Simulating the dissipation of two herbicides using micro paddy lysimeters

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ABSTRACT

A set of packed micro paddy lysimeters, placed in a greenhouse, was used to simulate the dissipation of two herbicides, simetryn and thiobencarb, in a controlled environment. Data from a field monitoring study in 2003, including the soil condition and water balances, were used in the simulation. The herbicides were applied and monitored over a period of 21 d. The water balances under two water management scenarios, intermittent irrigation management (AI) and continuous irrigation management (CI), were simulated. In the AI scenario, the pattern of herbicide dissipation in the surface water of the field were simulated, following the first-order kinetics. In the CI scenario, similarity was observed in most lysimeter and field concentrations, but there were differences in some data points. Dissipation curves of both herbicides in the surface water of the two simulated scenarios were not significantly different ($P > 0.05$) from the field data except for intercept of the thiobencarb curve in the CI scenario. The distribution of simetryn and thiobencarb in the soil profile after simulation were also similar to the field data. The highest concentrations of both herbicides were found on the topsoil layer at 0–2.5 cm depth. Only a small amount of herbicides moved down to the deeper soil layers. Micro paddy lysimeters are thus a good alternative for the dissipation study of pesticides in the paddy environment.

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1. Introduction

Lysimeters were initially used more than three hundred years ago, to study crop water balance and evaluate evapotranspiration (FAO, 1982). Recently, many studies on pesticide dissipation have been carried out using lysimeters (Bergstrom, 1990; Byers et al., 1995; Corwin, 2000; Beulke et al., 2002; Malone et al., 2004). Lysimeter experiments can provide data for risk assessment, or provide a database for modeling purposes. The environmental fate of pesticides can be studied at different levels: in the lab, with disturbed or undisturbed soil columns (Mallawantantri et al., 1996), or in the field, with suction cup lysimeters (Byers et al., 1995) or soil enclosure lysimeters (Bergstrom, 1990). However, most lysimeter studies have been carried out in upland field conditions. In Japan, Maru (1990) reported a pioneering research using paddy lysimeters to study the runoff pattern of 21 herbicides in paddy water. Later, outdoor lysimeters were also used to develop mitigation techniques for controlling pesticide runoff from paddy fields (Watanabe et al., 2008).

The European Union, in its Directive 91/414, has stressed the use of lysimeters for registration of plant protection products. The new registration guidelines for rice pesticides in Japan have also stipulated the use of paddy lysimeters for predicting environmental concentration of pesticides. However, lysimeters with undisturbed soil profiles were costly due to their larger size (Francaviglia and Capri, 2000; Watanabe et al., 2008). Moreover, undisturbed lysimeter experiments required laborious preparation. Therefore, a lysimeter system that is easy to set up and can provide reliable data is of great interest.

Water management is an important factor affecting the environmental fate of pesticides. Water management might affect pesticide persistence and transformation by dilution, runoff, and leaching into the soil, especially under paddy conditions. Different water management scenarios having significant different water input and output may also affect the ability of lysimeters to simulate the dissipation of rice pesticides. A lysimeter system that can acceptably perform the simulation under different water managements is desired.

The objective of this study was to investigate the ability of packed paddy lysimeters to simulate the dissipation of two herbicides, simetryn and thiobencarb, under two defined water management scenarios: intermittent irrigation (AI) and continuous irrigation with overflow drainage (CI).

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2. Materials and methods

2.1. Lysimeter setup

A set of three stainless steel lysimeters (50 cm × 35 cm × 30 cm) was used in the present study (Fig. 1). Under the surface water, from top to bottom, each lysimeter consisted of three layers: a plough soil layer (14 cm), a hardpan soil layer (2 cm), and a glass bead support (1 cm). A sheet of glass fiber filter paper (GF/A, Whatman) was used to separate the glass bead and hardpan layers. Three outlets were used for collecting percolation water at the bottom of the lysimeter. Each layer of the lysimeter was separately prepared during the setup. The hardpan soil layer was prepared by soaking finely sieved soil (soil particle size less than 2 mm) in water for 24 h, to achieve the saturated condition with the designed porosity of 0.61. For the plough layer, air-dried soils of different particle sizes (D) were mixed according to a preset ratio to achieve the aggregate distribution in the actual paddy plot (Watanabe et al., 2007). The mixture consisted of 12.8%, 20.0%, 20%, and 47.2% of soil particles with $D < 2$ mm, 2 mm $< D < 4.75$ mm, 4.75 mm $< D < 9.5$ mm, 9.5 mm $< D$, respectively. The mixed soil was soaked with 20 L of water for 24 h and then carefully stirred before transferring to the lysimeters. The lysimeters were filled up layer by layer, from bottom to top. The soil used in this experiment was a light clay soil (37.6:31.8:30.6%, sand/silt/clay) with an organic carbon content of 3.6%.

