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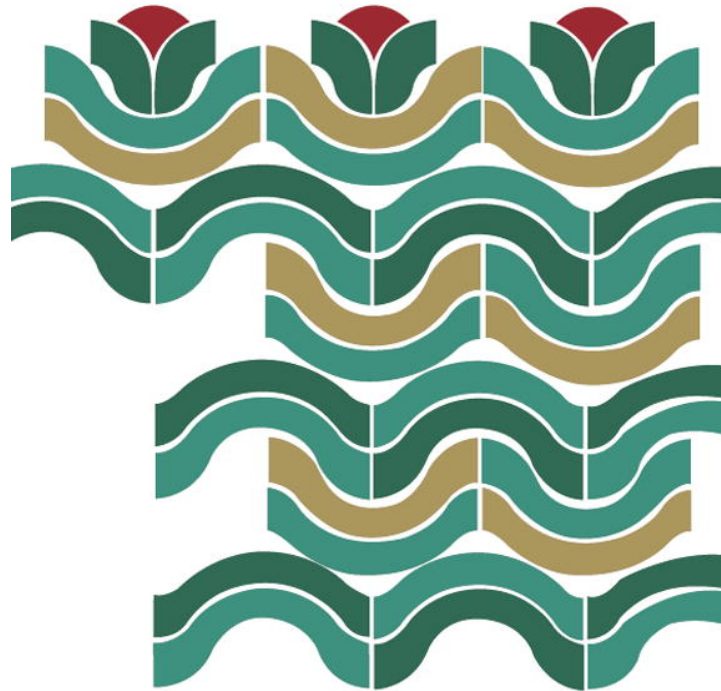


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## Effect of water management practice on pesticide behavior in paddy water

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### ABSTRACT

The fate and transport of three herbicides commonly used in rice production in Japan were compared using two water management practices. The herbicides were simetryn, thiobencarb and mefenacet. The first management practice was an intermittent irrigation scheme using an automatic irrigation system (AI) with a high drainage gate and the second one was a continuous irrigation and overflow drainage scheme (CI) in experimental paddy fields. Dissipation of the herbicides appeared to follow first order kinetics with the half-lives ( $DT_{50}$ ) of 1.6–3.4 days and the  $DT_{90}$  (90% dissipation) of 7.4–9.8 days. The AI scheme had little drainage even during large rainfall events thus resulting in losses of less than 4% of each applied herbicide through runoff. Meanwhile the CI scheme resulted in losses of about 37%, 12% and 35% of the applied masses of simetryn, thiobencarb and mefenacet, respectively.

The intermittent irrigation scheme using an automatic irrigation system with a high drainage gate saved irrigation water and prevented herbicide runoff whereas the continuous irrigation and overflow scheme resulted in significant losses of water as well as the herbicides. Maintaining the excess water storage is important for preventing paddy water runoff during significant rainfall events. The organic carbon partition coefficient  $K_{oc}$  seems to be a strong indicator of the aquatic fate of the herbicide as compared to the water solubility ( $S_w$ ). However, further investigations are required to understand the relation between  $K_{oc}$  and the agricultural practices upon the pesticide fate and transport. An extension of the water holding period up to 10 days after herbicide application based on the  $DT_{90}$  from the currently specified period of 3–4 days in Japan is recommended to be a good agricultural practice for controlling the herbicide runoff from paddy fields. Also, the best water management practice, which can be recommended for use during the water holding period, is the intermittent irrigation scheme using an automatic irrigation system with a high drainage gate.

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## 1. Introduction

Herbicide has brought a great benefit to rice cultivation (Matsunaka, 2001). Therefore, a large number of herbicides of various formulations are used in Japan, placing the country in second place in terms of the intensive use of pesticides worldwide (Sabik et al., 2000). However, monitoring studies for pesticide concentrations in river systems in Japan detected several herbicides commonly used in paddy fields (Nakamura, 1993; Ebise et al., 1993; Nagafuchi et al., 1994). Toxicology studies also showed the negative impact of herbicides on aquatic biota (Ueji and Inao, 2001; Hatakeyama et al., 1999).

Previous monitoring studies have demonstrated that the discharge of pesticide reaches its peak during the period shortly after the pesticide application time (Ebise and Inoue, 2002; Sudo et al., 2002). The surface drainage/runoff of paddy water containing appreciably high concentrations of pesticides is obviously responsible for this pollution.

Moreover, significant losses of pesticides used in the paddy fields seem to occur after significant rainfall events. While the pesticide loss without an intense rainfall after application was less than 5%, it reached 20–30% if a significant rainfall event follows pesticide application (Nagafuchi et al., 1994). A single rainfall event can cause substantial pesticide loss to the surface water (Flury, 1996). In Japan, Ebise and Inoue (2002) also indicated that the surface runoff from paddy fields increased during heavy storm events. Meanwhile, Vu et al. (2004) reported increased discharge from the paddies after rainfall events exceeding  $1.5 \text{ cm day}^{-1}$ . The excess water storage in a paddy to accommodate the excess precipitation can be an applicable solution for this matter. Mishra et al. (1998) reported that almost 100% of the intense rainfall can be stored in a rain-fed paddy plot having the weir height of 30 cm. Watanabe et al. (2006a) reported that excess water storage created by the high drainage gate prevented herbicide runoff during significant rain events.

