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Original Article

Landscape-Scale Simulation of Pesticide Behavior in River Basin due to Runoff from Paddy Fields Using Pesticide Paddy Field Model (PADDY)

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A landscape-scale simulation model (PADDY-Large) based on PADDY was developed for predicting pesticide concentrations in drainage canals and rivers due to runoff from paddy fields. Based on the irrigation systems used in agrohydrology, a rice-producing area was classified into a "field plot", "farm block", "district", and "river basin" and pesticide behavior was estimated focusing on the main drainage canals in the "district" area. To validate the model, a surveillance of pesticide residues was carried out in a rice-producing area. Herbicide concentrations in a main drainage canal in the area increased in early May, reached a maximum in mid May, and declined to below detection limits by early July. The correlation between simulated and observed concentrations of a herbicide mefenacet in the main canal were obtained by considering actual pesticide use and environmental conditions in the rice-producing area.

Key words: environmental fate, pesticides, paddy, river basin, runoff, simulation model.

INTRODUCTION

Public concern has recently been growing over the runoff of pesticides applied to agricultural land and the potential contamination of drinking water and adverse effects on aquatic ecosystems. In Japan, more than half of all agricultural land is paddy fields, from which pesticides can easily flow out through drainage into public water areas such as rivers and lakes. The Japanese Environmental Agency established a Working Party on the Ecological Risk Assessment of Pesticides in February 1998, with a mandate to make technical decisions about how to assess a pesticide's ecological risk. The party compiled an interim report on its basic approach in January 1999. The report states that for predicting environmental concentrations of pesticides, it is necessary to develop and validate mathematical models adapted to the rice paddy environment.

Previously,[1,2] we have developed and validated the pesticide paddy field model (PADDY) for predicting pesticide concentrations and runoff amounts. The PADDY model successfully simulated the observed concentration changes in a field plot (about 0.3 ha). However, PADDY cannot estimate the behavior of pesticides in a large area such as river basins.

In this study, we have developed a landscape-scale simulation model (PADDY-Large) based on PADDY for predicting pesticide concentrations in drainage canals and rivers due to runoff from paddy fields. To validate the model, an examination of pesticide residues was carried out in a rice-producing area. Concentrations predicted by the model were compared with the measured data.

THEORY, MATERIALS AND METHODS

1. *Model Concept*

1.1. *Standard scenario for evaluation*

In rice-producing areas in Japan, river water is a main source for irrigation (about 88% of total water use), which is introduced to a main canal by weirs and diverted to branch canals.[3] Drainage water from paddy fields is used again in other paddy fields downstream. Therefore, river water is reused many times by this an irrigation and drainage system.

Pesticide behavior in drainage canals was estimated by considering the following concept. From the viewpoint of agrohydrology,[3] it was assumed that a rice-producing area

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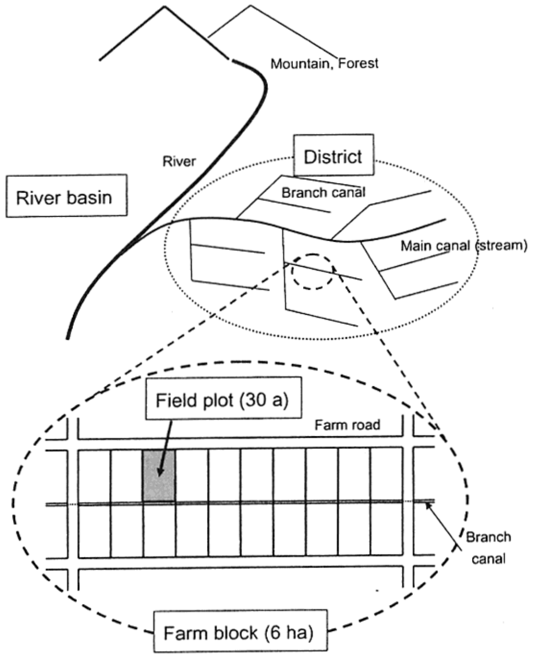

Fig. 1. Standard scenario for evaluating pesticide behavior in a rice-producing area.