After soil filling, the lysimeters were left undisturbed for 24 h to allow sedimentation without percolation. Next, water was drained freely through the bottom outlets for 7 d for the consolidation of the soil profile. Following this, a peristaltic pump (Cole-Palmer, USA) was connected to the drainage pipes of the lysimeters to control the percolation rate. The designed percolation rate of 0.5 cm d^{-1} was set according to the mean value of the measured percolation rates (0.57 cm d^{-1}) in the field (Watanabe et al., 2007). During the consolidation period, the water level was kept at 4 cm by irrigating the lysimeters twice a day. Rice crop was not planted in this study. All three lysimeters were placed in a greenhouse, in a controlled environment (temperature: 18 °C from 6 pm to 6 am, and 25 °C from 6 am to 6 pm; humidity: 65%).

2.2. Lysimeter monitoring

The dissipation simulations were conducted under two water management scenarios: the AI and CI scenarios, as in the field study in 2003 (Watanabe et al., 2007). The AI scenario refers to an intermittent irrigation scheme with a high drainage gate (7.5 cm) to prevent pesticide runoff. The CI scenario refers to a continuous irrigation and overflow drainage scheme with a low drainage gate (2.5 cm). The simulations of the AI and CI scenarios were conducted from September 13 to October 3, 2006, and from

November 28 to December 19, 2006, respectively. The use of two different water management scenarios was to evaluate the ability of lysimeters to simulate the herbicide dissipation when the amounts of water input and output are largely different.

Water balance data from the AI and CI scenarios in the field study were used for the simulation. As water level is assumed to have the greatest effect on the dissipation of pesticides through the dilution effect, the recorded water level of the field study was exactly followed for both AI and CI scenarios. Other water balance components, including irrigation and precipitation (input water), evaporation, seepage, drainage, and percolation (output water), were simulated in accordance with the field study, to assure the water balance.

Irrigation and precipitation were combined to make the water input, which was measured using a volumetric cylinder. Evaporation was determined by precise balance, by measuring water loss from a square pan placed next to the lysimeters. In this study, evaporation was assumed to be a loss of pure water (without herbicide), because simetryn and thiobencarb are not volatile (Kibe et al., 2000). Therefore, to maintain the water balance, the difference between field evapotranspiration (ET_{field}) and lysimeter evaporation ($ET_{lysimeter}$) ($\delta_{ET} = ET_{field} - ET_{lysimeter}$) was compensated by reducing the water input by the same amount.

$$\text{Water input (actual)} = \text{Water input (irrigation} + \text{precipitation)} - \delta_{ET}$$

When δ_{ET} was greater than the calculated water input, the input value became negative. In this case, no water was added to the lysimeters on that day and the negative value was further deducted from the water input on the following day(s).

The field percolation data was divided into two parts: lateral seepage and vertical percolation. Lateral seepage, which consists of losses through the macro pores and edge flow, was considered to bypass the soil matrix and concurrent interaction; therefore, it was added to the surface drainage component of the water balance. Vertical percolation through the soil matrix was simulated by controlling the water outflow from the bottom of the lysimeters at the designed rate (0.5 cm d^{-1}), as described in the previous section. Seepage and drainage were combined to make the surface water output, which was also measured using a volumetric cylinder. The sequence of daily monitoring activities was sampling (if needed), percolation rate measurement, calculating ET and δ_{ET}, withdrawing surface water output, and finally adding actual water input.

The physical properties of soil and surface water were monitored twice a day, using a pH meter (D-23, Horiba), an Eh meter (EHS-120, Fujiwara Scientific), and temperature loggers (UIZ 3633, Hioki). Platinum-tipped Eh electrodes were installed in the surface water and at 1 and 3 cm soil depths.

2.3. Herbicide application and sampling

After the lysimeter setup, a granular herbicide product, KumishotSM® (4.5% simetryn, 15.0% thiobencarb, 4.5% mefenacet, 2.4% MCPB), was applied at a rate of 10 kg ha^{-1}. The product and the application rate were the same as in the field experiment.