The water holding period seems to be a key practice for controlling the pesticide discharge from paddy fields. In California, the water holding requirement after pesticide application has successfully reduced the concentrations of rice pesticides in streams (Newhart, 2002). However in Japan, the water holding period, which is recommended and written on pesticide labels, is only 3–4 days after pesticide application without a proper extension or specific water quality program. The importance of extending the water holding period in Japan has been previously discussed (Ishii et al., 2004; Watanabe et al., 2006a). It should be noted that the popular practice in monsoon paddies is shallow water ponding, hence irrigation is still performed during the water holding period to keep the appropriate water level while maintaining an excess water storage capacity. Therefore, imposing the proper water holding period in Japan needs a detailed investigation on water management practices specific to the Asian monsoon climate.

The physico-chemical properties of pesticides such as the solubility ( $S_w$ ) and the soil water partitioning coefficient normalized for the organic carbon content ( $K_{oc}$ ) are important parameters for the preliminary assessment of the pesticide fate and exposure risks. Several studies have suggested that

the magnitude of the pesticide loss depends on the solubility of the pesticides in the paddy water (Ebise et al., 1993; Ueji and Inao, 2001; Sudo et al., 2002). Nevertheless, a number of studies have also pointed out a correlation between the sorption behaviors of pesticides ( $K_{oc}$  or  $\log P_{ow}$ ) with their loss (Fajardo et al., 2000; Nakano et al., 2004). More studies should thus be carried out to determine the correlation of the pesticide loss with their intrinsic properties.

In this study, we monitored the fate and transport of three commonly applied rice herbicides having distinctive physico-chemical properties. Two water management practices, one intermittent irrigation scheme using an automatic irrigation system with a high drainage gate and one continuous irrigation overflow drainage scheme with a low drainage gate were used. The objective of this study was to investigate the effect of the water management practice and pesticide chemical properties on their behaviors in paddy fields so that a good water management practice for reducing herbicide loss from paddy fields can be proposed.

## 2. Materials and methods

### 2.1. Field experiment

The pesticide fate and transport monitoring was conducted in two paddy plots ( $27.9 \text{ m} \times 49.0 \text{ m}$ ) on the experimental farm of the Tokyo University of Agriculture and Technology (TUAT) in Fuchu, Tokyo, from 27 May to 30 June 2003 (Fig. 1). The physico-chemical properties of the paddy soil in these plots are listed in Table 1.

One plot was assigned to the intermittent irrigation scheme with a high drainage gate (denoted as AI plot) using an automatic irrigation system (Rakutaro<sup>®</sup>, Nihon System Kaihatsu Co. Ltd., Saitama). Irrigation was set to start when the paddy water level is below about 2 then continue up to 5 cm. The height from the paddy soil to the bottom of the notch of the drainage gate for the AI plot was set at 7.5 cm in order to minimize the paddy water drainage. The other was assigned to the continuous irrigation and overflow drainage scheme with a lower drainage gate (denoted as CI plot). The CI plot was kept irrigated at all times, but the flow rate depended on the pressure head in the pipeline. The corresponding height of the drainage gate from the soil surface for the CI plot was 2.5 cm.

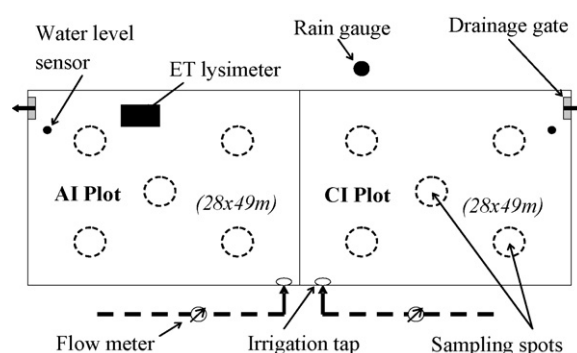


Fig. 1 – Layout of the experimental plots.

**Table 1 – Physico-chemical properties of paddy soil (0–15 cm) in experimental plot**

| Physico-chemical properties                                    | Value            |
|--|------------------|
| pH (H <sub>2</sub> O)  | 6.5              |
| Organic carbon content (%)                                     | 3.96             |
| Total carbon content (%)                                       | 4.77             |
| Total nitrogen content (%)                                     | 0.44             |
| Cation exchange capacity (cmol <sub>c</sub> kg <sup>-1</sup> ) | 22.5             |
| Particle density (g cm <sup>-3</sup> )                         | 2.50             |
| Sand (%)   | 37.6             |
| Silt (%)   | 31.8             |
| Clay (%)   | 30.6             |
| Soil texture (ISSS)  | Light clay (LiC) |

ISSS: International Society of Soil Science.

Following the general paddy field preparation and water ponding, the paddy soil was puddled and leveled by several passes of a rotary tiller under a few centimeters ponding-water condition. After the soil preparation, about 20-day-old rice seedlings (*Oryza sativa* L. cv. var. kogane-mochi) were transplanted with a spacing of 16 cm × 30 cm on 12 May 2003.

