

## Excess water storage depth—a water management practice to control simetryn and thiobencarb runoff from paddy fields

Thai Khanh PHONG, Hirozumi WATANABE<sup>\*</sup>, Thai Quoc HIEN<sup>†</sup>, Son Hong VU<sup>††</sup>,  
Taku TANAKA<sup>†††</sup>, Dang Thi Tuyet NHUNG and Takashi MOTOBAYASHI

*Tokyo University of Agriculture and Technology, 3–5–8, Saiwaicho, Fuchu, Tokyo 183–8509, Japan*

*† Vietnam Institute of Water Resources Research, 179 Tay Son Street, Hanoi, Vietnam*

*†† Department of Science and Technology, Ministry of Agriculture and Rural Development, 2 Ngoc Ha Street, Hanoi, Vietnam*

*††† University of Milan, via Festa del Perdono 7–20122 Milano, Italy*

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Experiments were carried out to verify the effectiveness of the excess water storage depth (EWSD) in reducing runoff losses of simetryn and thiobencarb from paddy fields upon appreciable rainfall events. A paddy plot having an EWSD of 2 cm was effective in controlling runoff with the herbicide losses of less than 1% of the applied herbicides. Meanwhile, a plot with 0-cm EWSD lost 18.1 and 3.7% of the applied mass of simetryn and thiobencarb, respectively. Therefore, an appropriate EWSD is essential during the recommended 7-day water holding period in order to completely hold the water inside the field in case of rainfall. ©Pesticide Science Society of Japan

**Keywords:** excess water storage depth, paddy fields, water management, runoff, simetryn, thiobencarb.

### Introduction

Pesticide contamination of surface water has long been attributed to non-point source pollution from agricultural fields. In Japan, a number of researches have been conducted to study the relation between agricultural practice and the concentrations of pesticide in surface water such as rivers or lakes. Because paddy fields account for more than 50% of agricultural lands in Japan, pesticide consumption in paddy fields is expected to be high. Consequently, it was found that the highest occurrence of pesticides in open water usually coincides with the application period of pesticides in paddy fields.<sup>1,2)</sup>

The discharge of water from paddy fields that contains appreciably high concentrations of pesticides is obviously responsible for this pollution. Besides water discharge by the drainage practice, an other significant cause of pesticide runoff from paddy fields is water discharge during and after major rainfall events. Nagafuchi *et al.*<sup>3)</sup> reported that losses of pesticides could reach 20–30% if a significant rainfall event followed pesticide application. Ebise and Inoue<sup>1)</sup> also indi-

cated that pesticide runoff from paddy fields increased during heavy storm events. Meanwhile, Vu *et al.*<sup>4)</sup> reported increased discharge from rice paddies after rainfall events exceeding 1.5 cm/day.

Therefore, controlling the discharge upon major rainfall events is important to prevent pesticide contamination in the aquatic environment. A solution for this matter could be the excess water storage depth (EWSD) which is extra depth obtained by the high boundary of a paddy to accommodate excess precipitation. The water storage depth has been known to be a key factor for many aspects of flood prevention in paddy fields; however, its ability to control pesticide runoff from paddy fields from a water quality point of view has been rarely discussed. The effectiveness of the EWSD was clearly demonstrated in rain-fed paddies where almost 100% of the intense rainfall can be stored with a 30 cm weir height<sup>5)</sup>; however, in Japan, the water level in the paddies is kept shallow to promote tilling and heading of the rice<sup>6)</sup> so only low bunds and weirs are available. Under this circumstance, several authors<sup>7–9)</sup> have reported that even small EWSDs created by the high drainage gate prevented herbicide runoff during significant rain events.

The EWSD is a complement to the water holding period in order to have better control of pesticide runoff from paddy fields, especially in the Asian monsoon region. The EWSD

\* To whom correspondence should be addressed.