A 5-cm-long stainless steel ring of 5 cm diameter, placed on a thin plate, was used to sample the entire profile of the surface water in each lysimeter, from five spots (the four corners and the center). The samples were then combined to make one composite sample. The samples were taken at 0, 1, 3, 5, 7, 15, and 21 d after herbicide application (DAHA). Volumes of the composite samples were 100 mL for 1, 3, 5, 7 DAHA, 200 mL for 15 DAHA, and 400 mL for 0 and 21 DAHA. All samples were stored at −20 °C until chemical analysis. To maintain the water balance, the volume of surface water samples was considered as part of the surface water

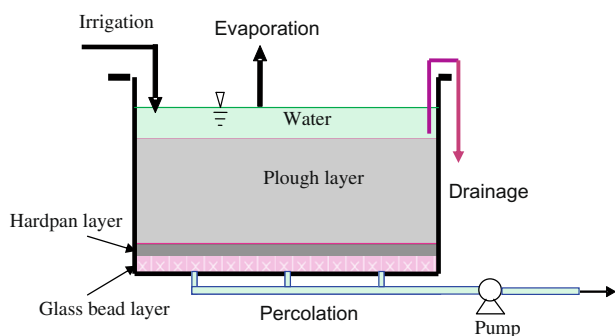**Fig. 1.** Design of a micro paddy lysimeter.

output. For percolation water, water in the collecting bottles was measured and stored at −20 °C for chemical analysis on the sampling day.

At the end of the experiment (21 DAHA), the soil profiles in the lysimeters were sampled after draining the paddy water completely. Soil layers at 0–2.5 cm, 2.5–5 cm, 5–7.5 cm, 7.5–10 cm, 10–12.5 cm, and 12.5–15 cm depths were taken manually, by driving a soil core sampler into the soil and then picking it up carefully, to avoid cross-contamination. Soil samples were also kept frozen until chemical analysis.

2.4. Chemicals and sample extraction

Simetryn and thiobencarb standards (purity >99%) and other chemicals of analytical grade (Wako Pure Chemical Industries, Osaka, Japan) were used in this experiment. Water used for chemical analysis was produced using a MilliQ Water Purification System (Millipore, Billerica, MA, USA).

Water samples were thawed and filtered through a 1.1 μm glass microfiber filter paper (GF/C, Whatman). Surface water samples were extracted by the solid phase extraction method, using Sep-Pak Plus PS-2 cartridges (Waters, Milford, USA). Prior to use, the cartridge was activated using 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}. The cartridges were washed with 10 mL of distilled water and air-dried for 10 min, after which they were mounted on a Visiprep vacuum manifold (Supelco, Bellefonte, USA), which was connected to an EYELA water aspirator (Tokyo Rikakikai, Tokyo, Japan). The herbicides were eluted from the cartridge with 6 mL of acetone at the rate of 1 mL min^{-1}. The acetone extracts were collected and then evaporated down to 1 mL, using a gentle stream of nitrogen. The final samples were transferred to the vials and kept at 4 °C until gas chromatography (GC) analysis.

For percolation water samples, as ferric hydroxide in the samples can easily clog the cartridges, the samples were extracted by liquid–liquid extraction with dichloromethane. Sample was poured in a separatory funnel and shaken vigorously, twice, with 100 mL dichloromethane. The organic layers were taken and combined. The dichloromethane solution was shaken with 40 g anhydrous sodium sulfate to eliminate the residual water and then filtered through silicon-treated filter paper (1 PS, Whatman). Dichloromethane was evaporated at 35–40 °C under vacuum pressure. The residue was dissolved with 1 mL acetone using an ultrasonic device. The final sample was transferred to the vials and kept at 4 °C until GC analysis.

Soil samples were air-dried to reduce the water content and then ground in a stainless steel bowl before herbicide extraction. Twenty grams of soil sample and 100 mL acetone were added into a 200 mL Erlenmeyer flask. The soil was then sonicated for 10 min. After being shaken for 2 h in an orbital shaker, the acetone extract was removed from the soil by filtering the slurry solution through a filter paper (GF/C, Whatman). The residual soil was washed twice with 20 mL of acetone. All the filtrates were combined and the acetone solution was then evaporated under vacuum pressure until 10 mL solution remained. The remaining solution was mixed with 20 mL NaCl 10% and loaded on a diatomaceous earth cartridge (Chem Elut, Varian). The cartridge was then eluted twice with 60 mL of dichloromethane. The dichloromethane extracts were combined and dried with 20 g of anhydrous sodium sulfate. The extract was then filtered through silicone-treated filter paper (1 PS, Whatman). Dichloromethane was evaporated at 35–40 °C under vacuum pressure. The residue was dissolved in 2 mL acetone using an ultrasonic device. The final sample was transferred to vials and kept at 4 °C until GC analysis.