The water balance variables included irrigation, surface drainage, evapotranspiration and percolation. Precipitation data were collected from a meteorological station in TUAT. The volume of the irrigation water in each treatment was monitored with a flow meter connected to a data logger. The depth of the paddy water was monitored with a water level sensor (LSP-100, UJIN Co. Ltd., Tokyo) and the volume of the surface runoff through the V-notch weir was calculated using the paddy water level data from the equation described by Rao and Muralidhar (1963). Evapotranspiration (ET) was observed using a water level sensor in a lysimeter box (35 cm × 50 cm × 30 cm) containing 15 cm of puddled soil in a flood condition with four growing rice plants. The total percolation including lateral seepage was calculated from the remaining monitored hydrological data in the following water balance equation:

$$\frac{dh_{PW}}{dt} = \text{RAIN} + \text{IRR} - \text{DRAIN} - \text{PERC} - \text{ET} \quad (1)$$

where  $h_{PW}$  is the depth of water in a paddy field (cm),  $t$  is the time (day), RAIN is the rainfall (cm day<sup>-1</sup>), IRR is the irrigation (cm day<sup>-1</sup>), DRAIN is the paddy water discharge from a paddy plot including the overflow from the drainage gate (cm day<sup>-1</sup>), PERC is the percolation (cm day<sup>-1</sup>) including the vertical percolation through the paddy soil and the seepage through the levees and plot borders, and ET is the evapotranspiration (cm day<sup>-1</sup>). In addition, the distribution of the vertical percolation through paddy soil was measured using PVC rings with a diameter of 16 cm for 53 spots in each plot.

Three active ingredients, simetryn (N<sub>2</sub>,N<sub>4</sub>-diethyl-6-methylthio-1,3,5-triazine-2,4-diamine), mefenacet (2-(1,3-benzothiazol-2-yloxy)-N-methylacetanilide) and thiobencarb (S-4-chlorobenzyl diethyl (thiocarbamate)) were applied as a granular formulation, KumishotSM<sup>®</sup> (4.5% simetryn, 4.5% mefenacet, 15.0% thiobencarb, 2.4% MCPB), at a rate of 10 kg ha<sup>-1</sup> on 27 May 2003, 21 days after transplanting. The paddy water samples were taken at 1, 3, 7, 14, 21, and 35 days after herbicide application (DAHA). At each sampling, five

100-ml samples of the paddy water taken from five spots (Fig. 1) were mixed together to make one composite sample. At the same time, 500 ml water samples were taken at the drainage gate. The samples were kept frozen until the chemical analysis.

## 2.2. Gas chromatography analysis

Mefenacet, thiobencarb and simetryn in the water samples were extracted by liquid-liquid extraction with dichloromethane. The thawed samples were filtered through 1.2 μm glass micro-fiber filters (GF/C, Whatman, Maidstone, UK) then the filtered water samples were mixed with 30 g of NaCl and extracted twice with 400 ml of dichloromethane. The samples with a high concentration (1, 3, 7 DAHA) were diluted with deionized water before extraction. The dichloromethane solution was dehydrated by sodium sulfate and filtered with silicon treated filter paper (1 PS, Whatman, Maidstone, UK). The dichloromethane in the filtrate was evaporated by a rotary evaporator up to a volume of 1 ml and then to complete dryness under a gentle nitrogen stream. The residue was resuspended in 5 ml of acetone in an ultrasonic device. All of the solution was transferred to a test tube and kept at 4 °C until the GC analysis. A gas chromatographic system (GC-17A, Shimadzu, Kyoto, Japan) was used for the analysis. The column was a DB-5 column (30 m × 0.25 μm × 0.32 mm) (J&W Scientific, Rancho Cordova, USA). The temperature was programmed as follows: 60 °C (2 min) ramped up to 140 °C at 10 °C min<sup>-1</sup> then to 270 °C at 5 °C min<sup>-1</sup>. The temperature was then held at 270 °C for 4 min. A splitless injection mode was used with an injection volume of 4 μl. The carrier gas pressure was set at 40 kPa for 2 min then increased to 64 kPa at 3 kPa min<sup>-1</sup> and continued to ramp at 1.5 kPa min<sup>-1</sup> to 103 kPa which was maintained for 4 min. The herbicides were detected by the flame thermoionic detector (FTD). The determination limit were 0.024, 0.039 and 0.016 mg l<sup>-1</sup> for simetryn, mefenacet and thiobencarb, respectively. The recovery values were 118%, 136% and 119% for simetryn, mefenacet and thiobencarb, respectively.

## 3. Results and discussion

### 3.1. Water balance

The monitored water balance in the two plots (AI and CI) are presented in Table 2. The precipitation for the study period of 2

**Table 2 – Water balance in paddy plots**

|               | AI plot | CI plot |
|---------------|---------|---------|
| Input (cm)    |         |         |
| Irrigation    | 34.8    | 56.5    |
| Precipitation | 17.6    | 17.6    |
| Total         | 52.4    | 74.1    |
| Output (cm)   |         |         |
| Drainage      | 3.5     | 24.5    |
| Percolation   | 34.1    | 34.1    |
| ET            | 15.5    | 15.5    |
| Total         | 53.1    | 74.2    |

months (May and June) was 17.6 cm. This amount was similar to the 22-year average precipitation (1979–2000) in the region. The average rates of percolation during the monitoring period were 0.97 cm day<sup>-1</sup> for both the AI and CI plots. Although the percolation rate was obtained from the rest of the measured variables, the obtained values were still in the range of the typical Japanese paddy field reported by Nakagawa (1967). The similar percolation rates between the two plots may be due to the consistent soil preparation and the equal ponding water depth (about 4 cm).

