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# Simulation of Pesticide Behavior in a Paddy Block by a Pesticide Fate and Transport Model

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A simulation model (PCPF–B) was developed based on the PCPF–1 model to predict the runoff of pesticides from paddy plots to a drainage canal in a paddy block. The block–scale model now comprises three modules: (1) a module for pesticide application, (2) a module for pesticide behavior in paddy fields, and (3) a module for pesticide concentration in the drainage canal. The PCPF–B model was first evaluated by published data in a single plot and then was applied to predict the concentration of bensulfuron–methyl in one paddy block in the Sakura river basin, Ibaraki, Japan, where a detailed field survey was conducted. The PCPF–B model simulated well the behavior of bensulfuron–methyl in individual paddy plots. It also reflected the runoff pattern of bensulfuron–methyl at the block outlet, although overestimation of bensulfuron–methyl concentrations occurred due to uncertainty in water balance estimation. Application of water management practice such as water–holding period and seepage control also affected the performance of the model. A probabilistic approach may be necessary for a comprehensive risk assessment in large–scale paddy areas

**Keywords**: PCPF–B; PCPF–1; predicted environmental concentration (PEC); pesticide modeling; pesticide application distribution

## INTRODUCTION

Rice is the second most important staple food in the world (Nguyen and Ferrero, 2006) and pesticide has become indispensable to maintain a stable yield. However, rice paddy field is susceptible to pesticide runoff since the chemical is applied directly to paddy water. Pesticide losses from paddy fields range from a few percentage to more than 50% of the applied mass, depending on water management (Watanabe *et al.*, 2008). A monitoring of river systems in Japan has detected several pesticides commonly used in paddy fields, with maximum concentrations ranging up to 10 $\mu$g/L (Phong, 2008). Therefore, controlling pesticide discharge from paddy is very important in protecting the aquatic ecosystems.

The use of simulation models to determine the predicted environmental concentration (PEC) has become the basis for assessing the potential environmental risk within the regulatory and registration process. In the European Union, advisory groups, such as MED–RICE, have produced general guidelines on how risk assessment should be performed in rice paddies; here, the standard tiered approach for pesticide risk assessment in rice production using mathematical models has been proposed (MED–RICE, 2003). Currently, a number of simulation models for pesticides used in paddy rice production are available. The RICEWQ model has been used to simulate PEC in surface water as well as in groundwater under EU conditions (Karpouza and Capri, 2006). The PCPF–1 and PADDY models have also been validated for paddy rice conditions in Japan (Inao and Kitamura, 1999; Watanabe and Takagi, 2000b). However, those models are used to simulate pesticide behavior in single paddy plots. Coupled RICEWQ–RIVWQ and PADDY–Large models were developed for predicting pesticide concentration in a riverine system, but their algorithms for pesticide application were either based on a simultaneous and homogeneous application or a normal distribution application (Inao *et al.*, 2003; Karpouza and Capri, 2006), which are not usually applicable for a small paddy catchment. In such a catchment, the number of pesticide application events are limited and are totally dependent on farmers' schedules. The deviation between the model assumption and the actual application events can easily lead to discrepancies between simulated and observed data.

In Japan, paddy fields can be classified into paddy plot, paddy block, irrigation district, and river basin. The paddy plot is the smallest unit with a standard plot size of 0.3 ha (30×100 m). The paddy block comprises several plots and irrigation and drainage canals. Generally, the paddy block is surrounded by farm roads with an area of about 6 ha (Inao *et al.*, 2003). Drainage water from a paddy block can flow into a main drainage canal of the irrigation district or can flow directly into a river tributary/stream. Therefore, prediction of pesticide con-

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centration in paddy block drainage water is essential for exposure risk assessment of rice pesticides. However, to our knowledge, this study will be among the first attempts to collect a comprehensive data set for modeling application at the paddy block scale.

Therefore, this study aims to develop a rice pesticide simulation model for predicting pesticide concentration in a drainage canal of a paddy block based on the single plot model PCPF–1. The developed model is then evaluated with monitored data and model performance is discussed.

## MATERIALS AND METHODS

### Behavior of rice pesticide in a paddy plot – PCPF–1 model

PCPF–1 is a validated rice pesticide simulation model, which simulates the behavior of rice pesticide in a single paddy plot. A full description of the development of the PCPF–1 model can be found in Watanabe and Takagi (2000a) and Watanabe *et al*. (2006b). Briefly, PCPF–1 simulates pesticide fate and transport in two compartments: the paddy water and the surface soil. The paddy water compartment is assumed to be a completely mixed reactor having variable water depths. The paddy surface soil compartment is also assumed to be a completely mixed reactor, with a constant depth of 1.0 cm. The conceptual pesticide fate and transport scenario used for the model is shown in **Fig. 1**.