2.5. Gas chromatography

The herbicides in the water and soil samples were analyzed using a Shimadzu 2010 gas chromatograph (Shimadzu, Kyoto, Japan) equipped with a Flame Thermionic Detector (FTD). The column was a DB-5 column (30 m × 0.25 μm × 0.32 mm) (J&W Scientific, Rancho Cordova, USA). Helium was used as the carrier gas. The temperature was programmed as follows: 60 °C for 2 min, ramped up to 140 °C at 10 °C min^{-1}, then to 325 °C at 5 °C min^{-1}. The temperature was then maintained at 325 °C for 4 min. A splitless injection mode was used, with an injection volume of 2 μL. The carrier gas pressure was set at 40 kPa for 2 min, then increased to 64 kPa at 3 kPa min^{-1}, and continued to be ramped up at 1.5 kPa min^{-1} to 103 kPa, which was maintained for 4 min. The limits of detection of both simetryn and thiobencarb were 0.1 μg L^{-1} and 0.5 μg kg^{-1} for water samples and soil samples, respectively. The recovery ratios were 100% for simetryn and 85% for thiobencarb in surface and percolation water samples. The recovery ratios of soil samples were 109% and 99% for simetryn and thiobencarb, respectively.

2.6. Statistical methods

To verify the ability of the lysimeters to simulate the herbicide concentrations in surface water of the field, equalities of slope and intercept were tested for linear regressed lines of herbicides concentrations (on logarithmic scale) over DAHA. The test, using the analysis of covariance (ANCOVA), was to determine whether the dissipation process of herbicides in the lysimeters and the field were identical.

The movement of the herbicides in paddy soil was investigated by comparing the means of herbicide concentrations in different soil layers using t-test. The statistical calculation was performed using the Graphpad Prism 5 software (Graphpad Software, Inc., USA).

3. Results and discussion

3.1. Physical conditions

The temperature of paddy water in the lysimeters had a mean of 25.5 °C and 21.6 °C for the AI and CI scenarios, respectively, with variations from the lowest of 14.1 °C to the highest of 39.0 °C. The difference in temperature between the two simulations can be attributed to the difference in daily sunshine hours between the two monitorings (late September for AI and early December for CI). They were comparable with the values in the field during the time of herbicide application (Genka, personal communication), which had a highest value of 35 °C and a lowest value of 13 °C, with an average temperature of approximately 21 °C.

In this experiment, the average pH value of the surface water was slightly alkaline (pH of approximately 8.3), and stable during the monitoring period. Takagi et al. (1998) reported that water pH in the experimental field fluctuated from neutral (pH 7 in the mornings) to alkaline (pH 9.5 in the afternoons) due to the photosynthetic processes. As there was no rice or any other comparable plant in the studied lysimeters, the photosynthetic activities might differ from those in the real field.

An oxidized state, with Eh > 400 mV, was observed in the surface water in both simulated scenarios. The soil was in the reduced state at both 1 and 3 cm depths. However, the Eh values varied remarkably (from −210 mV to 220 mV) between soil measurements. Greater variation was observed in the CI scenario than that in the AI scenario. Fiedler et al. (2007) have discussed that changes in external conditions, such as precipitation and water table fluctu-

ations (as indirect parameters of oxygen supply), temperature, and availability of organic matter, can all lead to changes in Eh value. Consequently, the redox potential can vary by several orders of magnitude, both temporally and spatially (Vepraskas et al., 1999; Gao et al., 2002). However, the observed data were still in agreement with those reported in the experimental paddy plots (Takagi et al., 1998).

In general, the physical conditions such as paddy water temperature, pH, and redox potential (Eh) in the lysimeters were similar to the conditions in the actual paddy field in Japan.

3.2. Simulation of water balance components

The water balance in the two simulated scenarios during the 21-d monitoring period is shown in Table 1. Some components of the water balance in the simulations were adjusted in accordance with the field data to keep the water level in the lysimeters as close to the field data as possible, as the water level greatly affects the concentrations of herbicides in water and thus determines their dissipation.

