Original Article

Prediction of Pesticide Behavior in Paddy Field by Water Balance on the Water Management Using Pesticide Paddy Field Model (PADDY)

Keiyo INAO,^{*,#} Yasuo ISHII, Yuso KOBARA and Yasuo KITAMURA[†]

*National Institute of Agro-Environmental Sciences, Ministry of Agriculture, Forestry and Fisheries,
Kannon-dai, Tsukuba, Ibaraki 305-8604, Japan*

[†] *Agricultural Chemicals Inspection Station, Ministry of Agriculture, Forestry and Fisheries,
Suzuki-cho, Kodaira, Tokyo 187-0011, Japan*

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The improved version of the pesticide paddy field model (PADDY) was evaluated for the prediction of pesticide concentrations in water and soil considering water balance on the water management. Field studies under the two different conditions on the water management practices, continuous irrigation and drainage, and water holding management that regulate drainage during the experimental periods, were performed to validate the improved model using molinate and simetryne. For both pesticides, concentrations in paddy water were the same level during the first day after the application on both fields. After second day, pesticide concentrations on the field for continuous irrigation and drainage were lower than those on the field of water holding management. Good fits between model predictions and field observations were obtained for the two pesticides by considering the water management and hydrological condition.

Key words: environmental fate, pesticides, paddy, water balance, simulation model.

INTRODUCTION

Recently, there has been growing concern about the risk related to the use of pesticide. Pesticides are intentionally applied to agricultural lands, and there is a possibility that a part of pesticides transfers to public water areas such as rivers and lakes. In Japan, over 50% of agricultural lands are paddy fields, and pesticides are used extensively in paddy fields to control pests and weeds that affect rice plants. Especially, herbicides used in paddy fields are detected often in river water from May to July after the pesticides application.^{1,2)}

In the previous paper,³⁾ we validated the pesticide paddy field model (PADDY) for predicting pesticide concentrations and pesticide runoff amounts. Accurate prediction of pesticide runoff loss is required to estimate the environmental concentration of pesticides in public water areas. In the previous version of PADDY, how-

ever, steady state was applied in water balance for the water management in paddy field and weather conditions were not considered. Therefore, under the outdoor conditions where outflow rate of paddy water changes by weather and water management, the model cannot accurately predict pesticide runoff.

In this study, to estimate the behavior of pesticides more accurately, we modified the PADDY for calculation of water balance in paddy field with site-specific environmental conditions. We also performed paddy field experiments under the different conditions on water management to validate the model, and calculated values by the modified model were compared with experimental results of measured concentrations.

THEORY, MATERIALS AND METHODS

1. Water Balance in Paddy Field

The water movement processes are inflow (irrigation), precipitation, evaporation, transpiration, outflow (overflow), and both vertical and horizontal percolation as shown in Fig. 1. The water balance equation in paddy field can be expressed as follows:

* To whom correspondence should be addressed.

Present address: Agricultural Chemicals Control Office, Water Environment Department, Environmental Management Bureau, Ministry of the Environment, Kasumigaseki, Chiyoda-ku, Tokyo 100-8975, Japan.

Fig. 1 Water balance and pesticide behavior in paddy field.
→: pesticide transport, ⇨: water movement.

$$A \frac{dh}{dt} = Q_{in} - Q_{out} + A(P - E - T) - q_v - q_h \quad (1)$$

Where A is area of paddy field (m^2), h is water depth (m) at time t , Q_{in} is irrigation rate (m^3/day), Q_{out} is outflow rate (m^3/day), P is precipitation (m/day), E is evaporation rate (m/day), T is transpiration rate (m/day), q_v is vertical percolation rate (m^3/day), and q_h is horizontal percolation rate (m^3/day). If h is smaller than height of outlet (h_{out}), Q_{out} is zero. In case h is higher than h_{out} , outflow is generated. Under these conditions, this equation can be solved by finite difference method (backward difference approximation) with daily inflow, rainfall, evaporation, transpiration, and both vertical and horizontal percolation data. As the results, h and Q_{out} are obtained as a function of time t .

