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RESEARCH PAPER

Behavior of simetryn and thiobencarb in rice paddy lysimeters and the effect of excess water storage depth in controlling herbicide run-off

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Eight small-scale lysimeters with different excess water storage depths (EWSDs) were used to investigate the behavior of two herbicides, simetryn and thiobencarb, under paddy conditions. The concentration of simetryn dissipated similarly in all the lysimeters, while the thiobencarb concentration varied significantly because thiobencarb can adsorb onto the dissolved organic matter in a manure slurry, which was applied to six of the lysimeters. The herbicide losses (the percentage of the applied mass) from the lysimeters were reversely proportional with the EWSD. The correlation was stronger for simetryn than for thiobencarb. An appropriate EWSD is required to effectively prevent herbicide run-off from the paddy field, especially when a rainfall event occurs soon after herbicide application.

Keywords: lysimeter, paddy, run-off, simetryn, thiobencarb.

INTRODUCTION

With increased concern about water quality around the world, more emphasis is being placed on understanding the behavior of agricultural chemicals and then finding the best management practise to reduce their impact on the environment. Experiments with various scales have been carried out to monitor the behavior of pesticides. Although the field experiment is time-consuming and costly, lysimeters can be a useful tool to investigate pesticide behavior.

Many studies on pesticide behavior have been carried out in lysimeters (Corwin 2000). The European Union, in its Directive 91/414 (Commission of the European Communities 1996), also has stressed the use of lysimeters for the registration of plant protection products. As paddy fields account for a major part of agricultural lands, especially in Asia, lysimeter experiments on pesticides' fate under paddy field conditions are necessary for the risk assessment process. In Japan, Maru (1990) pioneered the use of paddy lysimeters to investigate the fate of 21 pesticides in paddy water. Recently, the new registration guidelines for rice pesticides in Japan (MAFF 2000) also have stipulated the use of paddy lysimeters for the prediction of the environmental concentrations of pesticides. Thus, it is useful to study the behavior of rice pesticides using paddy lysimeters.

Controlling water overflow upon major rainfall events is important to prevent pesticide run-off from paddy fields. Several studies in Japan reported that heavy rainfall significantly increased pesticide run-off (Ebise & Inoue 2002; Vu *et al.* 2006). The excess water storage depth (EWSD), which is an extra depth obtained by the high levees of a paddy to accommodate the excess rainfall water, might be a good water management practise for this matter. The water storage property of paddy fields has been known for many aspects of flood prevention and ground water recharge. Also, its ability to control pollutant run-off from paddy fields has been discussed recently (Watanabe *et al.* 2007). Although a large EWSD,

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which means very high levees, might require a lot of infrastructure investment, we previously reported that even small EWSDs (up to 3 cm) can effectively prevent herbicide run-off during significant rainfall events (Phong *et al.* 2006; Watanabe *et al.* 2007). However, a detailed explanation of the relationship between the EWSD and herbicide behavior is desired in order to implement it as a good agricultural practise for controlling herbicide losses from paddy fields.

In this study, a set of lysimeters was utilized to monitor the behavior of two herbicides and to evaluate the effect of the EWSD on the amount of herbicide loss during a rainfall event.

MATERIALS AND METHODS

Lysimeter establishment

The lysimeter experiment was conducted in outdoor conditions in the experimental field of Tokyo University of Agriculture and Technology (TUAT) in Fuchu, Tokyo, Japan. Eight stainless steel lysimeters (1 m × 1 m × 0.5 m: width × diameter × height) were packed to ~40 cm height with, from top to bottom, a muddy soil layer (~22 cm), a hardpan soil layer (6–7 cm), and a gravel layer (~10 cm) (Fig. 1). The EWSD in each lysimeter was set by adjusting the height of the drainage hole. The percolation water was collected through the drainage pipe installed at the bottom of the lysimeter. These lysimeters were called L1, L2, L3, L4, L5, L6, L7, and L8. The soil used in this experiment was taken from a paddy plot of TUAT and was a light clay soil (Table 1) with an average 3.02% of organic carbon (C) content.