The ET_{field} was generally 3 or 4 times higher than the $ET_{lysimeter}$, except during some days of rain. The ET_{field} varied largely due to the influence of environmental factors such as wind and humidity, while the $ET_{lysimeter}$ values fluctuated within a narrow range (from 0.06 cm to 0.25 cm in the AI scenario, and from 0.04 cm to 0.16 cm in the CI scenario) due to the controlled environment of the greenhouse. Moreover, the average evaporation in the AI scenario was greater than that in the CI scenario as a result of the higher average temperature of the surface water during the monitoring period.

The smaller value of the total $ET_{lysimeter}$ led to an adjustment of water input as described in Section 2. As a result, the simulated water inputs were smaller than the field values for both scenarios (Table 1).

Other water output components, including drainage, seepage, and percolation, were kept the same as in the field monitoring study because they generate herbicide losses. Consequently, the values of those components were comparable between the simulation and the field output data.

The water levels in the lysimeters and the field were very similar (Fig. 2). This indicated that different water management practices can be simulated by micro paddy lysimeters.

3.3. Simulation of herbicide dissipation

3.3.1. In water

Fig. 3 shows the average herbicide concentrations with the standard deviations in surface waters in the lysimeters and the field data, for both AI and CI scenarios. In the AI scenario, the maximum concentrations of simetryn in the lysimeters at 1 DAHA ranged from 458 $\mu g\,L^{-1}$ to 646 $\mu g\,L^{-1}$, while that concentration in the field was reported at 951 $\mu g\,L^{-1}$. This large variation occurred only at 1 DAHA. It was observed that, depending on the experiments, the maximum concentrations of simetryn at 1 DAHA vary greatly, from as low as 300 $\mu g\,L^{-1}$ (Inao et al., 2001), to 496.3 $\mu g\,L^{-1}$ (Phong
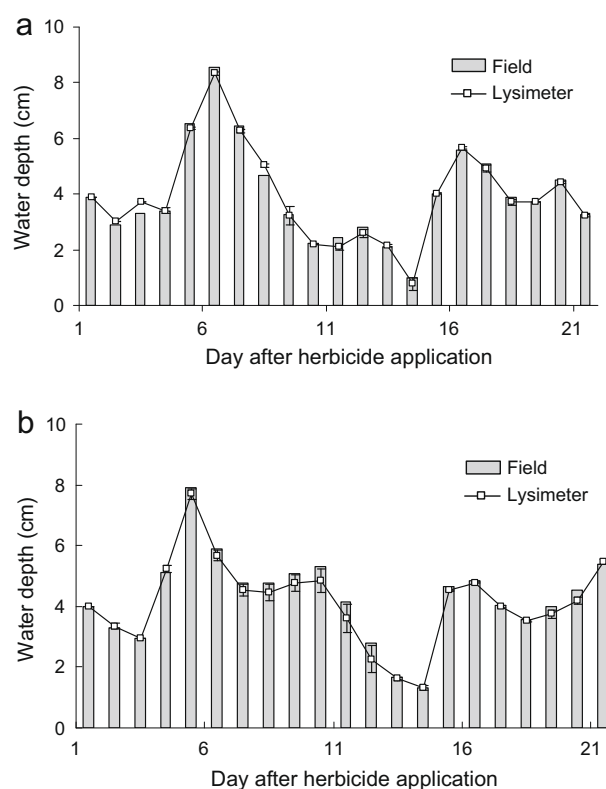
Fig. 2. Water level of AI scenario (a) and CI scenario (b) in the field and the lysimeters (average with standard deviation).

et al., 2006) and 951 $\mu g\,L^{-1}$ (Watanabe et al., 2007), given that all studies assigned the same simetryn application rate. The maximum concentrations of simetryn in the CI scenario were from 610 $\mu g\,L^{-1}$ to 807 $\mu g\,L^{-1}$ in the lysimeters and 838 $\mu g\,L^{-1}$ in the field. The variation of the maximum concentrations of simetryn could probably be explained by the difference in the initial hydrological conditions, as well as in the uniformity of the product itself. Flury (1996) stated that the release is gradual for granular formulations, because the active ingredient leaves the granules either by diffusion or is leached out of the granules by irrigation or precipitation. Therefore, granular formulations usually yield a less uniform spatial distribution than spray formulations, and this may affect the transport of the active ingredient. However, the variation of thiobencarb concentrations in the AI simulation was not significant. The simulated concentrations of thiobencarb in the AI scenario on all the sampling dates were similar to those recorded in the field.