2. Mass Balance of Pesticides in Paddy Field

Figure 1 shows water balance and the pesticide transport processes in paddy field for PADDY. In this model, the process of pesticide uptake by plants was not considered. If pesticide concentration in irrigation water is equal to zero, the mass balance equations on the surface of paddy field are given below:

For the water compartment,

$$Ah \frac{dC_w}{dt} = Ahk_s(C_{ws} - C_w) - Q_{out}C_w - (q_v + q_h)C_w - Mk_{des}(K_f C_w^{1/n} - C_s) - K_L A C_w - Ahk_{dw}C_w \quad (2)$$

For the soil solid compartment,

$$M \frac{dC_s}{dt} = Mk_{des}(K_f C_w^{1/n} - C_s) - Mk_{ds}C_s \quad (3)$$

Where C_w is pesticide concentration in water (mg/l), k_s is dissolution rate constant ($1/day$), C_{ws} is water solubility of pesticide (mg/l), M is weight of surface soil solid (kg), k_{des} is desorption rate constant ($1/day$), K_f is Freundlich adsorption coefficient ($1/kg$), $1/n$ is Freund-

lich exponent, C_s is pesticide concentration in soil solid (mg/kg), K_L is volatilization rate (m/day), and k_{dw} and k_{ds} is first-order degradation rate constant in paddy water and soil ($1/day$), respectively.

For the dissolution of the granule formulation,

$$\frac{dW}{dt} = -Ahk_s(C_{ws} - C_w) \quad (4)$$

Where W is amount of pesticide in the granule formulation (mg). When dissolution of the pesticide from the granule is completed ($W=0$), k_s is set to zero in equations 2 and 4. In the previous version of PADDY, hydrological and management condition was not considered, and water depth (h) and outflow rate (Q_{out}) were handled as constant values. In the modified version of PADDY, h and Q_{out} can be calculated by Equation 1 as a function of time t , and these values and input parameters are substituted in Equations 2–4, pesticide concentrations in water and soil can be obtained by numerical solution technique (Runge-Kutta-Gill method).

3. Model Validation

3.1 Pesticides

Molinate (*S*-ethyl hexahydro-1*H*-azepine-1-carbithioate) and simetryne [4,6-bis(ethylamino)-2-methylthio-1,3,5-triazine] were used to validate the modified version of PADDY. The formulated product used for experiment was the Mamet[®] SM One Kiro Granule (24.0% molinate, 4.5% simetryne and 2.4% MCPB ethyl). Table 1 shows physicochemical properties, equilibrium constants, and rate constants for molinate and simetryne, which were measured and estimated values.³⁾

Table 1 Model input parameters of molinate and simetryne.

Parameter	Molinate	Simetryne
Physicochemical properties		
molecular weight (g/mol)	187.3	213.3
water solubility (C_{ws} , mg/l)	800 (20°C)	450 (20°C)
vapor pressure (mm Hg)	5.7×10^{-3} (25°C)	7.1×10^{-7} (20°C)
Equilibrium constants		
Henry's constant (-)	7.2×10^{-5} a)	1.8×10^{-8} a)
adsorption coefficient (K_f , l/kg)	2.2 ^{b)}	3.0 ^{b)}
[Freundlich exponent (1/n)]	1	1
Rate constants		
dissolution (k_s , 1/day)	9.6×10^{-3} c)	3.9×10^{-3} c)
desorption (k_{des} , 1/day)	2.9×10^{-1} c)	1.5×10^{-1} c)
volatilization (K_L , m/day)	1.6×10^{-2} d)	3.8×10^{-6} d)
degradation in water (k_{dw} , 1/day)	1.9×10^{-2} c)	4.7×10^{-3} c)
degradation in soil (k_{ds} , 1/day)	1.7×10^{-2} e)	1.4×10^{-2} e)

a) Calculated by the dilling equation (reference 4).

b) Obtained from reference 5. Organic carbon content in soil is 2%. c) Measured value (reference 3). d) Calculated by the Liss & Slater method (reference 6). e) Obtained from references 7 and 8.

3.2 Field experiment

To validate the modified PADDY, a field experiment was carried out on paddy fields in National Institute of Agro-Environmental Sciences. The layout of paddy fields for the experiment is shown in Fig. 2. Paddy fields were surrounded by concrete frame to maintain flooded condition. Irrigation water was supplied by pipeline and an irrigation tap was installed on each field plot. The outlet, which controls water depth, was also assembled. The soil texture is light clay (clay 47%, silt 19%, sand 34%) having 2% organic carbon and pH of 5.2/ H_2O . The experiment was conducted between July 1st and August 1st, 1996. The average temperature was 24.4°C ($16.2\text{--}35.1^\circ\text{C}$), and pH in paddy water ranged from 6.6 to 7.9.

At 26 days after transplanting of rice plant (July 1st, 1996), the Mamet SM granule was applied uniformly by hand at a rate of 10 kg/ha (molinate 2400 g/ha, simetryne 450 g/ha as active ingredient) under the flooded conditions. The experiments were performed under two different conditions on water management. One is water-holding management, which means water depth was kept about 4 cm by supplying irrigation corresponding to water requirement in depth without excess water (Field 1). The other management is continuous irrigation, which is the outlet of field plot was adjusted so that maximum water level was 4 cm and irrigation water was supplied at a fixed flow rate (Field 2).