E-mail: pochi@cc.tuat.ac.jp

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helps to ensure that the water is held over the holding period, thus reducing pesticide loss during rainfall events. While the water holding period is now being paid significant attention, extended from 3–4 days to 7 days, the EWSD issue has rarely been discussed. Considering that rainfall in the region is high, the establishment of an appropriate EWSD is necessary to reduce potential pesticide runoff from paddy fields.

In their studies in 2001 and 2003, Watanabe *et al.*<sup>8,9)</sup> proved the advantage of the water holding period and the EWSD over the overflow drainage practice in reducing runoff of pesticides from paddy plots. In 2004, Phong *et al.*<sup>7)</sup> compared two EWSDs and reported that the higher EWSD of 3 cm is significantly more effective than that of 1 cm; however, in order to prove the usefulness of the EWSD in paddy fields, a systematic experiment with several EWSD values is needed. Therefore, our study aimed to further evaluate the effectiveness of the EWSD by providing systematic comparison in the control of simetryn and thiobencarb runoff from paddy fields. For this objective, two paddy plots with different EWSDs (2 and 0 cm) were used to monitor the fate and transport of two commonly applied rice herbicides, simetryn (2,4-bis(ethylamino)-6-methylthio-1,3,5-triazine and thiobencarb *S*-(4-chlorobenzyl) *N,N*-diethylthiocarbamate.

## Materials and Methods

### 1. Field experiment

Pesticide fate and transport monitoring was conducted at the experimental farm of Tokyo University of Agriculture and Technology (TUAT) in Fuchu, Tokyo in 2005. Two small paddy plots of similar size (138 m<sup>2</sup>) were set up inside a standard paddy plot (3000 m<sup>2</sup>), using plastic bund with enforced soil between two plastic sheets (Fig. 1). The soil in these plots is a light clay soil with an organic carbon content of 3.6%.

Both plots were intermittently irrigated, which started when the water level was lower than 3 cm and ceased when the level reached 5 cm. In Plot 1 (P1), a high drainage gate was installed with the height from the paddy soil to the bottom of the drainage gate set at 7.0 cm. In Plot 2 (P2), a lower drainage gate of 5 cm was installed. This setup provided a minimum EWSD of 2 cm in P1 and 0 cm in P2.

The water level was automatically measured in the two plots and the volume of water discharge through a 30-cm wide rectangular drainage weir was calculated using water level data. Other water balance components, including precipitation, irrigation, evapotranspiration, and percolation, were also monitored or calculated. Detailed procedures for measuring and calculating water balance can be found elsewhere.<sup>9)</sup>

Simetryn and thiobencarb as components of the commercial granular herbicide KumishotSM<sup>®</sup> (Kumiai Chemical Industry, Tokyo, Japan) were applied on June 20, 2005. The application rates of the active ingredient were 450 g/ha and 1500 g/ha for simetryn and thiobencarb, respectively.

Similar to the previous experiment,<sup>7)</sup> rainfall simulation was carried out to clarify the response of two management

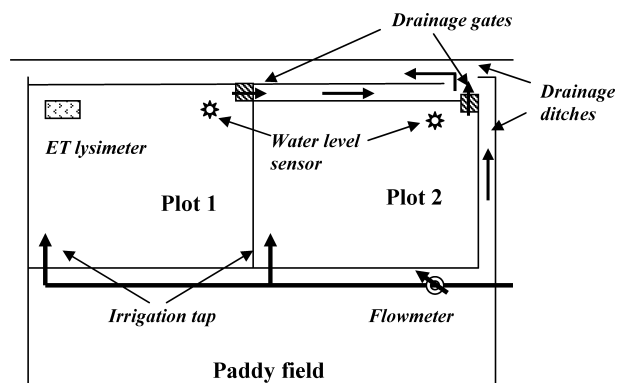


Fig. 1. Layout of the experimental plots.

scenarios to major rainfall events. Precipitation pattern in June 2002 was selected because it had a similar monthly total precipitation to the average in archival records (for 22 years) but concentrated in a short and intense rainfall pattern. This rainfall simulation was simply carried out by irrigating water directly at the center of the plots. Flow rate, water volume, and duration of the simulation were recorded to calculate the actual water depth.