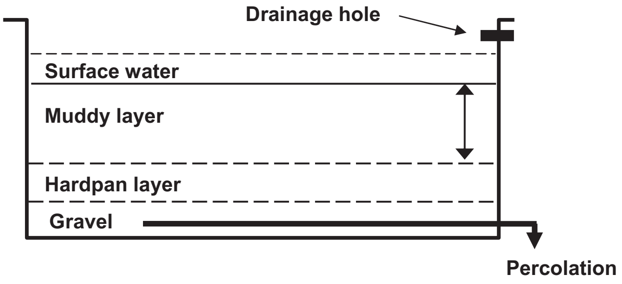

Fig. 1. Structure of the lysimeter used in this study.

Before packing, the soil was air-dried, ground, and passed through a 2 cm sieve to remove rocks, plant residue, and other large particles. Over the gravel layer, the moistened soil was packed by a rammer to make the hardpan layer. After that, the muddy soil, made by mixing soil with water using a concrete mixer, was poured in. The lysimeters were ponded and left to consolidate for 2 months prior to the experiment.

Eighteen (3 rows × 6 plants design) rice seedlings (*Oryza sativa* spp. Kusahonami) were transplanted on 20 June 2005 to each lysimeter after fertilization and plowing. Before the transplantation, fertilizer was applied to each lysimeter. Different doses of manure slurry were added as organic fertilizer to six lysimeters (L2–L7) (Table 2). The other two lysimeters, L1 and L8, received a chemical fertilizer.

Water balance

The water balance components, including the water depth, irrigation, rainfall, overflow, percolation, and

Table 1. Physico-chemical properties of the paddy soil

Physico-chemical property	Value
pH (H_2O)	6.30
Organic carbon content (%)	3.02
Total carbon content (%)	3.59
Total nitrogen content (%)	0.35
Cation exchange capacity ($\mathrm{cmol_c\ kg^{-1}}$)	20.10
Particle density ($\mathrm{g\ cm^{-3}}$)	2.58
Sand (%)	40.70
Silt (%)	32.90
Clay (%)	26.40
Soil texture (ISSS)	Light clay

ISSS, International Society of Soil Science.

Table 2. Fertilizer treatment of the lysimeters

Variable	Lysimeter							
	L1	L2	L3	L4	L5	L6	L7	L8
Treatment	CF	MS	MS	MS	MS	MS	MS	CF
Application rate (NH_4-N: kg ha^{-1})	100	100	150	75	75	150	100	100

CF, chemical fertilizer; MS, manure slurry.

evapo-transpiration, were recorded on a daily basis. The water depth and percolation were measured manually, while the irrigation volume was measured by flow meters installed at the inlets of each lysimeter and the rainfall amount was recorded by a rain gauge (Ota Keiki, Tokyo, Japan) placed near the lysimeters. The volume of water overflow was calculated from the water level and the rainfall data. Irrigation was performed when the water depth in the lysimeters was <4 cm.

Herbicide application and sampling

Simetryn (N^2,N^4-diethyl-6-methylthio-1,3,5-triazine-2,4-diamine) and thiobencarb (S-4-chlorobenzyl diethylthiocarbamate) (Table 3), two commonly used herbicides in Japan, were used in this experiment as the test substances. A granular herbicide (KumishotSM; Kumai Chemical Industry, Tokyo, Japan), containing 4.5% of simetryn and 15.0% of thiobencarb was applied at the rate of 1 g m^{-2} (10 kg ha^{-1}), as recommended by the product label. Before application, the water levels of all the lysimeters were adjusted to 5 cm for similar initial conditions.