3.3 Sampling

At various intervals of 3 hr, 6 hr, 1, 2, 4, 7, 14, 22, and 31 days after the application, water samples were collected at 1–2 cm depth in paddy water by a water collecting equipment composed of a manual suction pump and a glass bottle connected with a Teflon tube. A compos-

ite water sample from each field plot of five spots was analyzed for pesticide concentrations in paddy water. Soil samples were taken from two sites of the Field 1 at intervals of 1, 4, 7, 14, and 31 days after the application as shown in Fig. 2. The samples were collected 5.0 cm deep with stainless steel cylinder (20×5 cm I.D.) and divided into two layers (0–2.5 cm and 2.5–5.0 cm depth) and mixed for each layer and analyzed individually.

3.4 Observation of hydrological condition

Water depth, volume of irrigation water, and the fall in paddy water depth which resulted from vertical percolation and evapotranspiration were measured during the experimental periods. Polyvinyl chloride pipes (30×20 cm I.D.) were inserted into the soil of about 20 cm deep at two sites in the Field 1 (see Fig. 2). The falls in paddy water depth in a day were determined by measuring the differences of the water levels in these pipes during the day. Daily vertical percolation rate was calculated by subtracting daily evapotranspiration rate from the fall in paddy water depth in a day. Daily horizontal percolation rate was calculated by subtracting both daily evapotranspiration and vertical percolation rate from the daily difference of water depth in the field. Daily rainfall and pan evaporation data were obtained from meteorological observatory of the Institute. In general, evaporation amount from water surface is relatively large in the initial growth stage of rice plant, however, it decreases with the flourish of the rice. On the other hand, transpiration from rice plant depends on surface area of the rice plant, and it increases with the plant growth.⁹⁾ However, it is reported that evapotranspiration ranged from 0.96 to 1.22 times as much as pan evaporation through the growing period.¹⁰⁾ Therefore, evapotranspiration was assumed to be equal to pan evaporation from meteorological observatory data.

3.5 Pesticide analysis

Water samples (50 and/or 200 ml) were passed through a solid phase extraction cartridge (WATERS Sep-Pak PS-2), and the cartridge was eluted with ethyl acetate (10 ml). Then the eluate was concentrated in a rotary evaporator at 40°C to about 1 ml and dried up gently by N_2 gas purging and dissolved in acetone. Soil samples (25 g) were extracted for two times with 200 ml of a mixture of water and acetone (1 : 3, v/v) by shaker. The combined extract was concentrated until the acetone was removed. The residue was passed through a Sep-Pak PS-2 cartridge, and the cartridge was eluted with ethyl acetate (10 ml). Then the eluate was dried up and dissolved in 10% acetone in hexane. Clean-up was performed with glass columns ($30 \text{ cm} \times 8 \text{ mm}$ I.D.) packed with anhydrous Na_2SO_4 (1.5 g) layer overlaid on silica gel (630mg) layer.¹¹⁾ Silica gel was activated overnight at 130°C , and cooled in a desiccator, and deactivated with 4% water. The column was rinsed with *n*-hexane (10 ml) just before use. The soil extracts were

Fig. 2 Layout of the two model paddy fields experiment for sampling site.

○: sampling site of paddy water and measurement site of water depth, ●: sampling site of soil, △: measurement site of receded water depth. Arrows (→) indicate water movement.

placed on the top of the column. Then the column was eluted with 10 ml of 10% acetone in hexane. The eluate was dried up and dissolved in acetone with above-mentioned method. Pesticide residues were determined using a GC-FTD (Shimadzu GC-17A) with a column of DB-5 (0.32 mm I.D. $\times$ 30 m). The limits of determination for two herbicides in water and soil by the above method were 0.1 $\mu\text{g/l}$ and 1 $\mu\text{g/kg}$, respectively. The recovering ratio of each pesticide was 88–94% for water samples and 89–93% for soil samples. Duplicate analysis of pesticides was performed.