Fig. 2 shows the spatial distribution of the measured percolation rates. The measured vertical percolation followed a log normal distribution with the mean and standard deviation of -0.57 (0.57 for normal value) and 0.73, respectively. Note that there were two spots with extremely high percolation (24.2 cm day<sup>-1</sup> at the Northwest corner of the AI plot and 25.7 cm day<sup>-1</sup> at the Southwest corner of CI plot) therefore they were excluded from the statistical analysis. However, the average values of the measured percolation rates including these hot spots coincided with the monitored data. Some points with a high rate were also observed along the concrete banks of the plots that means the seepage and/or under-bund percolation may contribute a significant portion to the water flow at these points. According to Sharma and De Datta (1985), puddling of rice fields before transplanting or direct seeding reduces the percolation losses. However, for machinery puddling, the edges and corners along the banks are usually left undisturbed because the plow cannot reach these areas. Tuong et al. (1994) reported that unpuddled soil (about 1% of field area) increased the field percolation by a factor of five and under-bund percolation may cause a further two- to five-fold increase.

Fig. 3 shows the daily changes in precipitation, irrigation, runoff/drainage, and paddy water depth for the AI and CI plots.

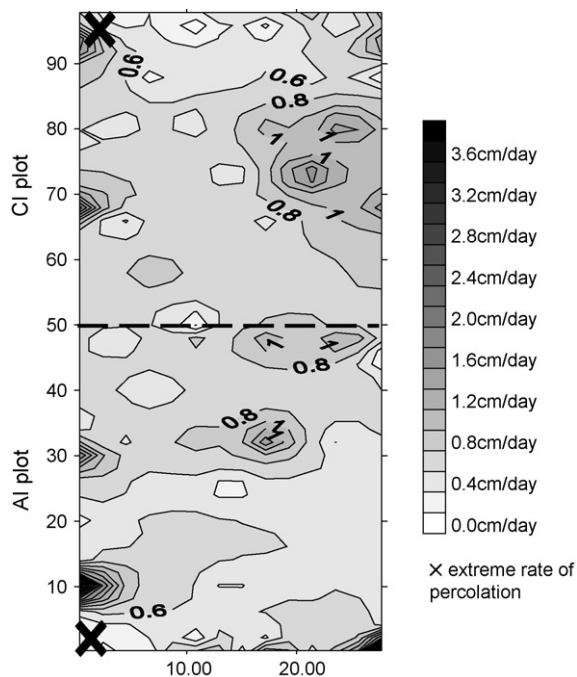


Fig. 2 – Spatial distribution of the percolation rate within the studied plots.

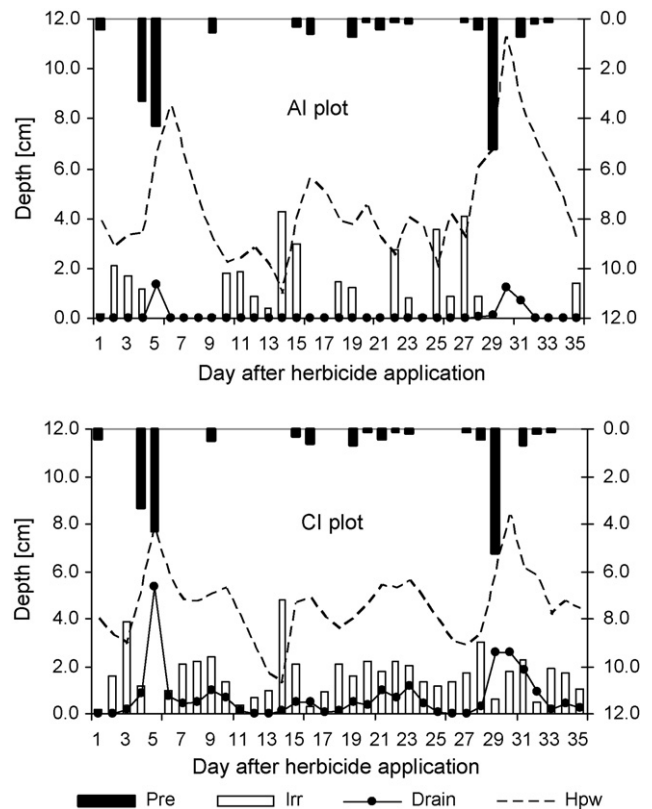


Fig. 3 – Observed water balance including precipitation (Pre), irrigation (Irr), drainage (Drain) and paddy water depth (Hpw) in AI plot (above) and CI plot.

Due to the continuous irrigation and overflow drainage scheme, the CI plot discharged a significant amount of water through the surface runoff. Also, the CI plot maintained a relatively deep paddy water (about 4–6 cm) although it had a lower drainage gate due to the discharge characteristics of the V notch gate. The discharge from the V notch gate in the CI plot was significant and that raised the paddy water level to drain excess water during the monitoring period. Runoff from the CI plot especially increased after significant rainfall events. The total depth of drainage in the CI plot contributed about 33% of the total output. Meanwhile, the AI plot with a high drainage gate had almost no surface runoff. Since the water depth set for the irrigation system in the AI plot was 4 cm while it had a 7.5 cm drainage gate, the AI plot basically had a 3.5-cm excess water storage depth (EWSD). This EWSD in the AI plot prevented the surface runoff during the rainfall events except for two cases of extremely large rainfall.

As a consequence, during the monitoring period the CI plot required 60% more irrigation water as compared to the AI plot. The excessive amount of irrigation water was wasted as runoff. This result confirmed the conclusion of Watanabe et al. (2006a) that important factors in water management for saving water used in paddy rice production are

- (1) reduction of overflow drainage from excess irrigation and
- (2) efficient utilization of precipitation by storing as much rain water as possible in the fields.

