ultrasonication. The final samples were kept at 4°C before the GC analysis.

The soil samples were analyzed using a Shimazu 2010 gas chromatograph equipped with a Flame Thermoionic Detector (FTD) and a DB-17capillary column (J&W Scientific, Rancho Cordova, USA). The limit of detection is 10.0μg kg^{-1}. The recovery values (n=3) are 108.8 ± 4.5% and 98.7 ± 1.8%, respectively, for simetryn and thiobencarb.

RESULTS AND DISCUSSION

The total precipitation during the monitoring period in 2004 was 13.6 cm that is remarkably lower than the average value for the period of 22 years of 16.1 and 17.0 cm for June and July, respectively. In addition, there was only one significant 3 cm day^{-1} rainfall event from the herbicide application date of June 24 until the end of the monitoring. Therefore, a short and intense rainfall pattern for June 2002 was simulated at 4, 7, 9 and 16 DAHA. Three main simulated rainfall events shortly after the herbicide application at 4, 7, 9 DAHA had depths of 3.06, 5.16 and 3.78 cm, respectively.

Table 1. Water balance in plot 1 and plot 2.

		Inflow (cm)		Outflow (cm)		
		Irrigation	Precipitation	Runoff	Percolation	ET
Plot 1	Total	63.01	19.41	0.16	52.91	29.86
	Average	1.66	0.51	0.00	1.39	0.79
Plot 2	Total	66.40	19.41	4.63	52.72	29.86
	Average	1.75	0.51	0.12	1.39	0.79

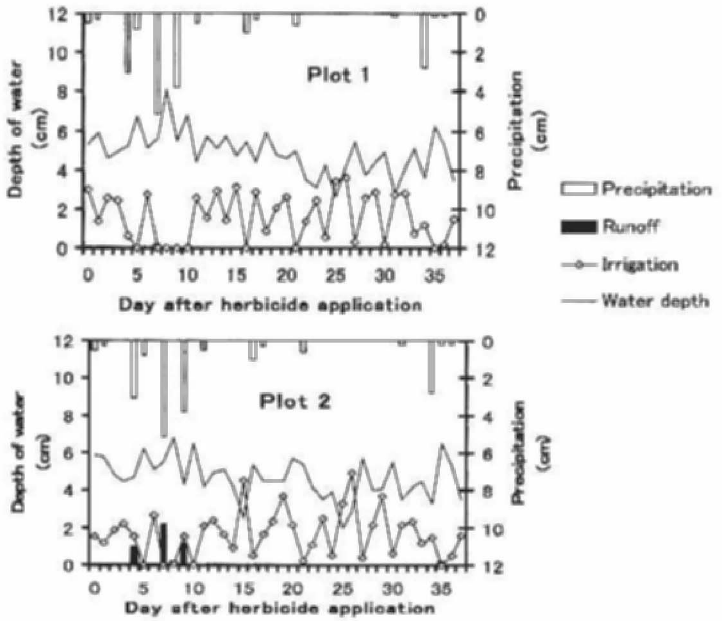

Figure 1. Water balance monitoring in plot 1 and plot 2

The average values of the daily irrigation, precipitation, runoff, percolation and evapotranspiration of the two experimental plots during the 38 day monitoring period (Table 1) were agreement with Japanese published data (Mizutani, 1995). The irrigation scheme managed by automatic irrigation systems in both plots reduced the paddy runoff and saved significant irrigation water as compared to the continuous irrigation and overflow drainage scheme in previous experiments (Watanabe et al. 2006).

Figure 1 shows the daily depth of the paddy water, irrigation and drainage in plots 1 and 2. Since the height of the drainage gate or the EWSC in plot 1 was 2 cm greater than that of plot 2, plot 1 had almost no runoff even for the intense rainfall event. The runoff depth of only 0.16 cm and 0.08 cm were observed in the significant rainfall events of 5.16 cm at 7 DAHA and 3.78 cm at 9 DAHA, respectively. Meanwhile, in plot 2 having only 1cm of EWSC, the paddy water

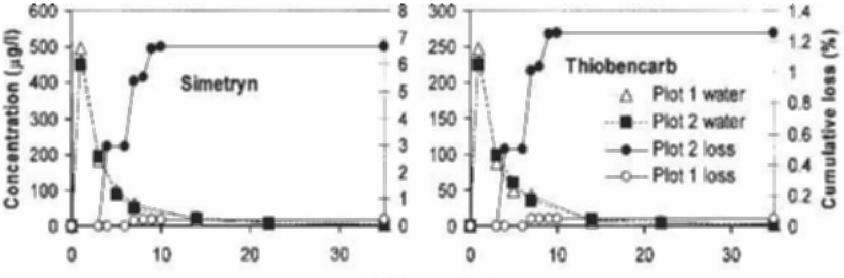

Figure 2. Concentrations of simetryn and thiobencarb in paddy water and cumulative losses through runoff