The composite surface paddy water samples from nine spots (3 × 3 spots) were taken from each lysimeter at 1, 3, 7, and 14 days after herbicide application (DAHA). At 1 DAHA, samples from the lysimeters with the same fertilizer treatment (L1 and L8, L2 and L7, L3 and L6, L4 and L5) were mixed to make volume-weighed, averaged samples for each treatment. At the other sampling dates, separate samples were taken from each lysimeter. The samples were immediately transported to the laboratory and kept frozen until chemical analysis.

Chemical analysis

The water samples were filtered through 0.45 μm disk filters (DISMIC-13CP; Advantec, Tokyo, Japan). The filtered water samples were solid phase-extracted by cartridges (PS-2, Sep-Pak Plus; Waters, Milford, MA, USA) mounted on a vacuum manifold (Visiprep; Supelco, Belleforke, PA, USA). Prior to use, the cartridges were washed with 5 mL of acetone, followed by 5 mL of distilled water. An appropriate volume of water sample was then loaded into the cartridge at a flow rate of 5 mL min^{-1}. After extraction, the cartridges were washed with 10 mL of distilled water. The cartridges were air-dried for 10 min before the herbicides were eluted by 6 mL of acetone at a rate of 1 mL min^{-1}. The acetone extracts were collected in glass, graduated centrifuge tubes and then evaporated down to 1 mL by a gentle nitrogen stream. The final samples were kept at −20°C before gas chromatography analysis.

Table 3. Properties of simetryn and thiobencarb (Kibe *et al.* 2000)

Herbicide	Molecular weight	Solubility in water (μg L^{-1} 20°C)	Normalized distribution coefficient (K_{oc})
Simetryn	213.2	450	737
Thiobencarb	257.8	30	4280

The samples were analyzed by a gas chromatograph (6890N; Agilent, Palo Alto, CA, USA), equipped with a mass spectrometer (5973 MSN; Agilent, Palo Alto, CA, USA) and a fused-silica capillary column (DB-5 MS; J&W Scientific, Rancho Cordova, CA, USA). Helium was used as the carrier gas (constant pressure of 70 kPa). The column temperature was programmed from 50°C (held for 1 min) to 200°C at a rate of 20°C min^{-1}, then to 280°C (held for 1.5 min) at a rate of 10°C min^{-1}. The injector temperature was set at 250°C. Splitless injection mode was used for 2 μL of the sample. The mass spectrometer was set in selected ion monitoring mode (at 213.2 m/z and 257.8 m/z for simetryn and thiobencarb, respectively). The detection limit was 0.1 μg L^{-1} for both herbicides and the recovery was 83.2 ± 3.5% and 86.6 ± 1.2% for simetryn and thiobencarb, respectively.

RESULTS AND DISCUSSION

Water balance

The water balance was calculated for 15 days from 8 July 2005 to 23 July 2005 to cover the period of pesticide monitoring. The water balance of this period is shown in Table 4. There were differences in the values of the water balance components among the lysimeters. The difference was small in terms of percolation but was significant in terms of irrigation.

There was a large rainfall (6.5 cm) at 2 DAHA. This severe rainfall flooded and resulted in the overflow of all the lysimeters (Table 4). The overflow volumes differed among the lysimeters because of the variation in the EWSD among them. This was the only overflow event during the monitoring period, but the volumes of overflow were significant (from 0.8–3.9 cm of water depth).

Although the percolation values could be as much as two times greater between lysimeters, the absolute values, ranging from 0.06–0.14 cm day, were small compared with typical field data. Nakagawa (1967) reported that