### 2. Sampling and analysis

#### 2.1. Sampling

Composite samples were taken similar to previous experiment.<sup>7)</sup> Water and soil were sampled at 0, 1, 3, 7, 14, 22, and 35 days after herbicide application (DAHA) during flooding. In addition, soil samples of 50, 70 and 80 DAHA in P1 were also taken when the soil was dry after the midterm drainage. All samples were kept frozen until chemical analysis.

#### 2.2. Sample extraction and analysis

The methods of extraction for water and soil samples are described elsewhere.<sup>7)</sup> Briefly, water samples were filtered and then solid phase extracted prior to chromatographic analysis. Soil samples were centrifuged and extracted with acetone before liquid–liquid extraction with the help of a diatomaceous earth cartridge.

Soil and 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 detection limits for water samples are 0.01 µg/l for both herbicides and the recoveries ( $n=3$ ) were  $86.8 \pm 0.2\%$  and  $81.4 \pm 1.4\%$  for simetryn and thiobencarb, respectively. The detection limits for soil samples are 10 µg/kg for both herbicides and the recoveries ( $n=3$ ) were  $83.0 \pm 5.6\%$  and  $60.7 \pm 2.2\%$  for simetryn and thiobencarb, respectively.

## Results and Discussion

### 1. Water balance monitoring

Water balance components, including irrigation, discharge,

**Table 1.** Water balance in the paddy plots

Input (cm)	P1		P2	
	Total	Average	Total	Average
Irrigation	31.4	0.90	23.0	0.66
Precipitation	30.3	0.87	30.3	0.87
Natural	20.5	0.59	20.5	0.59
Simulation	9.8	0.28	9.8	0.28
Total	61.7	1.76	53.3	1.52
Output (cm)				
Discharge	4.8	0.14	19.8	0.57
Percolation	43.3	1.24	25.3	0.72
ET	14.9	0.43	14.9	0.43
Total	63.0	1.80	60.0	1.71

percolation and evapotranspiration, of the two experimental plots during the 35-day monitoring period are shown in Table 1. Total precipitation, including simulated rainfall during the monitoring period, was 30.3 cm scattered over the first 3 weeks, which was greater than the average value of precipitation for the period of June and July. Six significant rainfalls of more than 2 cm that could cause discharge in studied plots occurred at 2, 4, 7, 9, 14 and 19 DAHA, respectively. Three of these were simulated at 4, 7 and 9 DAHA, respectively.

The intermittent irrigation practice in both plots again showed its effectiveness in reducing paddy discharge and saved significant irrigation water as compared to the continuous irrigation and overflow drainage scheme in previous experiments.<sup>8,9)</sup> The irrigation amount was also reduced due to the abundance of precipitation (natural and simulated) during this period. There was a significant difference in terms of percolation between the two plots, possibly because of the leak under the concrete bund of P1 and the inconsistency of the bed soil layer. This difference consequently resulted in a higher irrigation requirement for P1. Therefore, careful field preparation to control leaks and reduce percolation is also an important factor in saving water in rice cultivation.