In the CI scenario, the maximum concentrations of simetryn in the lysimeters at 1 DAHA were not markedly different from the field data. With the same water level at 1 DAHA, the maximum concentration of simetryn in the CI simulation ranged from 610 $\mu g\,L^{-1}$ to 807 $\mu g\,L^{-1}$ in the lysimeters, compared to the value of 838 $\mu g\,L^{-1}$ in the field. However, the maximum concentrations of thiobencarb in the lysimeters at 1 DAHA, ranging from 222 $\mu g\,L^{-1}$ to 259 $\mu g\,L^{-1}$, varied greatly from the peak of 641 $\mu g\,L^{-1}$ in the field. Phong et al. (2006) reported that the thiobencarb in the field peaked at 246.6 $\mu g\,L^{-1}$ at 1 DAHA, with the same application rate. Again, this discrepancy could be caused by the differences in hydrological and field conditions and by the difference in the dissolution process between the field and the lysimeters.

The large amounts of water input and output in the CI scenario had great impact on the dissipation of both simetryn and thioben-

Table 1
Water balance in the lysimeters and in the field.

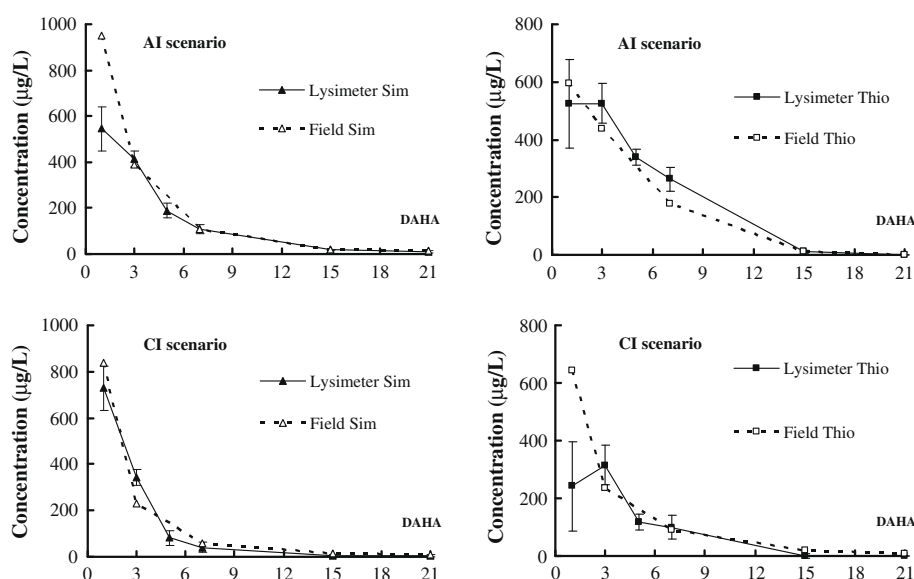|		AI scenario		CI scenario	
		Lysimeter	Field	Lysimeter	Field
Input (cm)		26.2	30.9	35.6	42.3
	Drainage	1.4	1.4	12.9	12.9
	Seepage	12.8	11.5	9.1	11.8
Output (cm)	Percolation	10.2	10.5	10.2	10.5
	ET	3.0	8.0	2.1	8.0
	Total	27.4	31.4	34.3	43.2

Fig. 3. Concentrations of simetryn (Sim) and thiobencarb (Thio) in the surface water of the field and the lysimeters (average with standard deviation).

carb. The concentration of thiobencarb in one lysimeter was unexpectedly low, from 5 DAHA until the end of the monitoring. A considerable difference was also found between the lysimeter and the field concentrations at 15 DAHA. The possible cause of this difference is the large error in water balance measurement in both field and lysimeter data in the CI scenario. The difference in the water balance simulation procedure of the lysimeter experiment and the irrigation/rainfall-runoff pattern in the field were also thought to contribute to this difference.

Although the field data on percolation water were not available, the percolation water from the lysimeters was analyzed to evaluate the performance of the lysimeters. In the CI scenario, no trace of herbicide was detected in the percolation water during the monitoring period. In the AI scenario, traces of both simetryn and thiobencarb (below $0.5\ \mu g\ L^{-1}$ for simetryn and below $0.3\ \mu g\ L^{-1}$ for thiobencarb, respectively) were spotted on some sampling dates, possibly due to cross-contamination or an error in the sampling process.