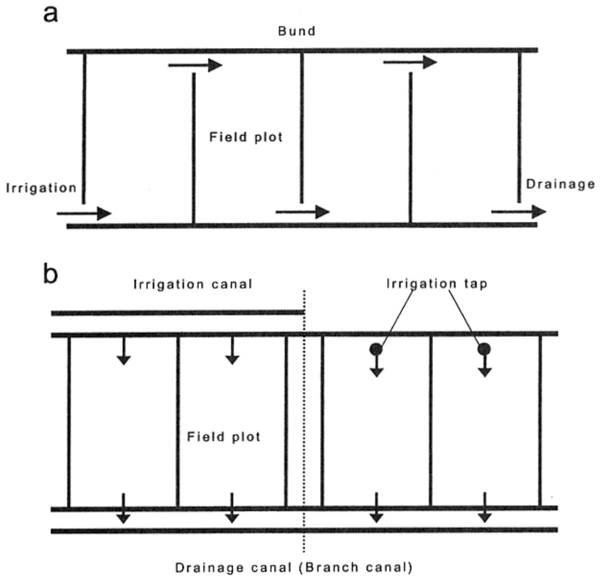

Fig. 2. Irrigation system in the farm block.
(a): Plot-to-plot irrigation system, (b): Individual irrigation system. Arrows (→) indicate water movement.

can be classified into a "field plot", "farm block", "district", and "river basin" (Fig. 1). The "field plot" is the smallest unit of the paddy field enclosed by a levee to store water. The size of a standard plot is 0.3 ha (30 × 100 m). The inlet for irrigation and outlet for drainage are attached to the field plot. The "farm block" usually comprises twenty field plots and branch canals. Generally, farm roads surround the farm block with an area of about 6 ha. The "district" area is composed of many farm blocks along a main canal (small river). The size of a district varies depending on local conditions. The "river basin" has a large river where agricultural drainage flows from districts. Therefore, drainage from paddy fields flows down through branch and main canals to the river.

1.2. Simulation in a field plot

In our previous papers,[1,2] the pesticide paddy field model (PADDY) was developed for predicting pesticide concentrations in water and soil of a "field plot". Pesticide concentrations in paddy drainage runoff from the field plot can be also calculated by PADDY as a function of time. Pesticide fate and transport processes in the field plot of the model include: (1) dissolution of pesticide from granules into paddy water, (2) adsorption and desorption between paddy water and soil solids, (3) runoff, (4) leaching, (5) volatilization from paddy water, and (6) degradation in paddy water and soil solids.

1.3. Simulation in a farm block

In a traditional farm block, the water for each field plot was supplied either by a ditch used also as a drain or by plot-to-plot irrigation (Fig. 2a). Under such conditions, it was difficult to control the water supply in individual field plots. Recently, land improvement of paddy fields has been undertaken by the Ministry of Agriculture, Forestry and Fisheries. In the improved fields, irrigation water is supplied by either irrigation canals or a pipeline as shown in Fig. 2b; in the latter case, a tap is installed in individual field plots. Since these improved field plots occupy most paddy fields in Japan, plot-to-plot irrigation was not considered in the model. In the case of individual irrigation systems, a farm block can be assumed to be a large field plot, and drainage from the farm block gathers into a branch canal.

When pesticides are used for pest and weed control by ground applications, generally, they are not applied all at once to a farm block. In this study, it was assumed that the distribution of application dates follows a normal distribution function, and the number of field plots where pesticides are applied at time t in a farm block [$N_P(t)$] was estimated by considering the amount of actual pesticide used and the timing of application in a district. When the day of the first application in a field plot among the farm block is defined as $t=0$, the pesticide concentration in paddy drainage in the branch canal at time t [$C_{drain}(t)$, g/m^3] can be calculated by the following equation.

$$\begin{aligned}C_{drain}(t)&=C_{Pw}(t)\times\frac{N_P(0)}{N_{Ptotal}}+C_{Pw}(t-1)\times\frac{N_P(1)}{N_{Ptotal}}\\&\quad+\cdots+C_{Pw}(t-T_{end})\times\frac{N_P(T_{end})}{N_{Ptotal}}\\&=\sum_{i=0}^{T_{end}}\left[C_{Pw}(t-i)\times\frac{N_P(i)}{N_{Ptotal}}\right]\qquad(1)\end{aligned}$$

Where:

$C_{Pw}(t)$ = Pesticide concentration in paddy drainage from a field plot at time t (g/m^3), derived from the PADDY estimation focusing on one field plot

N_{Ptotal} = Total number of field plots in a farm block

T_{end} = The day of last pesticide application in a field plot of the farm block

The first, second and last term on the right-hand side of Equation 1 indicate the pesticide concentration in paddy drainage from the field plot where pesticides are applied at $t=0$, at $t=1$ and at $t=T_{end}$, respectively. In case $t-i<0$ in Eq. 1, $C_{Pw}(t-i)=0$. The model does not consider pesticide dissipation processes (degradation, volatilization and adsorption by sediment) in the branch canals.