RESULTS AND DISCUSSION

1. Field Experiment

1.1 Hydrological condition

Conditions of the experimental paddy fields are shown in Table 2. The average vertical and horizontal percolation rates of water during the experimental period were 0.4 and 0.3 cm/day, respectively. For continuous irrigation method on the Field 2, water was supplied at an average rate of 0.92 m^3/day , which was equivalent to 2.3 cm/day increase in the water level. Precipitation (observed), discharge (simulated) and water depth (observed and simulated) are shown in Fig. 3. On the Field 2, the fraction of discharged water over total volume of paddy water was about 30% per day at no rainfall condition. At 7–9 days after the application, daily precipitation exceeded 20 mm/day, and overflow was also generated on the Field 1 by water holding management. Simulated water depth on the Field 1 increased with precipitation. Calculated water depth by modified PADDY agreed well with the trend of measured values. The model prediction reflected observed hydrological condition.

1.2 Measured concentrations of pesticides in paddy water

Figure 4 shows the measured changes of two pesticide concentrations in paddy water. Pesticide concentrations on the Field 1 increased immediately after the applica-

Fig. 3 Changes in environmental conditions.

(a) daily rainfall recorded at NIAES; (b) discharge simulated by PADDY; (c) water depth.

Fig. 4 Comparison between simulated and measured pesticide concentrations in paddy water.

(a) Molinate; (b) Simetryne.

Table 2 Conditions of experimental paddy field.

Parameter	Values	
	Field 1	Field 2
Area of paddy field (A , m^2)	40	40
Height of outlet (h_{out} , m)	0.06	0.043
Initial water depth (m)	0.036	0.043
Percolation rate		
Vertical (q_v , m^3/day)	0.16 ^{a)}	0.16 ^{a)}
Horizontal (q_h , m^3/day)	0.12 ^{a)}	0.12 ^{a)}
Irrigation rate (Q_{in} , m^3/day)	— ^{b)}	0.92 ^{a)}
Soil bulk density (g/cm^3)	0.9	0.9
Porosity	0.4	0.4

^{a)} Average value during the experimental periods. ^{b)} Water depth was kept about 4 cm to supplement irrigation water corresponding to water requirement in depth.

tion, and reached the maximum around 3–6 hr after the application (molinate: 1.05 mg/l at 3 hr, simetryne: 0.30 mg/l at 6 hr). Then pesticide concentrations declined rapidly with time, and were 0.7 and 4 $\mu\text{g/l}$ for molinate and simetryne at day 31, respectively. Pesticide concentrations on the Field 2 were the same level as those on the Field 1 during the first day after the application because dissolution of two pesticides in paddy water from the granule was not released. After second day, however, pesticide concentrations on the Field 2 were lower than those on the Field 1. It is assumed that the main reason for the difference of pesticide concentration was due to runoff loss of pesticide with continuous irrigation.

1.3 Measured concentrations of pesticides in soil

The measured pesticide concentration profiles in soil on the Field 1 are shown in Fig. 5. In 0–2.5 cm soil layer, pesticide concentrations increased immediately after the application, and peaked around 4 to 7 days (molinate: 1.42 mg/kg at 4 days, simetryne: 0.59 mg/kg at 7 days), then declined gradually. In 2.5–5.0 cm depth, pesticide concentrations increased gradually and reached the maximum (molinate: 0.35 mg/kg, simetryne: 0.057 mg/kg) at 14 days after the application, then decreased slowly with the lapse of time. The time lag of the maximum concentrations in two different layers was probably the result of the pesticide percolation through paddy soil. For example, cumulative depth of percolation was 2.4 cm at 6th day after the pesticide application and 4.8 cm at 12th day after the application, which correspond to the peak concentrations of pesticides in the soil for those two layers.

2. Mass Distribution in Paddy Field

Mass distribution of pesticides was calculated from measured concentrations in paddy water and soil on the Field 1 (Table 3). About 16% of initially applied

molinate was distributed in paddy water at 3 hr after the application. Four days later, as much as 5% was found and after 22 days, less 0.1% was in water. About 23% of applied simetryne was distributed in water at 6 hr after

Fig. 5 Comparison between simulated and measured pesticide concentrations in soil on the Field 1.
(a) Molinate; (b) Simetryne.

Table 3 Time course of mass distribution of pesticides in paddy water and soil on the Field 1.