Table 4. Water balance of the studied lysimeters

Characteristic	Lysimeter							
	L1	L2	L3	L4	L5	L6	L7	L8
EWSD (cm)	5.20	2.50	5.60	4.20	3.20	5.20	5.20	4.40
Irrigation								
Daily (cm day^{-1})	0.11	0.23	0.04	0.08	0.08	0.01	0.00	0.10
Total (cm)	1.70	3.40	0.60	1.20	1.20	0.10	0.00	1.50
Rainfall								
Daily (cm day^{-1})	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45
Total (cm)	6.70	6.70	6.70	6.70	6.70	6.70	6.70	6.70
Overflow								
Daily (cm day^{-1})	0.08	0.26	0.05	0.15	0.19	0.08	0.09	0.13
Total (cm)	1.20	3.90	0.80	2.30	2.80	1.20	1.30	2.00
Percolation								
Daily (cm day^{-1})	0.13	0.13	0.13	0.07	0.12	0.14	0.08	0.08
Total (cm)	1.90	1.90	2.00	1.00	1.80	2.10	1.20	1.20
Evapo-transpiration								
Daily (cm day^{-1})	0.43	0.37	0.37	0.36	0.27	0.30	0.32	0.39
Total (cm)	6.40	5.50	5.50	5.40	4.10	4.50	4.80	5.80

EWSD, excess water storage depth.

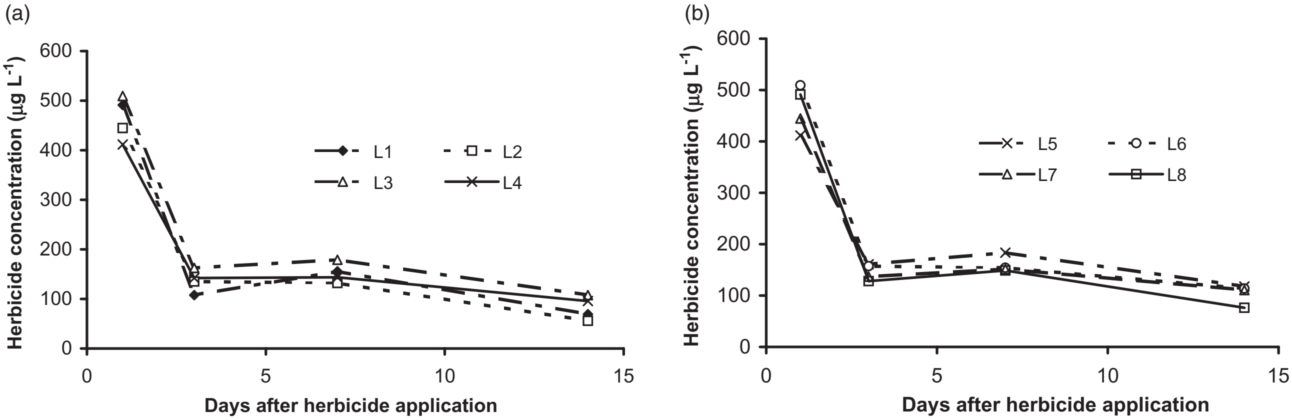

Fig. 2. Concentrations of simetryn in the surface water of the paddy lysimeters (L). (a) L1–4 and (b) L5–8.

the percolation rates were from 0.5–3.0 cm day^{-1} for typical Japanese paddy fields. In the lysimeter procedure for pesticide registration in Japan (MAFF 2000), the percolation rate of ~1–2 cm day^{-1} was recommended for paddy lysimeters. The small percolation values in the studied lysimeters might be related to the clogging of the outlet with sediment and suspended particles.

The evapo-transpiration values also varied significantly among the lysimeters. Besides the natural variation in evapo-transpiration, the uneven placement of the lysimeters and the different fertilizer treatments among the lysimeters also could have contributed to this variation. The difference in evapo-transpiration might also influence pesticide behavior because it is directly related to the amount of irrigation.

Behavior of herbicides in the paddy surface water

Similar simetryn concentrations in the surface water of all the lysimeters were observed during the experiment (Fig. 2), while the thiobencarb concentrations varied remarkably (Fig. 3). The concentration peaks occurred at