### 3.2. Pesticide fate and transport in paddy water

Fig. 4 shows the changes in the concentrations in the paddy water of the three studied herbicides in the AI plot, the CI plot as well as the water collected at the drainage gate of the CI plot. In general, the dissipation trend of the three herbicides was similar. The applied herbicides reached their peak concentrations in the day following the application date. These concentrations then rapidly declined during the 2 weeks after herbicide application. The peak concentration of simetryn was the highest followed by thiobencarb and mefenacet with the values of 0.951, 0.595 and 0.498 mg l<sup>-1</sup>, respectively. At the end of the monitoring period (35 DAHA), the measured concentrations of the studied herbicides were lower than the advisory levels (0.06 mg l<sup>-1</sup> for simetryn, 0.009 mg l<sup>-1</sup> for mefenacet, the level for thiobencarb is not available) for public surface water quality in Japan (MOE, 1994). The highest concentration at 35 DAHA is that of simetryn at the drainage gate with the

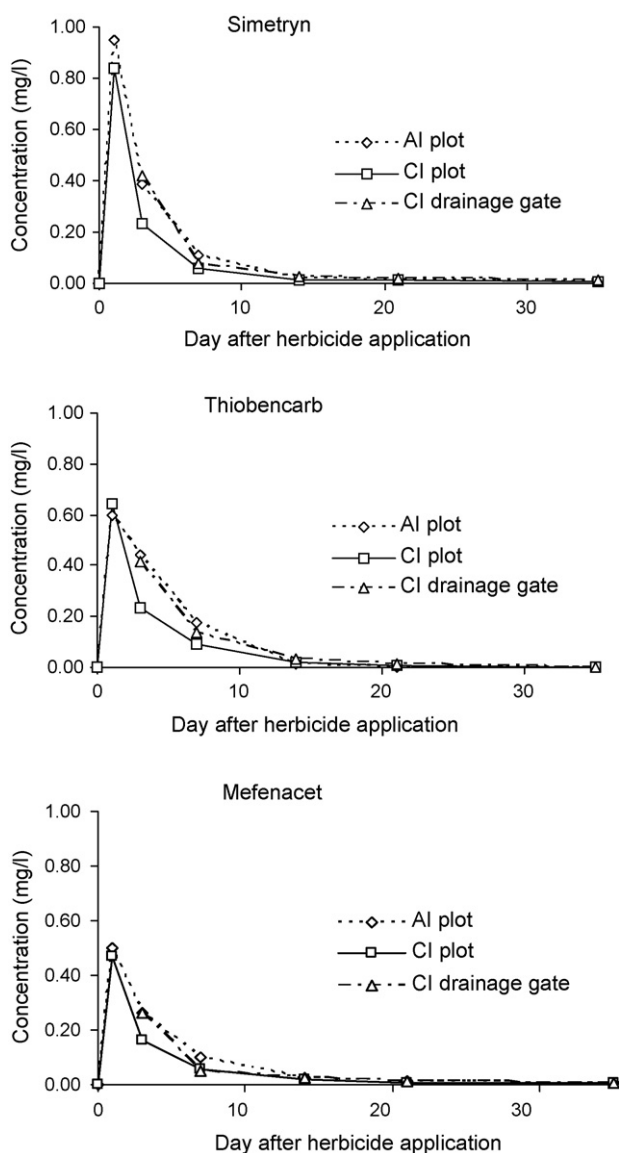


Fig. 4 – Concentration of the studied herbicides in paddy water and drainage water of the studied plots AI and CI.

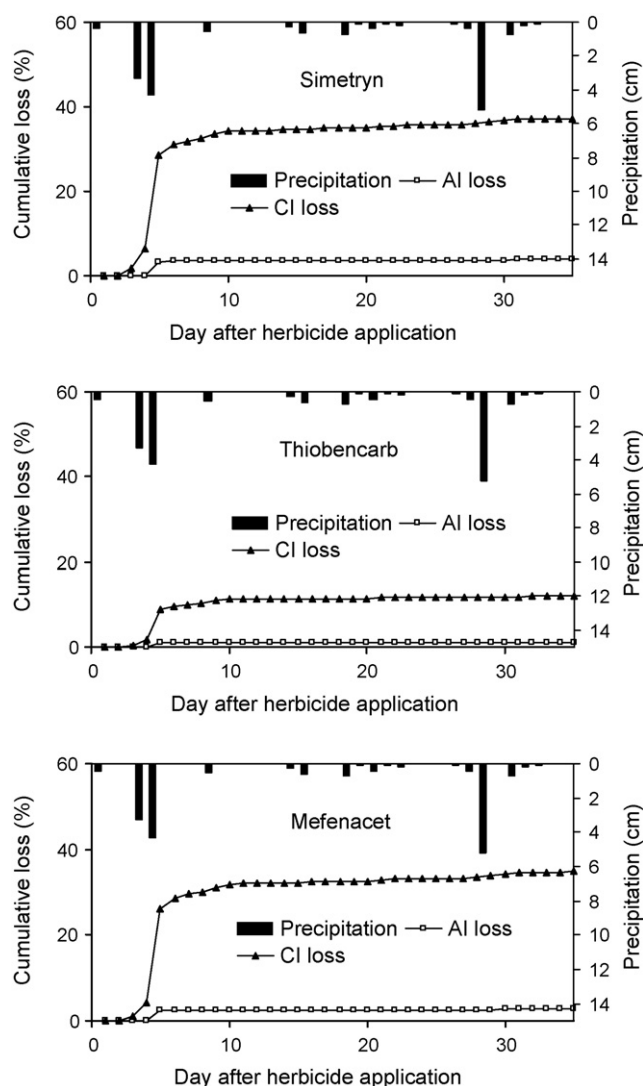
value of 0.01 mg l<sup>-1</sup>. The 3-year pesticide monitoring study at NIAES (Fajardo et al., 2000) also provided a comparable dissipation pattern of mefenacet in paddy water considering that the present experiment only had a third of the application rate of the NIAES study. A similar pattern for simetryn was also reported by Inao et al. (2001). However, the maximum concentration observed in that study was only 0.3 mg l<sup>-1</sup> for simetryn, while in both studies, the same application rate was used.