3.3.2. In soil

Fig. 4 presents the concentrations of simetryn in the soil profile in the AI and CI scenarios, respectively. The simetryn concentrations were highest at $970\ \mu g\ kg^{-1}$ in the AI scenario and $906\ \mu g\ kg^{-1}$ in the CI scenario in the topsoil layer (0–2.5 cm), and declined sharply to approximately $60\ \mu g\ kg^{-1}$ in the next layer. With the same application rate of simetryn, Inao et al. (2001) reported that the simetryn concentrations peaked at $590\ \mu g\ kg^{-1}$ at 7 DAHA for the 0–2.5 cm soil layer and $57\ \mu g\ kg^{-1}$ at 14 DAHA for the 2.5–5 cm soil layer, respectively. The simetryn concentration then decreased gradually in the soil layers below 5 cm.

As with simetryn, most of the thiobencarb mass remained in the topsoil layer, at 0–2.5 cm depth (Fig. 4). While the simetryn concentrations in the first soil layers were approximately 15–20 times higher than those in the next layer, the thiobencarb concentrations in the topsoil layer were recorded as being approximately 40–45 times higher than those in the next layer. A higher ratio of thiobencarb in the topsoil layer is because thiobencarb is relatively immobile due to its hydrophobic nature (high K_{oc} and low solubility) (Kibe et al., 2000). Therefore, thiobencarb tends to adsorb strongly into the soil (Braverman et al., 1990; Kibe et al., 2000; Chiang et al., 2001). The maximum concentrations of thiobencarb were
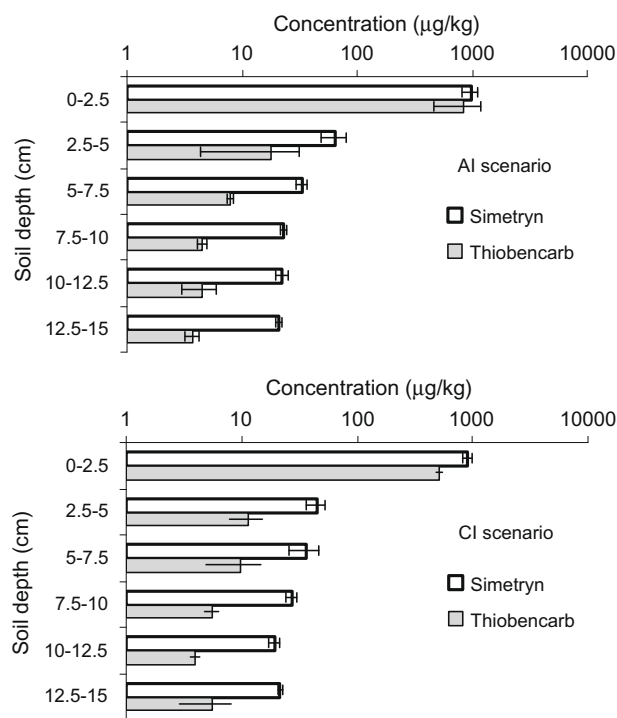

Fig. 4. Concentrations of simetryn and thiobencarb in the soil profile of the lysimeters in two simulated scenarios.

Table 2
Pesticide mass distribution (as % applied) in lysimeters at the end of the 21-d monitoring period.

	Simetryn		Thiobencarb	
	AI	CI	AI	CI
Residue in surface water	0.50	0.45	0.02	0
Residue in soil	58.60	54.69	13.52	8.55
Loss through water discharge	40.33	40.00	18.73	16.37
Dissipation[a]	0.57	5.21	67.72	75.08

[a] Dissipation including pesticide mass lost through other paths such as microbial degradation, hydrolysis, and photolysis, etc.

Table 3
Results of the statistical analysis between the dissipation curves of lysimeter simulation and field monitoring.

		Slope			Intercept		
		Pooled value	F	P	Pooled value	F	P
AI	Simetryn	−0.094	0.292	0.83[a]	−0.195	1.000	0.42[a]
	Thiobencarb	−0.146	1.442	0.27[a]	0.135	1.587	0.23[a]
CI	Simetryn	−0.110	0.759	0.54[a]	−0.305	0.899	0.46[a]
	Thiobencarb	−0.162	2.112	0.15[a]	NA[a]	14.54	0.003[b]

NA: not available because the intercepts were significantly different, it was impossible to calculate a pooled intercept for these curves.
[a] Nonsignificant difference.
[b] Significant difference.

834 µg kg^{-1} (AI scenario) and 515 µg kg^{-1} (CI scenario) in the first soil layers, and reduced to 3.7 µg kg^{-1} (AI scenario) and 5.5 µg kg^{-1} (CI scenario) in the bottom soil layers (Fig. 4).