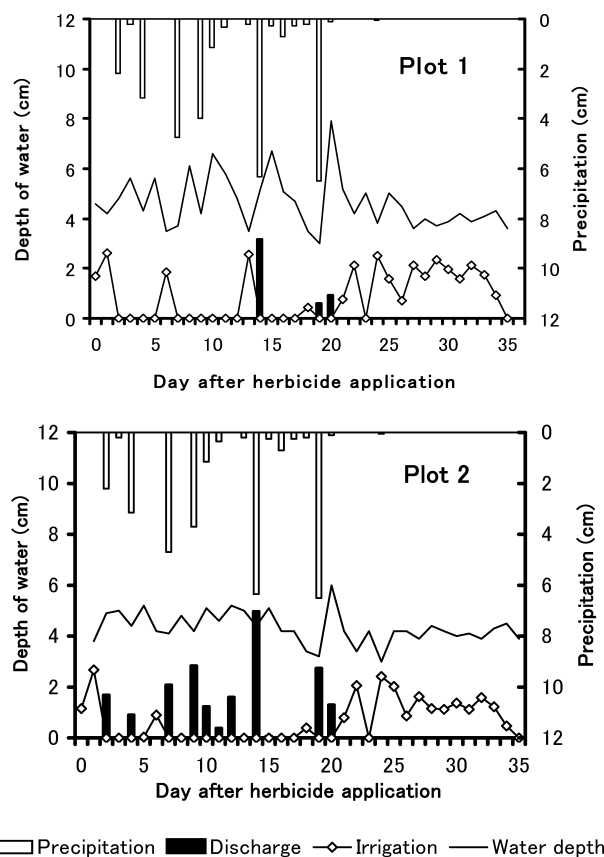
The depth of paddy water fluctuated more in P1 than in P2 (Fig. 2), especially during the first 3 weeks because P1 could store more rainfall water than P2. The EWSD has shown its effectiveness in utilizing rainfall water and, moreover, it has helped to control discharge caused by rainfall. Since the EWSD of P1 was about 2 cm greater than that of P2, P1 had little discharge except for during very large rainfall events of more than 4 cm. Meanwhile, in P2 with an average EWSD of only 0.65 cm, paddy water discharge often occurred even in ordinary rainfall events. The average discharge values were 0.96 and 1.65 cm per event for P1 and P2, respectively. The largest discharge volume of P2 was 4.96 cm while that of P1 was 3.19 cm in response to rainfall of 6.35 cm at 14 DAHA. It

should be noted that the water balance in P2 was not fulfilled because there was an inflow leak from the surrounding plot (Fig. 1) that lasted for 5 days from 9 to 13 DAHA. At that moment, the percolation rate was assumed to be equal to the mean value of the percolation rate during the monitoring period. This accident also contributed to the high ratio of discharge from P2.

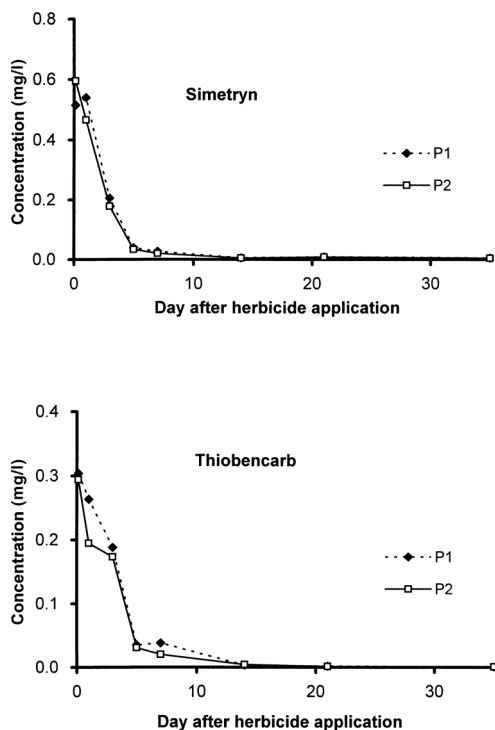
A similar effect of the EWSD was also demonstrated in previous studies. Watanabe *et al.*<sup>8)</sup> reported no discharge during a monitoring study of an intermittent irrigation scheme with 3.5 centimeters of EWSD. The same setting prevented discharge in most rainfall events, except for two extremely large events of 5.6 and 7.6 cm.<sup>9)</sup> Phong *et al.*<sup>7)</sup> reported almost no discharge in a paddy plot with an EWSD of 3 cm but there were three discharge cases in the plot with an EWSD of 1 cm.