Concerning the effect of the different water management practices on the behavior of the applied herbicides, the concentrations of herbicides in the CI plot were consistently lower than the concentrations in the AI plot. This was probably due to dilution and loss of the dissolved herbicides, which were greater in the continuous irrigation and overflow drainage scheme. As shown by the water balance, both the water input as well as the water drainage in the CI plot were much higher than those in the AI plot.

The herbicide concentrations in the drainage water from the CI plot were always higher than the concentrations measured in the composite samples of the same sampling date (representing the average concentration of the plot). The average difference was about 70% throughout the monitoring period. This phenomenon resulted from the structure of the plot with irrigation water coming in one side and drainage water going out the other side. Newly irrigated water therefore swept the standing water that contained a high concentration of herbicides toward the drainage gate creating a spatial variation in the herbicide concentrations within the plot. The evidence for this phenomenon was reported by Watanabe et al. (2006b), who discussed the application of the ELISA kit for the risk assessment of rice herbicides used in the same paddy field. The bensulfuron-methyl concentrations in this paddy field at 43 DAHA ranged from below 0.03 µg l<sup>-1</sup> at the sampling point near the irrigation inlet to about 1 µg l<sup>-1</sup> at points close to the drainage gate.

Considering the cumulative losses of the three studied herbicides (Fig. 5), the losses in the CI plot were significantly higher than those in the AI plot for all the herbicides. From the CI plot, the total herbicide losses were about 37%, 12% and 35% of the applied mass for simetryn, thiobencarb and mefenacet, respectively. Meanwhile, almost no herbicide lost from the AI plot since the drainage was very small. The total losses in the AI plot were 3.8%, 1.2% and 2.7% for simetryn, thiobencarb and mefenacet, respectively. The losses of thiobencarb were significantly lower than the other two herbicides. This is possibly due to its lower  $K_{oc}$  value as compared to the others. More discussion on the herbicide properties and their fate will be presented in a later section.

Most of herbicide mass was lost during the first week after application (Fig. 5). It should be noted that about 60% of the total loss in the CI plot and about 90% of the total loss in the AI plot occurred at 4 DAHA in a significant rainfall event consisting of two consecutive rain days. Therefore, pesticide runoff control during the earlier period is extremely important. As reported from the simulation of the rice herbicide fate and transport (Watanabe and Takagi, 2000), a paddy plot managed by a continuous irrigation and overflow drainage scheme had 86% of the total mefenacet loss during the first week. Especially, the pesticide losses by the runoff at 2 and 3



**Fig. 5 – Cumulative losses of the studied herbicides in the two studied plots.**

DAHA were 12% and 11%, respectively, since these days had significant precipitations of 1.7 and 3.3 cm (Watanabe and Takagi, 2000). Precipitation during this event was almost 8 cm (Fig. 3), which resulted in an appreciable runoff. In such an event, the height of the drainage gate plays a key role in preventing runoff. Since the AI plot had a considerable excess water storage created by a high drainage gate, the volume of the runoff from the AI plot in this large rainfall event was much less than that from the CI plot. Watanabe et al. (2006a)

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 runoff nor herbicide runoff due to sufficient excess water storage during the monitoring period.

The result implies that water management is important in order to control the herbicide runoff from a paddy field especially during the earlier period with a higher herbicide concentration in the paddy water. A continuous irrigation and overflow drainage scheme is not recommended during this vulnerable period. The disadvantages of the continuous irrigation and overflow drainage scheme have been reported by previous studies and mainly focused on the significant herbicide losses, up to about 60% of the applied mass, depending on the volume of irrigation and precipitation (Watanabe and Takagi, 2000; Inao et al., 2001; Watanabe et al., 2006a,b). In addition, the use of a higher drainage gate for excess water storage should be encouraged to prevent runoff from such a large rainfall event. Watanabe et al. (2006a) also concluded from their previous study that an intermittent irrigation scheme using an automatic irrigation system with a high drainage gate was recommended as the best management practice for controlling the herbicide losses from paddy fields.

A water holding practice should be recommended especially during the earlier period when the herbicide concentrations are high. Ishii et al. (2004) suggested that increasing the water holding period from 3 to 7 days would reduce the herbicide concentrations in the paddy water from 50% to 10% of the maximum concentrations. However, the appropriate holding time may need to be investigated for each herbicide as in California where different water holding periods were set depending on the herbicides (Newhart, 2002). Watanabe et al. (2006a) discussed the advantages of extending the current water holding period specified in Japan and suggested that the water holding period to be at least 10 days according to the DT<sub>90</sub> index. Note that the DT<sub>90</sub> values of the studied herbicides ranged up to 9.8 days as discussed in the next section.