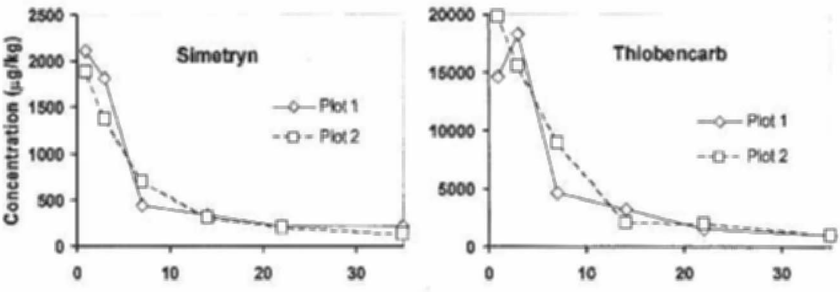

Figure 3. Concentrations of simetryn and thiobencarb in surface soil (0-1cm)

runoff often occurred even in ordinary rainfall events. The substantial runoff volumes were 0.95, 2.16 and 1.14 cm at 4, 7 and 9 DAHA corresponding to the precipitations of 3.06, 5.16 and 3.78 cm, respectively. Nevertheless, the amount of runoff water in plot 2 was less than 5% of the total water input since the intermittent irrigation scheme (as opposed to the continuous irrigation and overflow drainage scheme) was imposed during the monitoring period.

Figure 2 shows the herbicide concentrations and their losses through runoff from plots 1 and 2 during the monitoring period. The concentrations of both simetryn and thiobencarb in the water peaked at 1 DAHA and then exponentially decreased thereafter. The simetryn concentrations ranged from the maximum of 496.3 and 450.7 µg l^{-1} at 1 DAHA, respectively, in plot 1 and plot 2 to 3.5 µg l^{-1} in both plots at the end of the monitoring (35 DAHA). The thiobencarb concentrations peaked at 246.6 µg l^{-1} in plot 1 and at 225.6 µg l^{-1} in plot 2 at 1 DAHA and were 2.2 and 1.7 µg l^{-1}, respectively, for plot 1 and plot 2 at 35 DAHA.

The general trend of simetryn in both plots was comparable with the pattern reported by Inao et al. (2001). However, the maximum concentration observed by Inao et al. (2001) was only 300 µg l^{-1} knowing that all the experimental plots received the same simetryn application rate. This variation may be due to the difference in the hydrological conditions, especially the ponding depth at the time of sampling as well as the difference in the formulation, and therefore, implicates the importance of the farming practice to the fate of the agrochemicals. For the case of thiobencarb, Amano et al. (2001) reported similar results with the maximum concentration of 40.5g $10a^{-1}$ at 1 DAHA using a similar application rate. During the monitoring period, the concentrations of herbicides in water between the two plots were not significantly different. This similarity was probably due to the almost identical hydrological data between the plots that resulted in similar dilution factors for the compound. However, Watanabe et al. (2006) reported that there was an appreciable difference in the herbicide concentrations between the two plots with different dilution factors caused by a continuous irrigation and overflow drainage scheme in one plot and a water holding practice in the other.

Figure 3 shows the herbicide concentrations in the 0-1cm surface paddy soil of plots 1 and 2 during the monitoring period. The simetryn concentrations in the surface soil ranged from 2106 μg kg^{-1} to 218 μg kg^{-1} in plot 1 and from 1886 μg kg^{-1} to 130 μg kg^{-1} in plot 2. The thiobencarb concentrations ranged from the maximum of 14654 and 19672 μg kg^{-1} at 1 DAHA down to 953 and 926 μg kg^{-1} at 35 DAHA for plot 1 and plot 2, respectively. For both herbicides, the concentrations in the surface soil between the two plots were not significantly different during the monitoring period. It should be noted that the herbicide transport process through the vertical percolation to the subsurface layer also contributed to the dissipation of the herbicide in the 0-1 cm surface soil.

In this study, both herbicides dissipated slower in the soil than in the water. The dissipation of both herbicides in the water as well as the soil surface compartment seemed to follow the biphasic first order kinetics as reported by Fajardo et al. (2000). Data from the first week (for water) and from the first two weeks were used for the first phase kinetic analysis. In this study, the DT_{50} and DT_{90} of simetryn and thiobencarb (Table 2) from the first phase are shorter than those previously reported. In the paddy water, Amano et al. (2001) provided a DT_{50} of about 4 days for thiobencarb while the DT_{50} of simetryn was estimated to be about 3 days from the data of Inao et al. (2001).