1.4. Simulation in a district and river basin

A CSTR (continuous stirred-tank reactor) model concept[4] was employed for predicting pesticide concentrations in a main canal of a district. A main canal can be visualized as a series of continuous stirred flow compartments as shown in Fig. 3. The following assumptions were made in the development of the model: (1) The main canal consists of surface water and sediment; the latter is composed of interstitial pore water and sediment solid. (2) The pore water is included in the surface water. (3) The main canal is divided longitudinally into a number of segments w in width, l in length, h in the depth of surface water and d in the depth of sediment. (4) In each segment, pesticides flowing from the upper segment or farm block are uniformly well mixed with the entire contents (i.e. completely mixed condition).

Mass balance equations for the surface water and sediment solid compartments can be expressed as follows:

For the i th segment of the surface water compartments,

$$A_i h_i \frac{dC_{wi}}{dt} = Q_{i-1} C_{wi-1} + N_{Bi} Q_{drain} C_{drain}(t) - Q_i C_{wi} - A_i d_i \rho_b k_{ads} K_f C_{wi}^{1/n} + A_i d_i \rho_b k_{des} C_{si} - K_L A_i C_{wi} - A_i h_i k_{dw} C_{wi} \quad (2)$$

For the ith segment of the sediment solid compartments,

$$A_i d_i \rho_b \frac{dC_{si}}{dt} = A_i d_i \rho_b k_{ads} K_f C_{wi}^{1/n} - A_i d_i \rho_b k_{des} C_{si} - A_i d_i \rho_b k_{ds} C_{si} \quad (3)$$

Where:

Subscript i is denoting the ith segment.

C_{wi} = Pesticide concentration in surface water (g/m^3)

C_{si} = Pesticide concentration in sediment solid (g/ton)

A_i = Surface area of main canal ($=w \times l$, m^2)

h_i = depth of surface water (m)

d_i = depth of sediment solid (m)

ρ_b = bulk density of sediment solid (ton/m^3)

N_{Bi} = Number of farm blocks

Q_{drain} = Volumetric flow rate of drainage from one farm block (m^3/day)

Q_i = Volumetric flow rate of main canal (m^3/day)

k_{ads} = Adsorption rate constant for sediment solid (1/day)

k_{des} = Desorption rate constant for sediment solid (1/day)

K_f = Freundlich adsorption coefficient (m^3/ton)

$1/n$ = Freundlich exponent

K_L = Volatilization rate constant for surface water (m/day)

k_{dw} = First-order degradation rate constant for surface water (1/day)

k_{ds} = First-order degradation rate constant for sediment solid (1/day)

Pesticide concentrations in paddy drainage from one farm block [$C_{drain}(t)$] can be calculated by Eq. 1 as a function of time t, and substituted in Eq. 2. In the case where there is no drainage from a farm block in a segment, $N_{Bi}=0$, $Q_{drain}=0$ and $Q_i=Q_{i-1}$ in Eq. 2. If drainage from a farm block flows into a segment, then $Q_i=Q_{i-1}+N_{Bi}Q_{drain}$ in Eq. 2. Sites and the number of drainage emission points from farm blocks to the main canal are set by considering the location of paddy fields in the district.

These ordinary differential equations can be solved by the Runge-Kutta-Gill method, and numerical solutions provide

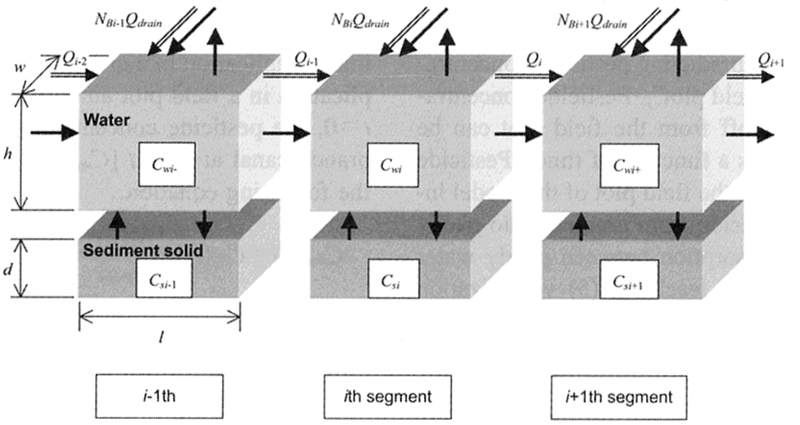

Fig. 3. Model of the river visualized as a series of continuous stirred compartments. (→): Pesticide movement, (⇒): Water movement.

pesticide concentrations in each segment as a function of time t. A computer simulation program was developed utilizing the BASIC language.