**2. Pesticide behavior in paddy water**

The concentration of both simetryn and thiobencarb peaked within 1 DAHA and then quickly decreased during the early period (Fig. 3). The concentrations between the two plots were not significantly different but concentrations in P2 were consistently lower than those in P1. The maximum concentrations of simetryn were 540 and 595  $\mu\text{g/l}$  for P1 and P2, respectively while the corresponding values of thiobencarb were 304 and 294  $\mu\text{g/l}$ . At the end of monitoring (35 DAHA),



**Fig. 2.** Water balance monitoring in plots 1 and 2.



**Fig. 3.** Observed simetryn and thiobencarb concentrations in paddy water for plots 1 and 2.

simetryn concentrations remained at about  $5 \mu\text{g/l}$ . but those of thiobencarb had decreased to  $1 \mu\text{g/l}$ . The results of this study were comparable with other data reported previously.<sup>7,9,10)</sup>

The dissipation process of both herbicides in this study fitted with biphasic first order kinetics, indicating an initial rapid dissipation phase followed by a slow phase in which herbicide concentrations remain fairly stable. However, the turning point between the two phases was at 7 DAHA for simetryn and at 14 DAHA for thiobencarb. This type of kinetics was reported by several authors for the behavior of pesticides under flooded conditions.<sup>2,11,12)</sup> This phenomenon is probably typical for paddy conditions because of the dynamic adsorption-desorption equilibrium between water and soil compartments.

Using biphasic first order kinetics, the half-life ( $DT_{50}$ ) of simetryn and thiobencarb were calculated (Table 2). The half-lives of both herbicides in the first phase were much shorter than in the second phase. For simetryn, similar  $DT_{50}$  values of about 2 days under paddy conditions have been reported previously.<sup>7,8)</sup> The  $DT_{50}$  of simetryn was also estimated to be about 3 days from the data of Inao *et al.*<sup>10)</sup> For thiobencarb, the  $DT_{50}$  values were slightly more than 2 days in this study, comparable with recent studies in Japanese paddies.<sup>7-9)</sup> Also in Japanese paddies, Amano *et al.*<sup>13)</sup> provided a  $DT_{50}$  of about 4 days for thiobencarb and Parveen *et al.*<sup>14)</sup> determined the  $DT_{50}$  as 2.9 and 6.9 on a large farm and in an experimental plot, respectively. In other studies from different countries, half-lives of thiobencarb have been reported to be from 3.4 to

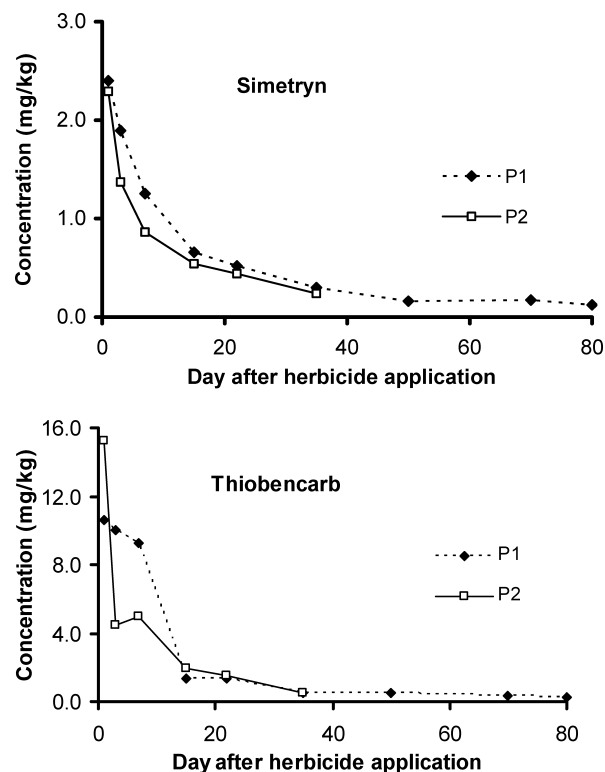
**Table 2.**  $DT_{50}$  of herbicides in paddy water and surface soil

		Simetryn		Thiobencarb	
		Plot 1	Plot 2	Plot 1	Plot 2
Paddy water (day)	1 <sup>st</sup> phase	1.4	1.3	2.1	2.2
	2 <sup>nd</sup> phase	16.2	17.7	9.2	9.7
Surface soil (day)		11.5	11.5	7.2	8.1

9 days.<sup>15,16)</sup> Several factors may contribute to this variation, including differences in formulation, field condition (soil type, climate) and management practices among the studies. Among them, the soil condition is of great importance because it can affect the adsorption-desorption equilibrium between water and soil as well as the degradation process.