Table 2. DT_{50} and DT_{90} of herbicides in paddy water and surface soil.

	Plot 1				Plot 2			
	Paddy water		Surface soil		Paddy water		Surface soil	
	DT_{50}	DT_{90}	DT_{50}	DT_{90}	DT_{50}	DT_{90}	DT_{50}	DT_{90}
Simetryn	2.0	6.6	4.61	15.2	1.9	6.3	5.0	16.7
Thiobencarb	2.4	7.9	5.1	17.1	2.3	7.6	4.0	13.2

Figure 2 shows the simetryn and thiobencarb losses by runoff during the monitoring period as a percent of the applied mass. These losses were significantly different between the two plots as a result of the different water managements. In plot 2, the first runoff event happened at 4 DAHA after a significant rainfall of 3cm (simulated) and then at 7 and 9 DAHA upon 5.1 and 3.8cm of rainfall. Meanwhile only one runoff occurred in plot 1 at 7 DAHA under a simulated 5-cm rainfall. This observation proved the effectiveness of the higher EWSC in plot 1 to store excessive rainfall water and consequently to prevent herbicide runoff. At 7 DAHA, plot 1 lost only 0.21% of the applied simetryn and 0.045% of the applied thiobencarb since the runoff was very small. These losses in plot 2 amounted for 2.96, 2.57 and 1.11% of simetryn and 0.51, 0.50 and 0.21% of thiobencarb at 4, 7 and 9 DAHA, respectively. The extent of these losses, however, is less than those previously reported especially in the paddy plot managed with a continuous irrigation and overflow drainage scheme. Watanabe et al. (2006) reported the mefenacet losses by runoff at 2 and 3 DAHA of respectively 12% and 11% of the applied mass during continuous irrigation and overflow drainage with the corresponding precipitations of 1.7 and 3.3 cm, respectively.

No comparison of loss among the runoff events can be made in plot 1 since there was only one event at 7 DAHA. For plot 2, although the runoff volume in the second event (7 DAHA) was the largest, the herbicide loss in this event was less than that of the first even (4 DAHA) because the herbicide concentrations have already diminished. The simetryn concentrations in the runoff decreased from 140 $\mu g\ l^{-1}$ to 50.6 $\mu g\ l^{-1}$ in the first and second events (4 and 7 DAHA) and the corresponding values of thiobencarb were 79.7 and 34.8 $\mu g\ l^{-1}$ with the corresponding runoff volumes of 0.95 and 2.2 cm, respectively. Therefore, controlling the water runoff in the period shortly after the herbicide application is critical, and increasing the EWSC proved to be a good alternative management for this purpose.

The total losses of simetryn in plot 1 and plot 2 were 0.21% and 6.67% of the applied mass, respectively. The thiobencarb runoff amounted to 0.045% and 1.26%, respectively, for plot 1 and plot 2. However, the two experimental plots did not lose as much herbicide when compared to other studies. Inao et al. (2001) reported that a continuous irrigation scheme might lose 60.4% and 40.5% of the applied simetryn and molinate, respectively. Similarly Watanabe et al. (2006) also indicated that the total mefenacet and bensulforon-methyl runoff losses might go up to 38% and 49% of the applied mass, respectively, in a continuous irrigation scheme. The reduction of the herbicide losses from the plots with some EWSC in this study was apparent and the continuous irrigation practice inducing significant amounts of herbicide losses should be discouraged.

Therefore, an appropriate EWSC is important for controlling herbicide runoff from paddy fields especially during the earlier period when the herbicide concentration in the paddy water is high. The recommended key periods for herbicide runoff control could be 7 and 8 days, respectively, for the simetryn and thiobencarb from their DT_{90} dissipation period. In California, rice growers are required to hold treated water on site to promote the dissipation up to 30 days when using granular thiobencarb (Helliker, 2002). However, in Japan, no appropriate extension program as well as regulations are in place except the recommendation by pesticide manufacturers of a water holding period of 3-4 days after application.

As a good agricultural practice for controlling simetryn and thiobencarb runoff from paddy fields pointed out from this study, the appropriate water holding practice should be at least 8 days. Also,during the water holding period, a paddy field should be managed with a EWSC of at least 2cm. However, in order to facilitate the effective extension program for herbicide runoff control, the appropriate WESC and its practical application in the paddy rice production depending on the local climate need to be investigated.

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