Time after pesticide application (days)	% of initial pesticides applied					
	Molinate			Simetryne		
	Water ^{a)}	Soil ^{b)} (0–2.5 cm)	Soil ^{b)} (2.5–5 cm)	Water ^{a)}	Soil ^{b)} (0–2.5 cm)	Soil ^{b)} (2.5–5 cm)
3 hr	15.8	— ^{c)}	—	19.5	—	—
6 hr	15.2	—	—	23.2	—	—
1	11.1	8.0	0.1	15.8	20.1	0.6
2	6.7	—	—	11.6	—	—
4	5.2	13.3	1.0	12.3	24.7	0.9
7	1.6	7.3	2.1	6.8	15.7	1.1
14	0.2	4.1	3.2	1.3	16.1	2.9
22	<0.1	—	—	0.6	—	—
31	<0.1	2.5	2.1	0.2	12.6	1.2

These values were calculated using measured concentrations in experimental paddy field as percent of molinate (2400 g/ha) and simetryne (450 g/ha) applied. ^{a)} Volume of paddy water $\times$ pesticide concentration in paddy water $\div$ applied amount of pesticide. ^{b)} Volume of soil $\times$ soil bulk density $\times$ pesticide concentration in soil $\div$ applied amount of pesticide. ^{c)} —: Not measured.

the application, however, the dissipation of simetryne was slower than that of molinate.

The difference of dissipation pattern reflects the fact that volatilization rate of molinate is much larger than simetryne. Mass distribution of simetryne in soil was higher than that of molinate, reflecting different adsorption coefficients (Table 1).

3. Validation of Modified PADDY

Validation of the modified PADDY was performed using the result of field experiment as shown in Figs. 4 and 5. The model input data for both pesticide parameters and environmental conditions considering water balance in paddy fields are listed on Tables 1 and 2. The PADDY generally tended to overestimate pesticide concentrations in paddy water. Simulated pesticide concentrations in paddy water were about five times as much as measured concentrations within 2 days after the application. In the model, paddy water compartment was assumed to be completely mixed conditions, and the diffusion between upper and lower layer in paddy water was not considered. Therefore, simulated pesticide concentrations may not reflect such process in actual paddy water. On the other hand, good fits between simulated and observed concentrations in both 0–2.5 and 2.5–5.0 cm soil layers were obtained for the two pesticides used.

Around 12 days after the application, there was the rise of pesticide concentrations in water on the simulation curve. It is assumed that rainfall exceed 20 mm/day caused the rapid dilution of pesticide concentrations in water for 7–9 days after the application, and that afterward, it increased due to desorption of pesticides from soil to paddy water. The modified PADDY is capable of simulating the concentration changes dependent on water balance.

Fig. 6 Runoff amounts and the cumulative runoff of pesticides simulated on the Field 2 by the modified PADDY. (a) Molinate; (b) Simetryne. — : the ratio of cumulative runoff to initial applied of pesticides, ■ : daily runoff amount of pesticides.

Runoff loss was also calculated by the modified PADDY over the experimental period of 32 days (Fig. 6). On the Field 2 of continuous irrigation and drainage, the cumulative runoff contributions of molinate and simetryne were 40.5% and 60.4% of initial applied, respectively. The modified PADDY calculates runoff loss according to the daily discharges as shown in Fig. 3, whereas previous PADDY calculates using average discharge during the simulation period. The modified model can predict runoff loss more accurately under the actual condition of water balance in paddy field.

Generally, for granule formulations used on paddy field as herbicides, the required water-holding period is 3–5 days for both persistence of effect and prevention of environmental load. Ross and Sava¹²⁾ reported the effect of water-holding periods on reducing herbicide loss to the environment. In this report, for pesticides with low volatility and low degradability, required holding period of 3–5 days was not sufficient to facilitate significant dissipation in order to lower the pesticide concentrations in paddy water. Our estimation was in agreement with this report. From a viewpoint of reducing the environmental load of pesticides due to surface runoff, it is important to regulate the drainage during the water-holding periods. Moreover, after this period, it is necessary to prevent overflow of paddy water on high soluble, low volatile and low degradable pesticides.

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要 約

水収支を考慮した農薬水田圃場モデル (PADDY) による農薬の動態予測

稲生圭哉, 石井康雄, 小原裕三, 北村恭朗

水田中での農薬濃度予測モデルとして開発した PADDY について, 水管理や気象要因等の環境条件から水田における水収支を計算して農薬動態の予測が可能な数値モデルの改良を行った. 改良したモデルの検証を行うため, 水田圃場に除草剤モリネートとシメトリンを散布して, 水

田水中及び土壌中の農薬濃度を経時的に測定した. 水管理は水深を一定に保持して, 落水や掛け流しを行わない止水管理及び一定の流量で用水を流入する掛け流し管理をして, 水収支の異なる条件で試験した. 水田水の農薬濃度は施用後短時間内 (<1 日) で両区での相違はみられなかったが, 時間が経つと掛け流し区が止水区に比較してその濃度は低くなった. 改良したモデルは圃場の水管理や降雨等の気象要因を考慮した水田の水収支を把握することにより, 水収支の異なる条件下における農薬の消長をほぼ予測することができた.