Pesticide concentrations in a large river basin can be estimated in the manner mentioned above.

2. *Surveillance of Pesticides in a Rice-Producing Area*

2.1. *Study site*

A study of pesticide residues was carried out in a rice-producing area in the southern part of Ibaraki prefecture (Fig. 4). A small river used as a main irrigation canal was located in the center of the district with a catchment area of 2.71 km^2. Rice paddy fields were spread along the basin of the river, and the total planted area was 0.55 km^2. Upstream of the river was a forest. The width of the river was 1.7 and 2.9 m at Station B and A, respectively. The riverbanks on both sides were protected by concrete blocks. Because there was only a small quantity of water in the river, water from a lake close to the region was supplied to the main canal at Station C. In the area, water was distributed to individual field plots by pipeline and a tap was installed in each plot.

2.2. *Environmental conditions*

Water gauges were installed at Station A and B on the main canal and water levels were monitored continuously. Volumetric flow rates in the canal were estimated from a discharge-rating curve based on the water levels. Rainfall was observed using a pluviometer set at Station B. The inflow rate of supply to the main canal was also monitored at Station C. Pesticide use (amount of actual use and application timing) in the district was investigated by questionnaire.

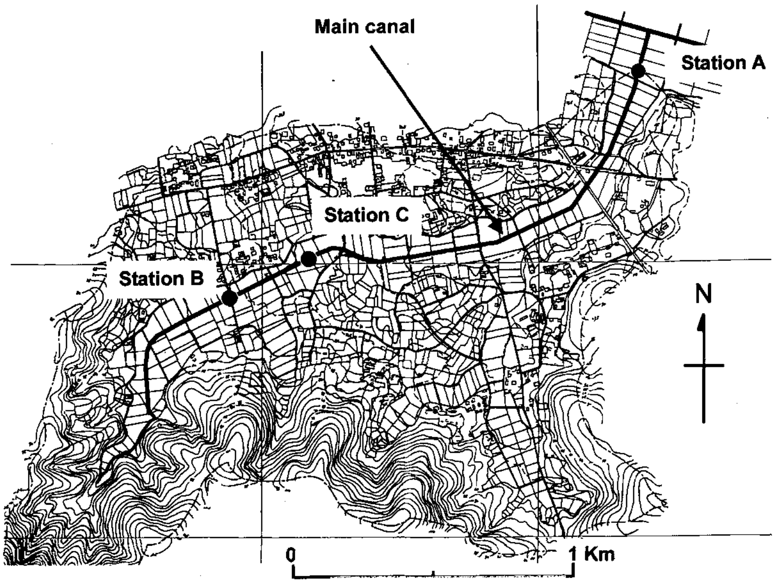

Fig. 4. Map of sampling locations in the district.

Table 1. Herbicides used for the analysis

Common name	Chemical name	Limit of determination (μg/l)	Recovering ratio (%)
dimepiperate	*S*-(1-methyl-1-phenylethyl)piperidine-1-carbotioate	0.2	90.4
dimethametryn	2-ethylamino-4-(1,2-dimethylpropylamino)-6-methylthio-1,3,5-triazine	0.05	86.1
esprocarb	*S*-benzyl 1,2-dimethylpropyl(ethyl)thiocarbamate	0.2	86.7
mefenacet	2-benzothiazol-2-yloxy-*N*-methylacetanilide	0.1	93.7
molinate	*S*-ethyl hexahydro-1 *H*-azepine-1-carbotioate	0.1	82.3
pretilachlor	2-chloro-2',6'-diethyl-*N*-(2-propoxyethyl)acetanilide	0.3	89.1
simazine	2-chloro-4,6-bis(ethylamino)-1,3,5-triazine	0.05	92.1
simetryne	4,6-bis(ethylamino)-2-methylthio-1,3,5-triazine	0.05	83.2
thibencarb	*S*-4-chlorobenzyl diethylthiocarbamate	0.1	88.1

2.3. *Monitoring of pesticide concentrations*

In the monitoring area, rice was transplanted from late April to early May, and harvested in the middle of September. One-shot herbicides were usually applied at 5–15 days after transplant. Therefore, the surveillance was carried out from late April to late August in both 1996 and 1997. By considering the actual use of pesticides in the district, nine herbicides were selected for analysis (Table 1).