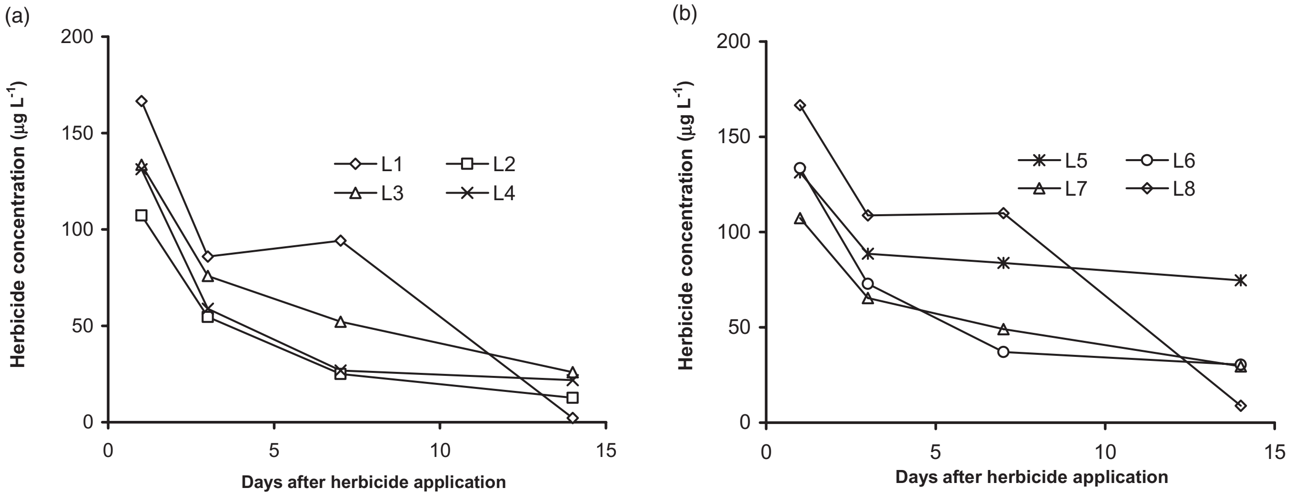

Fig. 3. Concentrations of thiobencarb in the surface water of the paddy lysimeters (L). (a) L1–4 and (b) L5–8.

1 DAHA, similar to other studies (Inao *et al.* 2001; Phong *et al.* 2006; Watanabe *et al.* 2007). However, only the results of the simetryn concentrations were comparable with those in the fields. The thiobencarb peak concentrations were significantly lower than those of the field concentrations. Among the eight lysimeters of L1–L8, the simetryn concentrations at 1 DAHA ranged from 411.6 μg L^{-1} in a sample from L4 and L5 to 509.3 μg L^{-1} in a sample from L3 and L6. The thiobencarb peaks were from 107.3 μg L^{-1} in a sample from L2 and L7 to 166.6 μg L^{-1} in a sample from L1 and L8. In the actual paddies, which shared similar initial conditions with the lysimeters, Phong *et al.* (2006) reported peak concentrations at 1 DAHA of 496.3 and 450.7 μg L^{-1} for simetryn and 246.6 μg L^{-1} and 225.6 μg L^{-1} for thiobencarb in two identical paddy plots. The remarkable lower level of thiobencarb in the six lysimeters treated with manure slurry can be explained by the adsorption of the herbicide molecule to the organic matter. It is because the applied manure slurry contained a significant amount of dissolved organic matter (DOM) (Table 5) and because, between the two herbicides, thiobencarb is less water-soluble and has a higher organic C normalized distribution coefficient (K_{oc}) than simetryn (Table 3); thus, it probably adsorbs strongly to the DOM present in the lysimeter surface water. Huang and Lee (2001) reported that chlopyrifos, a hydrophobic compound similar to thiobencarb, had a strong affinity to DOM, resulting in even less sorption of this pesticide to the soil surface.