### 3. Pesticide behavior in paddy surface soil

Herbicide concentrations in the 0–1 cm surface paddy soil of plots 1 and 2 during the monitoring period were much greater than the corresponding values in the water compartment. Maximum concentrations of both herbicides were reached at 1 DAHA (Fig. 4). Simetryn concentrations in the surface soil ranged from the maximum of 2400 and 2293  $\mu\text{g/kg}$  to 299  $\mu\text{g/kg}$  in P1 and 238  $\mu\text{g/kg}$  in P2 at 35 DAHA, respectively. With a higher application rate, thiobencarb concentrations decreased from 10,610 and 15,240  $\mu\text{g/kg}$  at 1



**Fig. 4.** Observed simetryn and thiobencarb concentrations in paddy surface soil for plots 1 and 2.

DAHA down to 524 and 502  $\mu\text{g}/\text{kg}$  at 35 DAHA for P1 and P2, respectively. The concentrations of the soil samples in P1 in the later period continued to decrease but they were still as high as 123  $\mu\text{g}/\text{kg}$  and 263  $\mu\text{g}/\text{kg}$  at 80 DAHA for simetryn and thiobencarb, respectively. Although there were variations, the concentrations of the two herbicides in P2 were observed to be lower than those in P1. This was consistent with the results in the previous section that the concentrations in water of P2 were also lower than those of P1.

In contrast to the behavior in the water compartment, both herbicides followed the simple first order kinetics in the soil surface compartment. The  $\text{DT}_{50}$  of simetryn and thiobencarb in this study (Table 2) are the same magnitude as those recently reported;<sup>7)</sup> however, for thiobencarb, half-lives from 100 to 200 days have been reported for the soils in Japan, Australia, and the United States.<sup>15)</sup> The probable cause of this significant difference among studies on thiobencarb is the difference in sample volume and soil condition including the redox potential of the soil.<sup>17)</sup> Thiobencarb in shallower soil samples usually has a shorter  $\text{DT}_{50}$  because the samples are more oxidative.<sup>7,18)</sup>

#### 4. Pesticide losses from paddy fields

Since water is the conveying phase of pesticide in paddy fields, the loss of water would correspond with the loss of pesticide. In this study, the cumulative losses of the two studied herbicides were significantly different between P1 and P2. The total herbicide losses in P2, where there was significant water discharge, were 18.1 and 3.7% of the applied mass for simetryn and thiobencarb, respectively. Meanwhile, since drainage was small in P1, only 0.7% of simetryn and 0.1% of thiobencarb were lost from the plot. The relative losses of thiobencarb were significantly lower than simetryn in both plots. This is clearly because of its stronger affinity toward the soil (higher  $K_{oc}$  therefore more adsorption to soil aggregates); thus, most of its applied mass remained in the soil compartment and was not available for loss through discharge.

While major loss of herbicides in P1 occurred only until 14 DAHA after a large rainfall of 6.35 cm, most of the herbicide mass was lost in P2 during the first week after application. In P2, until 7 DAHA, 83.8% of the total thiobencarb loss and 80.6% of the total simetryn loss occurred with the highest single loss at 2 DAHA (Fig. 5). This result indicated that pesticide runoff control during the earlier period is extremely important and the management practice in P2 should be improved to reduce the runoff of pesticide to the environment.