3.3.3. Mass balance calculation

Table 2 shows pesticide mass distribution in surface water and soil in the lysimeters at the end of the 21-d monitoring period. For both AI and CI scenarios, there was almost no pesticide residue in surface water. However, there was still a remarkable amount of pesticides remaining in the soil layers, especially for simetryn. Loss through water discharge accounted for almost all losses of simetryn mass during the monitoring period and thus dissipation through other paths such as microbial degradation, hydrolysis, and photolysis was not important for simetryn. Meanwhile, losses by dissipation through other paths was markedly important for thiobencarb fate. Losses of thiobencarb caused by those degradation paths were several times higher than the masses lost through water discharge or remained in the soil.

3.4. Statistical analysis

3.4.1. For herbicide dissipation in water

The natural logarithms of pesticide concentrations in surface water were plotted versus sample timing. These semi-log plots resulted in a straight line with all pesticides in both scenarios experimented in the lysimeters and in the field (except the case of thiobencarb in L3 in the CI scenario). It meant that the pesticide dissipation pattern can be attributed to a first-order process whose rate constant equals the slope of the line and extrapolated initial concentration equals the intercept of the line. Equalities of the slopes and intercepts obtained from a set of data in each lysimeter and in the field were tested to verify the ability of lysimeters to simulate the pesticide dissipation in surface water of the field. Results for which the reported P was less than 0.05 indicate statistical significance at the 5% level. When nonsignificant difference occurred, pooled values were calculated and used to estimate the time for dissipation of 50% of the initial concentration (half-life or DT$_{50}$).

Table 3 shows that for simetryn, the slopes and intercepts of the dissipation lines were not statistically different between the lysimeters and the field in both AI and CI scenarios (P > 0.05). Therefore, the pooled values were computed and DT$_{50}$ were 7.37 and 6.30 d for AI and CI, respectively. In case of thiobencarb, the slopes of the lines were not significantly different while the intercepts were. The estimated DT$_{50}$ of thiobencarb in both scenarios was similar (4.75 and 4.28 d for AI and CI scenarios, respectively) and shorter than that of simetryn.

The difference in the intercepts in the CI scenario was probably due to the irregularity of thiobencarb fate in one lysimeter in the late period of the CI simulation, as described in the previous section.

3.4.2. For herbicide dissipation in soil

Simple *t*-test was used to compare the concentration of herbicides in different soil layers. For simetryn, while the concentration drastically decreased from the surface soil to the next layer, no significant difference was detected in the soil layers below a 7.5 cm depth in either the AI or the CI scenarios (P > 0.05).

Similarly for thiobencarb, from a soil depth of 5 cm downward, there was no statistical difference in the concentrations in the soil layers and in the lysimeters in both simulated scenarios (P > 0.05).

A study by Phong et al. (in press) also showed that the concentrations of simetryn and thiobencarb in the field were similar at a soil depth of 5 cm downward. In this study, at 22 DAHA, simetryn concentrations were about 50 µg kg^{-1} in the 5–10 cm depth and were lower, from 20 to 40 µg kg^{-1}, in the 10–15 cm depth. Meanwhile, thiobencarb concentrations at 22 DAHA were shown very similar in the 5–10 cm and 10–15 cm depths, being about 10 µg kg^{-1} in 2005 and about 75 µg kg^{-1} in 2004 (Phong et al., in press). The similarity between the field and lysimeter data again proved the ability of micro paddy lysimeters to simulate the dissipation of pesticides under paddy conditions.

4. Conclusion

The dissipation of simetryn and thiobencarb in the field were simulated by using a set of three lysimeters for two water management scenarios: AI and CI. Soil profile and hydrological conditions of the field were mimicked in the lysimeters as much as possible. The dissipation of both simetryn and thiobencarb in surface water of the lysimeters followed the first-order kinetics as those in the field. While the dissipation lines of all pesticides in the AI scenario showed insignificant difference in the slopes and intercepts, the CI scenario gained only the equality of slopes, meaning that the pesticide dissipation in surface water was simulated better under the AI scenario than the CI one. Unremarkable concentrations of pesticides were found in surface water at the end of the 21-d monitoring period but considerable amounts remained in soil layers, especially for simetryn. Loss through water discharge was more important for simetryn than for thiobencarb and dissipation through other paths accounted for almost all losses of thiobencarb.

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