There was a maximum flow rate at Station A on the main canal, where all drainage gathered from the district. Therefore, drainage samples were taken at Station A. Irrigation water at Station C was also collected to measure the background levels of herbicides. Water samples were collected in 3-liter amber glass bottles at 1-week intervals. A 500-ml water sample was 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 passed through a phase separation filter paper (WHATMAN 1PS) and concentrated in a rotary evaporator at 40°C to about 1 ml and dried up gently by N_2 gas purging and dissolved in 5 ml of acetone. Pesticides residues were determined using a GC-FTD (Shimadzu GC-17A) with a column of DB-5 (0.32 mm I.D. × 30 m). Duplicate analysis of pesticides was performed.

3. *Model Validation*

3.1. *Field experiment in a field plot*

To validate the PADDY-Large model in a field plot, a field experiment was carried out in a paddy field of the National Institute for Agro-Environmental Sciences. Six days after the rice had been transplanted (June 11, 1996), Zark-D17 granules (bensulfuron-methyl 0.17%, daimuron 1.5% and mefenacet 3.5%) were applied uniformly by hand at a rate of 30 kg/ha under the flooded conditions. The experiment was performed with water-holding management. The experimental conditions, and sampling and analytical methods used were the same as those in a previous paper.[2] The measured concentrations of pesticides in a field plot were compared with the concentrations predicted by the model using input parameters (Table 2). In input parameters, it was assumed that the adsorption rate is equal to the desorption rate and that the degradation rate in water is equal to that in soil.

3.2. *Validation in a district*

The following assumptions were made in the validation of the model with monitoring data: (1) Water balance in the field plot is in a steady state (i.e. volume of paddy water is constant and inflow rate = outflow rate + evapotranspiration rate + percolation rate). (2) Water depth is kept at 5 cm by supplying irrigation corresponding to water requirements. (3) Paddy water is regulated to prevent outflow for 4 days after the pesticide application (water-holding period). (4)

Table 2. Model input parameters for mefenacet

Parameter	Value
Physicochemical properties	
molecular weight (g/mol)	298.4
water solubility (C_{ws}, mg/l)	4 (20°C)
vapor pressure (mm Hg)	4.8×10^{-11} (20°C)
Equilibrium constants	
Henry's constant (-)	2.0×10^{-10} [a]
adsorption constant related to organic carbon (K_{oc})	1000 [b]
adsorption coefficient (K_f, liter/kg)	20 [c]
[Freundlich exponent ($1/n$)]	1
Rate constants	
dissolution (k_s, 1/day)	3.0×10^{-1} [d]
adsorption (k_{ads}, 1/day)	4.0×10^{-2} [e]
desorption (k_{des}, 1/day)	4.0×10^{-2} [f]
volatilization (K_L, m/day)	3.5×10^{-8} [g]
degradation in water (k_{dw}, 1/day)	2.8×10^{-2} [h]
degradation in sediment solid (k_{ds}, 1/day)	2.8×10^{-2} [i]

[a] Calculated by the dilling equation (Ref. 5). [b] Obtained from Ref. 6. [c] Estimated from K_{oc} with organic carbon content in soil (2%). [d] Measured value. [e] Assumed to be equal to k_{des}. [f] Obtained from Ref. 7. [g] Calculated by the Liss & Slater method (Ref. 8). [h] Assumed to be equal to k_{ds}. [i] Obtained from Ref. 9. This value is the measured data of a laboratory experiment on degradation in paddy soil under flooded conditions.