Plotting the natural logarithm of the herbicide concentrations in paddy water versus DAHA indicated a first order kinetic dissipation for each herbicide. Note that the herbicide concentrations at the drainage gate were excluded from the analysis. The regression equations and their R values for the three herbicides in the two plots are presented in Table 3. All the R<sup>2</sup> values showed a good reliability (P > 0.05) yet the R<sup>2</sup> values of the CI plot were always lower than the corresponding number of the AI plot. The difference in the factors in the equations and the R<sup>2</sup> values between the two plots may be explained by the assumption that the herbicides in the CI plot were more affected by physical factors such as dilution and chemical loss from the excessive irrigation, and drainage thus

**Table 3 – Results of linear regression of herbicide concentrations in paddy water during the monitoring period**

|             | AI plot               |                | CI plot               |                |
|-------------|-----------------------|----------------|-----------------------|----------------|
|             | Equation              | R <sup>2</sup> | Equation              | R <sup>2</sup> |
| Simetryn    | $y = -0.301x + 0.065$ | 0.991          | $y = -0.291x - 0.350$ | 0.936          |
| Thiobencarb | $y = -0.309x + 0.045$ | 0.974          | $y = -0.257x - 0.455$ | 0.977          |
| Mefenacet   | $y = -0.235x - 0.565$ | 0.995          | $y = -0.245x - 0.880$ | 0.946          |

shifted the dissipation mechanism away from the first order kinetics.

The calculated dissipation times for the herbicide concentrations in the paddy water to reach 50% and 10% of the initial concentration of the three herbicides ( $DT_{50}$  and  $DT_{90}$ ) are shown in Table 4. The  $DT_{50}$  was calculated from the data of an 1–7 DAHA period and the  $DT_{90}$  was calculated from the data of an 1–14 DAHA period. The  $DT_{50}$  and  $DT_{90}$  of mefenacet of about 3 and 10 days were in accordance with other studies. Ishii et al. (2004) reported the  $DT_{50}$  of 1.8 days for mefenacet while Fajardo et al. (2000) reported 4.1 days. Ishii et al. (2004) also reported that the  $DT_{90}$  in the paddy water was 9.7 days for mefenacet. For simetryn, the estimation of the  $DT_{50}$  and  $DT_{90}$  from the data of Inao et al. (2001) also gave similar values.

Meanwhile, the  $DT_{50}$  values of thiobencarb found in this experiment were lower than that available in the literature. Yusa and Ishikawa (1977) determined the half-life ( $DT_{50}$ ) in the paddy water of thiobencarb to be 6–9 days while Ross and Sava (1986) predicted a half-life longer than 6 days in field water. The difference may be due to the product formulation because the peak concentration in the study of Ross and Sava (1986) was observed at 4 DAHA. The remarkably shorter  $DT_{50}$  of all the herbicides in the CI plot than in the AI plot were due to the herbicide losses through the runoff resulted from the continuous irrigation and overflow drainage scheme.

All the above-mentioned studies indicated that the herbicide concentrations in the paddy water were not significantly reduced during the first week after herbicide application. Watanabe et al. (2006a) also found similar phenomena in their experiment. This is in contrast to the current recommendation of the Japanese pesticide manufacturers of only a 4-day water holding period. In their monitored paddy water, Watanabe et al. (2006a) reported significant herbicide concentrations and concurrent losses were still observed after 4 DAHA. Furthermore, as they reviewed the literature, most of the  $DT_{90}$ s of the rice herbicides ranged from about 8–10 days. Therefore, it is essential to extend the Japanese water holding period to prevent discharge of the paddy water/pesticide after pesticide application.

For the present study, the estimated herbicide concentrations at 4 DAHA in the AI plot were 22.3%, 31.0%, and 39.2% of the maximum concentrations of simetryn, thiobencarb and mefenacet, respectively, and the corresponding herbicide losses at 4 DAHA were 22.2%, 7.1%, and 24.0% of the applied masses, respectively. High herbicide concentrations during the earlier period (longer than 3–4 days) have also been observed for pretilachlor (Fajardo et al., 2000), thiobencarb (Ross and Sava, 1986), carbofuran, molinate, tryclopypyr, 2,4-D (Johnson and Lavy, 1995; Johnson et al., 1995), and azimsulfuron (Armbrust et al., 1999).

**Table 4 –  $DT_{50}$  and  $DT_{90}$  of studied herbicides in two plots**

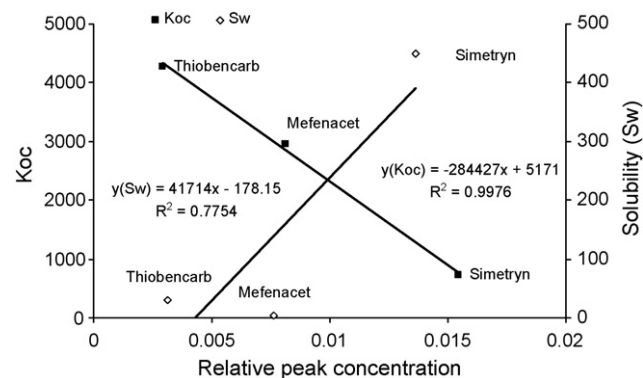
|             | $DT_{50}$ (day) |     | $DT_{90}$ (day) |     |
|-------------|-----------------|-----|-----------------|-----|
|             | AI              | CI  | AI              | CI  |
| Simetryn    | 2.0             | 1.6 | 7.9             | 7.7 |
| Thiobencarb | 3.4             | 2.2 | 9.0             | 3.4 |
| Mefenacet   | 2.6             | 2.0 | 9.4             | 9.8 |

Study by Ishii et al. (2004) suggested that increasing the water holding period would significantly reduce the herbicide concentrations. A longer water holding period of at least 10 days after herbicide application based on the  $DT_{90}$  for further dissipation might thus be a good agricultural practice for controlling the herbicide runoff from paddy fields. Therefore, the currently recommended water holding of 3–4 days in Japan needs to be re-evaluated. In addition, the best water management practice, which can be recommended for use during the water holding period, is the intermittent irrigation scheme using an automatic irrigation system with a high drainage gate. The proper extension of the water management practice for obtaining the optimum excess water storage during the water holding period is very important in order to have an effective control of the herbicide runoff from paddy fields. However, the optimum excess water storage and its control of the water management are dependent on hydrological parameters such as precipitation, percolation and evapotranspiration, and a detailed analysis may be required for future studies.