#### 5. Effect of management using EWSD to control pesticide runoff

In order to avoid undesired runoff of rice pesticides, water in paddy fields should be held inside the field for a certain period after pesticide application. In the United States or Australia where precipitation rarely occurs during the application time, water can be held in the field only by stopping the irri-

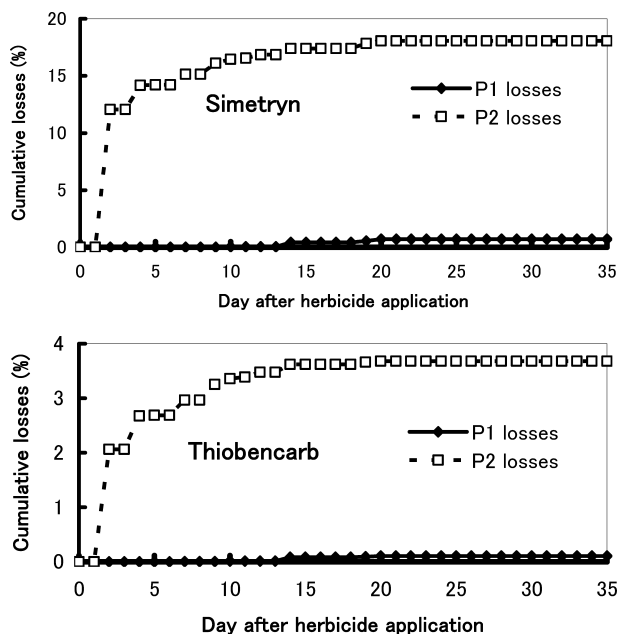
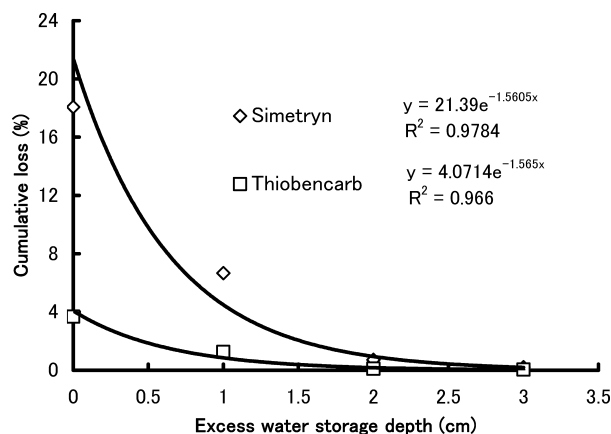


Fig. 5. Cumulative simetryn and thiobencarb losses as % mass applied during the monitoring period.

gation system. However, this practice is not always applicable in Japan or other countries in the monsoon region because of the high frequency of precipitation during the crop season. Moreover, most Japanese farmers practice shallow water management, which requires regular irrigation to ensure ponding conditions. In a survey in the Sakura river basin, Vu *et al.*<sup>4)</sup> reported the water level and EWSD of 296 paddy plots on a randomly selected non-rainy day followed normal distribution functions, with mean values of 5.2 and 0.5 cm for the water level and EWSD, respectively. The data also showed that 113 of 296 surveyed plots had overflow drainage; therefore, the establishment of the EWSD is necessary to control pesticide runoff.

From this study, the reduction of herbicide losses from the plots with a certain EWSD was apparent when plot P1 with an average EWSD of 2.35 cm lost less than 1% of applied herbicides in contrast with heavy losses of up to 18% in plot P2 with an average EWSD of 0.65 cm. The effect of the EWSD is significant, especially during the early period when herbicide concentration in the paddy water is high. With its high EWSD, P1 had no loss until 7 DAHA under rainfall of 4.7 cm. Meanwhile, about 66.7% of simetryn loss and 56% of thiobencarb loss in P2 took place at 2 DAHA under a rainfall of 2.2 cm. Other authors also demonstrated the key role of the EWSD in preventing pesticide loss through water discharge. Phong *et al.*<sup>7)</sup> reported smaller losses of simetryn and thiobencarb in a plot having an EWSD of 3 cm. Watanabe *et al.*<sup>8)</sup> also reported that a paddy plot and a similar set up with a high drainage gate of 7.5 cm in 2001 had neither paddy water discharge nor pesticide runoff due to sufficient excess water storage during the monitoring period. Watanabe *et al.*<sup>19)</sup> eluci-