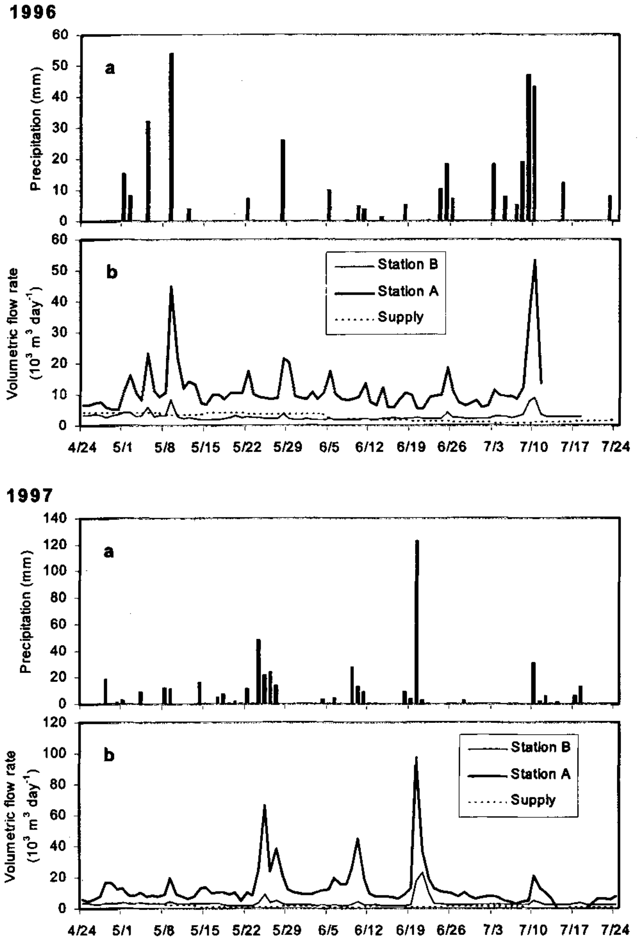

Fig. 5. Changes in environmental conditions.
(a): Precipitation; (b): Volumetric flow rate.

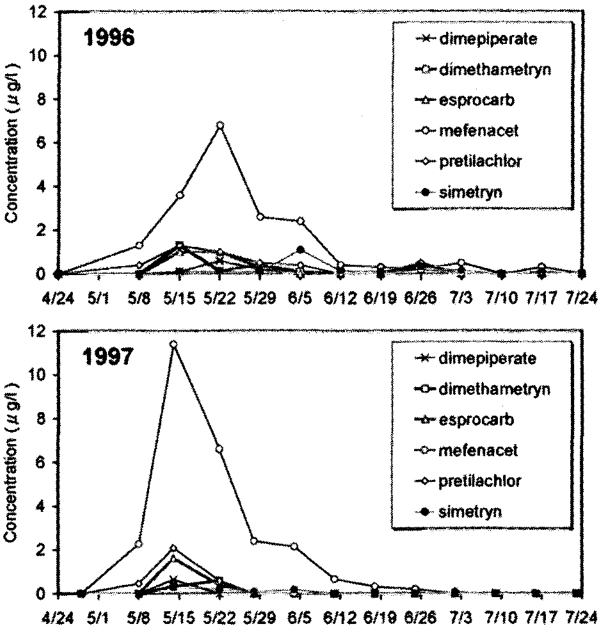

Fig. 6. Measured concentration-time profiles of herbicides detected in the main canal at Station A.

The fraction of daily discharged water over the volume of paddy water is 5%/day[10,11] in all the field plots of the district after the water-holding period. (5) Conditions of pesticide use (amount of actual use and application timing) in farm blocks are the same in the district. (6) Distribution of application date follows a normal distribution curve. (7) Farm blocks locate uniformly along the main canal. (8) Adsorption coefficient, adsorption and desorption rates, and degradation rate in water of pesticides in each main canal segment are equal to those in the paddy field. (9) The rate of degradation in sediment solid is equal to that in paddy soil.

RESULTS AND DISCUSSION

1. Surveillance of Pesticides in a Rice-Producing Area

1.1. Environmental conditions

In the district, the surface layer of the paddy fields comprised alluvial soil classified as Gray Lowland or Gley having around 2% organic carbon, a bulk density of 0.75 g/ml, and a porosity of 0.72. The measured vertical percolation