### 3.3. Herbicide properties and their fate

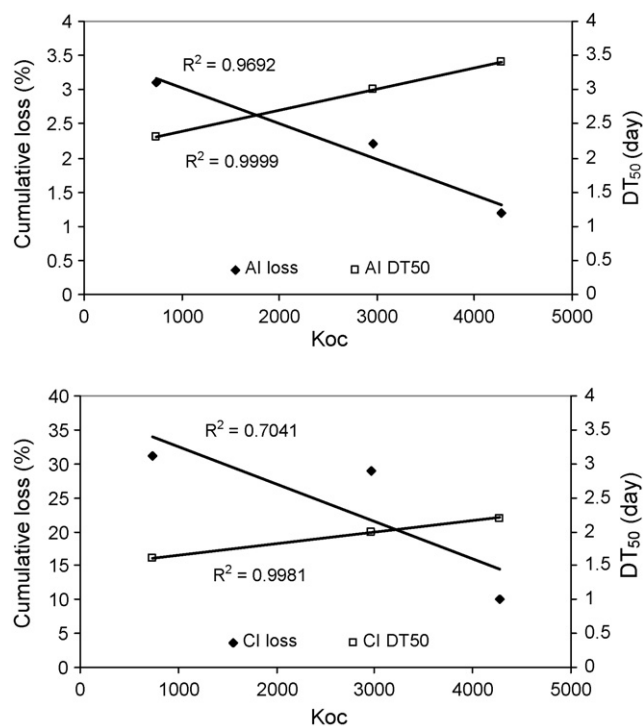
The peak concentration value of each active ingredient correlated with its physico-chemical properties. Although thiobencarb has an application rate 3 times higher than that of mefenacet and simetryn, the highest thiobencarb concentration in the paddy water was only about half that of simetryn and slightly higher than that of mefenacet. A negative correlation was found between the maximum concentration in the paddy water divided by the applied mass or the relative peak concentration and its  $K_{oc}$  value as shown in Fig. 6. The linear regression indicated a weaker positive correlation (Fig. 6) between the relative peak value and its water solubility value ( $S_w$ ). However,  $S_w$  has been used as a parameter for evaluating the pesticide fate and transport including the prediction of herbicide losses in the field as well as in the watershed (Maru, 1990; Sudo et al., 2002).

In the next step, the  $K_{oc}$  as well as the  $S_w$  of the herbicides were also correlated with the dissipation time and the herbicide loss through runoff. A similar observation was recorded such that the  $S_w$  has a weaker correlation with the  $DT_{50}$  of the compound and the herbicide loss than does the  $K_{oc}$  (Fig. 7). In this study, the greater the  $K_{oc}$ , the longer the  $DT_{50}$  and the smaller the herbicide loss by runoff. Also, the greater



**Fig. 6 – Linear regression of the relative peak concentration of the studied herbicides vs.  $K_{oc}$  ( $y(K_{oc})$ ) and vs.  $S_w$  ( $y(S_w)$ ).**





**Fig. 7 – Correlations of  $K_{oc}$  vs. cumulative loss and  $K_{oc}$  vs.  $DT_{50}$ .**

the  $K_{oc}$ , the lower the relative peak concentration of the applied herbicide. Among the three herbicides, thiobencarb, which had the highest  $K_{oc}$ , had the lowest runoff loss. Consequently, it is indicated that  $K_{oc}$  is a good indicator of the fate of herbicides in paddy fields and can be used together with  $S_w$  to make a good prediction of pesticide fate. However, the importance of  $K_{oc}$  (and  $S_w$ ) for the herbicide fate and transport in paddy fields and its relation to agricultural practices, such as water management and soil preparation, should be further studied for the pesticide risk assessment.

#### 4. Conclusions

From this study, controlling paddy water runoff by the intermittent irrigation scheme using an automatic irrigation system with a high drainage gate saved irrigation water and prevented herbicide runoff whereas the continuous irrigation and overflow scheme lost significant amount of water as well as herbicides from the paddy fields. Maintaining the excess water storage is important for reducing paddy water runoff during significant rainfall events.  $K_{oc}$  seems to be a good indicator of the aquatic fate of herbicides as compared to  $S_w$ . However, further investigations are required to understand the relation between  $K_{oc}$  and agricultural practices upon the pesticide fate and transport.

An extension of the water holding period to 10 days after herbicide application based on the  $DT_{90}$  from the currently recommended period of 3–4 days in Japan is recommended to be a good agricultural practice for controlling herbicide runoff from paddy fields. Also, the best water management practice,

which can be recommended for use during the water holding period, is the intermittent irrigation scheme using an automatic irrigation system with a high drainage gate. The proper extension of the water management practice for obtaining the optimum excess water storage during the water holding period is very important in order to have effective control of the herbicide runoff from paddy fields.

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