**Fig. 6.** Correlations of EWSD vs. cumulative losses of simetryn and thiobencarb.

dated the importance of EWSD for controlling herbicide losses from rice paddy upon appreciable rainfall events using their model simulation, and Vu *et al.*<sup>4)</sup> also analyzed the potential of the EWSD though the Monte Carlo simulation using precipitation and field data for a 3-year period.

Using the data from this study and from Phong *et al.*<sup>7)</sup> the relation between the EWSD and cumulative herbicide losses in the paddy plot is derived (Fig. 6). Cumulative losses (%) of applied herbicides exponentially declined as EWSD increased. The two exponential functions have similar bases but different leading coefficients. The similar bases indicate that any change in EWSD would have relatively the same effect on simetryn and thiobencarb losses. The leading coefficient of simetryn is greater than that of thiobencarb, which indicates greater loss of simetryn than that of thiobencarb over the range of EWSD investigated. The functions also showed that the effectiveness of the EWSD correlates well with the values of the  $K_{oc}$  of the pesticides in this study. At any EWSD, the relative loss of simetryn was 5-times greater than that of thiobencarb. The loss of thiobencarb through water discharge was low because its  $K_{oc}$  is about 6-times greater than that of simetryn (Table 3); however, this was not always applicable to other cases. Vu *et al.*<sup>4)</sup> demonstrated a similar exponential relation between the EWSD and the cumulative losses of two

**Table 3.** Properties of herbicides

Herbicide	Solubility in water (mg/l) <sup>a)</sup>	Normalized distribution coefficient ( $K_{oc}$ ) <sup>b)</sup>
Simetryn	450	737
Thiobencarb	30	4280
Imazosulfuron	308 (pH 7)	5.5
Dymron	1.7	3760

<sup>a)</sup> Taken from SciFinder Scholar database (2006). <sup>b)</sup> Taken from ref. 20.

different herbicides, dymron and imazosulfuron. Dymron possesses a greater  $K_{oc}$  than imazosulfuron (Table 3), but the loss of dymron was always higher than that of imazosulfuron. If the  $K_{oc}$  may vary depending on soil type, a more general parameter, such as solubility, can be used; however, the same situation occurred. Between simetryn and thiobencarb, the higher the solubility of the compound, the greater it was lost through water discharge. For dymron and imazosulfuron, the latter had higher solubility but smaller loss than dymron. In a different study, Nakano *et al.*<sup>21)</sup> also reported the irregularity of dymron behavior when it had the highest runoff rate among 9 herbicides but its water solubility was much lower than most other herbicides. Therefore, further study that includes several pesticides simultaneously with comparable water balance conditions is needed to draw a general conclusion about the relation between the effect of EWSD and the physico-chemical properties of pesticides.

Observation from Fig. 6 and data from Vu *et al.*<sup>4)</sup> suggested that only an EWSD of about 3 cm is required to control pesticide runoff, because the increase of the EWSD higher than 3 cm will not significantly reduce the loss of pesticide from paddy fields.

The effectiveness of EWSD may depend on both management practice as well as field conditions. The percolation rate and rainfall pattern can influence the outcome of the preventive action. Optimum EWSD may be set considering local field conditions and rainfall pattern; therefore, caution must be taken when interpreting the above results.

### Conclusion

The EWSD is effective for controlling pesticide runoff from paddy fields in case of a rainfall event. Higher EWSD is more effective than lower EWSD; however, the effectiveness of the EWSD depended on the physico-chemical properties of the pesticide. Only moderate EWSD (about 3 cm) is suggested to prevent most pesticide runoff. The EWSD is essential during the recommended 7-day water holding period in order to effectively hold the water inside the field in case of major rainfall.

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