Table 5. Physico-chemical properties of the manure slurry

Physico-chemical property	Unit	Value
pH		7.8
Suspended solid	mg L^{-1}	4200
Total solids	mg L^{-1}	20 000
Total organic carbon	mg L^{-1}	6800
Dissolved organic carbon	mg L^{-1}	4800

As a result of a large rainfall at 2 DAHA, the concentrations of both simetryn and thiobencarb at 3 DAHA were low. The large amount of water input brought by the heavy rainfall diluted the herbicide concentrations in all the lysimeters. Consequently, the concentrations at 3 DAHA in all the lysimeters were only about half of the concentration at 3 DAHA that was reported by Phong *et al.* (2006). At 7 DAHA, the concentrations in the lysimeters were higher or similar to those at 3 DAHA. The first-order kinetics was used to describe the behavior of the herbicides. The estimated first-order dissipation half-lives in the paddy water ranged from 8.9–13.6 days for simetryn and from 3.1–11 days for thiobencarb, except for an extreme value of 28.5 days for thiobencarb in L5 (Table 6). These values are much greater compared with the data reported for Japanese paddy fields, of ~2 days for simetryn and 2–3 days for thiobencarb in the surface water (Phong *et al.* 2006). However, a similarity in the thiobencarb half-life was reported by Ross and Sava (1986) in Californian paddies, where the herbicide concentration reduced to half in >6 days.

Table 6. Estimated first-order half-life of simetryn and thiobencarb

Herbicide	Lysimeter							
	L1	L8	L2	L7	L3	L6	L4	L5
	CF (100 kg ha^{-1})		MS (100 kg ha^{-1})		MS (150 kg ha^{-1})		MS (75 kg ha^{-1})	
Simetryn (days)	8.9	9.0	7.5	12.7	10.8	11.4	11.4	13.6
Thiobencarb (days)	3.1	4.6	6.4	11.0	8.5	9.4	7.9	28.7

CF, chemical fertilizer; MS, manure slurry.

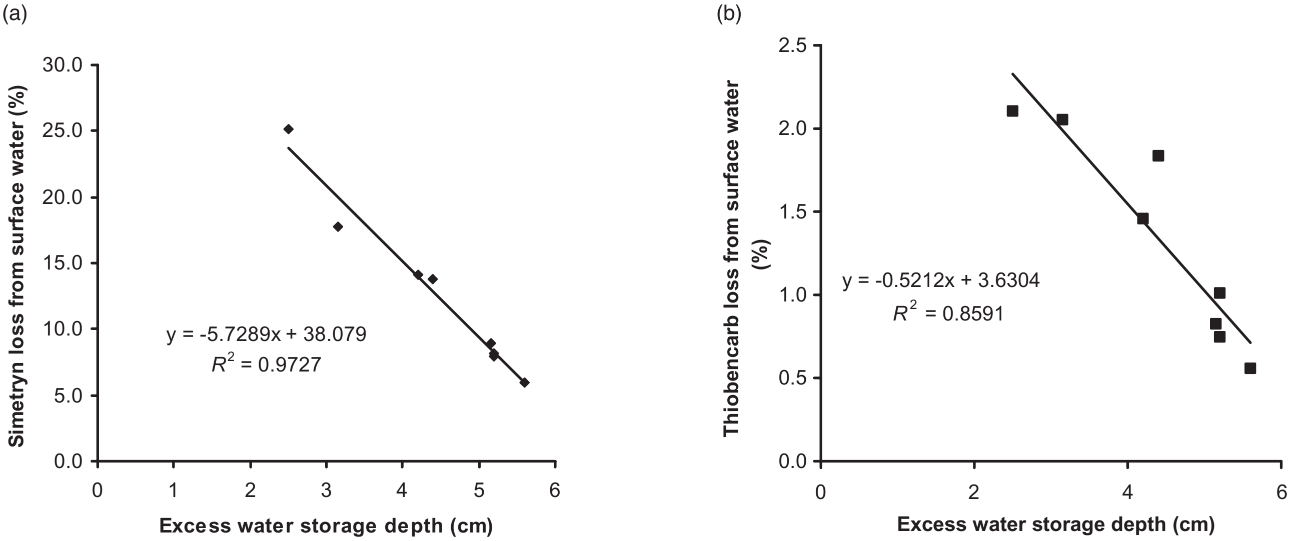

Fig. 4. Relationship between the herbicide losses from the surface water and the excess water storage depth. (a) Simetryn and (b) thiobencarb.