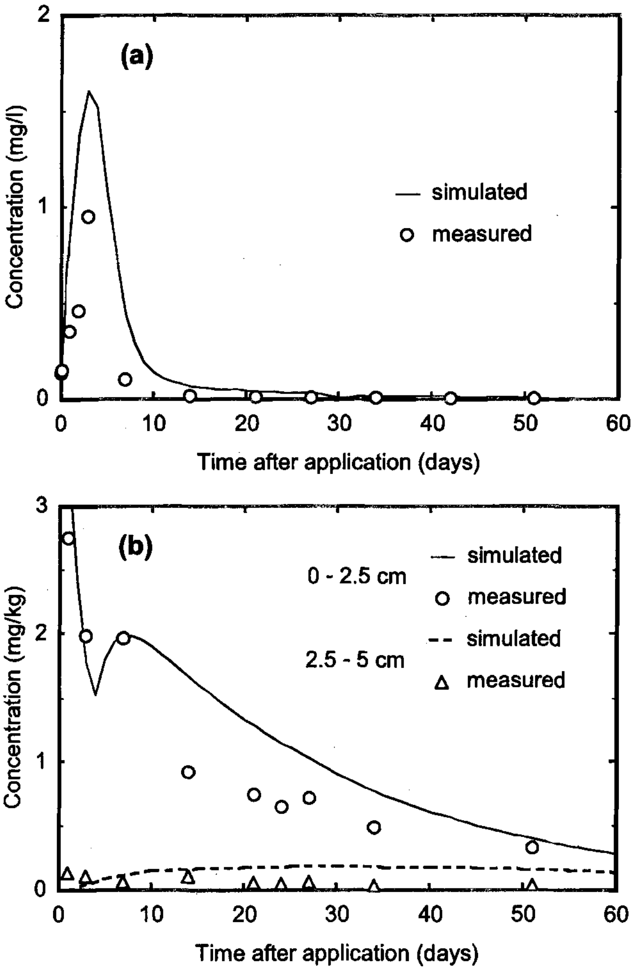

Fig. 7. Comparison between simulated and measured concentrations of mefenacet in the field plot.
(a): Paddy water; (b): Soil.

Table 3. The actual use of main herbicides in the monitoring area (1994)

Formulated product	Active ingredient	Content (%)	Actual use rate (g/10a)[2]	Occupation of the use (%)[3]	Estimated use in the district (kg)
Act GR[1]	pyrazosulfuron-ethyl	0.07	1,832	61.1	1,034
	mefenacet	3.5			
Kusakarin GR	butachlor	2.5	438	14.6	247
	pyrazolate	6			
Oneall GR	pretilachlor	1.5	279	9.3	158
	pyrazoxyfen	6			
Dysec-SM GR	MCPB	0.8	212	7.1	120
	simetryne	1.5			
	SAP	9			
Sparkstar GR	dimethametryn	0.2	142	4.7	80
	esprocarb	5			
	pretilachlor	1.5			
	pyrazosulfuron-ethyl	0.07			
Leadal GR	bifenox	6	119	4.0	67
	SAP	5			
Gorbo GR	bensulfuron-methyl	0.17	106	3.5	60
	pretilachlor	2			

[1] GR: granule formulation.

[2] Obtained from the result of a questionnaire given to rice growers.

[3] Percentage of actual use rate (g/10 a) per normal use rate (g/10 a) estimated under the assumption that the normal use rate for all the formulated products is 3000 g/10 a.

rate was 0–12 mm/day (average 7.3 mm/day). Precipitation and volumetric flow rates in the main canal are shown in Fig. 5. There were several rainfalls of more than 20 mm/day during the monitoring period. Water depth in the main canal at Station A was 5–28 cm (average 10 cm) during the monitoring period. The pH value of drainage water in 1996 and 1997 ranged from 6.4 to 7.3 and from 6.7 to 7.2, respectively.

Table 3 shows the actual use of main herbicides in the district. One-shot herbicides were used widely in the area. In particular, the use of Act granules (pyrazosulfuron-ethyl 0.07% and mefenacet 3.5%) covered 61% of the planted area in 1994.

1.2. Pesticide concentrations in the main drainage canal

Measured concentrations of herbicides at Station A on the main canal are shown in Fig. 6. Herbicide concentrations increased in early May, reached maximum levels in mid May, and then decreased to below detection limits by early July. The pattern of change in herbicide concentrations showed a similar tendency across two years. Since mefenacet was widely used for weed control in the district, concentrations of mefenacet were higher than those of other herbicides. The maximum concentrations of mefenacet in 1996 and 1997 were 6.8 and 11.4 μg/l, respectively. The cumulative runoff contributions of mefenacet at Station A were estimated to be 4.2% and 6.9% of the total applied in 1996 and 1997, respectively, using measured concentrations