The fact that simetryn and thiobencarb were more persistent in the surface water of the lysimeters than in actual Japanese paddy fields could be explained by the high water level and low percolation rate of the lysimeters. These conditions of the lysimeters require less irrigation and therefore reduce the dilution effect on herbicide concentrations. In addition, the high water level might also reduce the effect of sunlight on thiobencarb, as this herbicide is sensitive to sunlight (Ferrando *et al.* 1992). These conditions in the lysimeters were similar to those in California (Ross & Sava 1986), which led to the similar half-life data in these two studies.

Effect of the excess water storage depth on the herbicide run-off losses

There were variations in the depth of the soil layer and, thus, the EWSD varied from 2.5 cm in L2 to 5.6 cm in L3. These differences resulted in an unequal volume of overflow water from each lysimeter (Table 4). As the herbicides were lost through the overflow water to the open environment, the mass of herbicide run-off was calculated by multiplying the overflow volume by the concentration of the herbicides at the day that the overflow occurred. The simetryn losses were from 6.0% in L3 to 25.1% in L2 of the applied mass, while the corresponding losses of thiobencarb were from 0.6–2.1%, respectively. The herbicide losses from the studied lysimeters were reversely proportional to their EWSD (Fig. 4). The slope of the linear curves showed that the loss of simetryn through run-off was more sensitive to the change of EWSD, probably because simetryn is more soluble than thiobencarb. Meanwhile, the R^2 value of the curves indicated that the correlation between thiobencarb and the EWSD was not as good as that of simetryn. The cause of this phenomenon was the effect of the manure on the behavior of thiobencarb, as discussed previously.

In addition to the relationship between herbicide run-off and the EWSD, it is also important to consider the timing of the run-off. In this study, the losses were greater than the losses of simetryn and thiobencarb in the actual paddy reported by Phong *et al*. (2006), whose maximum values were 6.7% and 1.3% for simetryn and thiobencarb, respectively. The main cause of this difference in the loss is the relative time interval between the rainfall/run-off event and the application date. In this study, the herbicide run-off occurred unexpectedly soon at 2 DAHA, while Phong *et al*. (2006) reported the first run-off occurrence only at 4 DAHA, with less intense rainfall. Therefore, a significant EWSD is required to prevent herbicide run-off in the case of a rainfall event close to the herbicide application date.

However, compared to other studies using a continuous irrigation scheme (EWSD = 0), the EWSD significantly reduced the loss of herbicide through run-off. Inao *et al*. (2001) reported that a continuous irrigation scheme can lose 60.4% and 40.5% of the applied simetryn and molinate, respectively. A simulated scenario, reported by Watanabe & Takagi (2000), also indicated that the total mefenacet losses from a paddy can be ≤62% and 49% of the applied mass, respectively, for 3.0 cm day and 1.0 cm day^{-1} of continuous irrigation. From these results, it is understood that a water management scheme with an appropriate EWSD is recommended as an environment-friendly practise in rice cultivation.

CONCLUSION

The lysimeter seems to be a good tool to investigate the behavior of rice herbicides under paddy conditions. In this study, the water balance and concentration of two herbicides, simetryn and thiobencarb, were monitored from eight lysimeters. The behavior of simetryn was similar among the lysimeters, but thiobencarb behaved differently. It might be related to the effect of the applied slurry onto which thiobencarb adsorbed.

The effect of the EWSD, which is designed to hold excessive rainfall water, showed great influence on the herbicide run-off from paddy fields. The correlation between the herbicide run-off and the EWSD was stronger for simetryn than for thiobencarb because simetryn was less affected by the presence of manure in the lysimeters compared with thiobencarb. An appropriate EWSD is required to effectively prevent herbicide run-off from paddy fields, especially when the rainfall event is close to the herbicide application date.

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