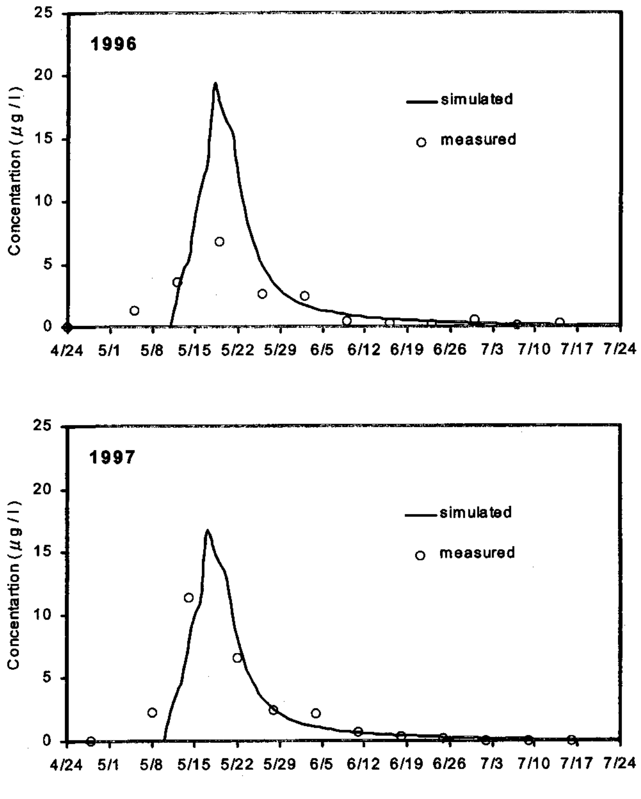

Fig. 8. Comparison between simulated and measured concentrations of mefenacet in the main canal at Station A.

and volumetric flow rates. Herbicide concentrations in irrigation water at Station C were lower than or the same as detection limits.

2. *Model Validation*

2.1. *Validation in a field plot with field experimental data*

Validation of the model in a field plot was performed using the results of the field experiment as shown in Fig. 7. The measured concentration of mefenacet in paddy water increased immediately after the application, and reached a maximum (0.95 mg/l) at 3 days, then decreased rapidly. In the 0–2.5 and 2.5–5.0 cm soil layer, peak concentrations measured were 2.75 and 0.13 mg/kg, respectively, at 1 day after the application. Then the concentration decreased gradually. Good fits between the simulated and observed concentrations were obtained in paddy water and soil as shown in Fig. 7.

2.2. *Validation in a district with monitoring data*

Mefenacet concentrations in the main canal were simulated with PADDY-Large using the pesticide property data (Table 2), the actual pesticides use (Table 3) and the environmental conditions in the district (Figure 5 and Table 4). The model successfully simulated the change of mefenacet concentrations in the main canal as shown in Fig. 8. The ratio of the simulated concentration to the observed value ranged from 0.41 to 2.62.

The cumulative runoff of mefenacet was calculated by PADDY-Large to be 11.2% of the initial amount applied to the field plot. On the other hand, that from the district in 1996 and 1997 was estimated to be 6.5% and 6.0% of the total applied, respectively, in the drainage at Station A by PADDY-Large, which was about 0.5 times that from the field plot. Moreover, the maximum concentration in the drainage canal was about 0.02 times that in the field plot, and the concentration-profile was broader than for the field plot. These results were appropriate under the following considerations: (1) The use of mefenacet covered 61% of the area. (2) Application dates of herbicides varied over about 2 weeks. (3) Pesticides in paddy drainage were diluted with water from the main canal 8–9 fold (Estimated total volume of paddy drainage was 1375 m^3/day from the district. Average volumetric flow rates in 1996 and 1997 were 11,587 and 12,487 m^3/day, respectively, at Station A on the main canal.). (4) Pesticide runoff from paddy fields

Table 4. Site-specific conditions in the district for simulation

Specific conditions in the district	1996	1997
Frequency of rice transplanting date	5/3	5/2
Application timing of herbicides (Act granule*)		
Distribution of application date	Normal distribution	
Frequency of application date	5/13	5/12
Standard deviation of application date (day)	3.5	3.5
Water-holding period (day)	4	
Paddy field conditions		
Area of field plot (m^2)	1627	
Total number of field plots in the district	338	
Number of farm blocks in the district	13	
Number of field plots in the farm block (N_{Ptotal})	26	
Distribution of farm blocks along the main canal	Uniform distribution	
Main canal conditions		
Length of main canal (m)	2000	
Number of drainage emission points	8	
Interval of emission point (m)	250	
River segment		
Length (l, m)	50	
Width (w, m)	1–3	
Depth of water (h, m)	0.1–0.2	
Depth of sediment (d, m)	0.03	
Bulk density of sediment (ρ_b, g/cm^3)	1.0	
Average volumetric flow rate at Station A (m^3/day)	11,587	12,487

*Act granules are used at 5–15 days after transplant and paddy water should be held for 3–4 days after the application.

decreased in the main canal due to degradation and adsorption by sediment.

The PADDY-Large model is a beneficial tool for predicting pesticide concentrations in drainage canals in rice-producing areas by considering actual pesticide use, application timing, and environmental conditions in rice-producing areas. Therefore, it is anticipated that the PADDY-Large model can predict pesticide concentrations in rivers accurately and that the model is applicable to ecological risk assessment.

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