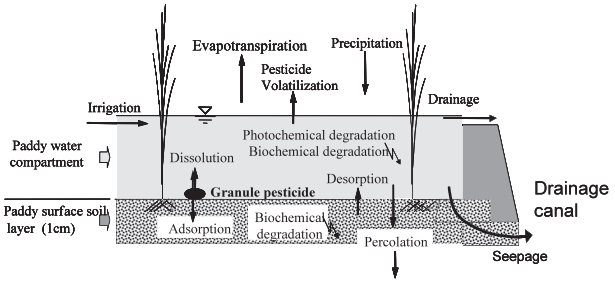


**Fig. 1.** Conceptual pesticide fate and transport in a paddy–rice field.

The PCPF–1 model is based on three governing equations, including water balance in the paddy–water compartment and the pesticide mass balances of both in paddy water and in the surface–soil layer. The daily water balance within the water compartment is given by

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

where $h_{PW}$ is the depth of water in paddy field (cm), $t$ is time (day), $RAIN$ is the average rainfall rate during $dt$ (cm/day), $IRR$ is the rate of irrigation water supply (cm/day), $DRAIN$ is the surface drainage or overflow rate (cm/day), $LSEEP$ is the rate of lateral seepage out of the plot through levees or bunds (cm/day), $PERC$ is the rate of vertical percolation (cm/day), and $ET_C$ is the rate of crop evapotranspiration (cm/day) for rice.

The pesticide mass balance in the paddy–water compartment is expressed by

$$\frac{dC_{PW}}{dt} = k_{DISS}\,(C_{SLB} - C_{PW}) + \frac{1}{h_{PW}}\left[C_{PW}\,\frac{dh_{PW}}{dt}\right]_{DISS}$$
$$+ \frac{1}{h_{PW}}\,d_{PSL}\,\rho_{b-PSL}\,k_{DES}\,C_{S-PSL}$$
$$+ \frac{1}{h_{PW}}\,IRRC_{W-IRR} - \frac{1}{h_{PW}}\,(DRAIN + LSEEP$$
$$+ PERC)\,C_{PW} - \frac{1}{h_{PW}}\,k_{L-A}C_{PW}$$
$$+ (-k_{PHOTO}f_{US}\,R_{S-a}\,(1 - f_{R-ab}\,t\,) - k_{BIOCHEM-PW})\,C_{PW}$$
$$- \frac{1}{h_{PW}}\,\frac{dh_{PW}}{dt}\,C_{PW} \quad (2)$$

where $C_{PW}$ is pesticide concentration in paddy water (mg/L), $k_{DISS}$ is the first–order rate constant of pesticide dissolution in water (1/day), $C_{SLB}$ is the solubility of pesticide in water (mg/L), $d_{PSL}$ is the depth of the paddy surface soil layer (cm), $\rho_{b-PSL}$ is the bulk density of the paddy surface soil layer (g/cm$^3$), $k_{DES}$ is the first–order rate constant for pesticide desorption from the paddy surface soil layer (1/day), $C_{S-PSL}$ is the pesticide concentration in the paddy surface soil (mg/kg dry soil basis), $C_{W-IRR}$ is the pesticide concentration in irrigation water, $k_{L-A}$ is the pesticide mass–transfer coefficient from paddy water to atmosphere (m/day), $k_{BIOCHEM-PW}$ is the first–order rate constant of biochemical degradation in paddy water (1/day), and $k_{PHOTO}$ is the first–order rate coefficient of photochemical degradation with respect to the cumulative UV–B radiation (m$^2$/kJ) as measured in ambient or laboratory conditions. $R_{S-a}$ is the daily solar radiation (kJ/m) above the rice canopy and the model accounts. The photochemical degradation accounts for the attenuation by plant growth of the sunlight entering the paddy water (factor $f_{R-ab}$) and also for the fraction of UV–B radiation over the solar radiation.

Similarly, the pesticide mass balance in the paddy surface–soil layer is expressed as

$$\frac{dC_{S-PSL}}{dt} = k_{d-PSL}\,k_{DISS}(C_{SLB} - C_{PW})$$
$$+ k_{d-PSL}\left[\frac{C_{PW}}{d_{PSL}}\,\frac{d(d_{PSL})}{dt}\right]_{DISS}$$
$$+ \frac{k_{d-PSL}}{(\theta_{Sat-PSL} + \rho_{b-PSL}k_{d-PSL})}\,\frac{1}{d_{PSL}}\,PERC\,(C_{PW}$$
$$- \frac{1}{k_{d-PSL}}\,C_{S-PSL})$$
$$- \frac{k_{d-PSL}}{(\theta_{Sat-PSL} + \rho_{b-PSL}k_{d-PSL})}\,\rho_{b-PSL}\,k_{BIOCHEM-PSL}\,C_{S-PSL}$$
$$- \frac{k_{d-PSL}}{(\theta_{Sat-PSL} + \rho_{b-PSL}k_{d-PSL})}\,\rho_{b-PSL}\,k_{DES}\,C_{S-PSL}$$

$$- \frac{C_{S-PSL}}{d_{PSL}} \frac{d(d_{PSL})}{dt} \quad (3)$$

where $k_{d-PSL}$ is the soil adsorption coefficient of the pesticide (L/kg), $\theta_{sat-PSL}$ is the volumetric saturated water content ($cm^3/cm^3$), $k_{BIOCHEM-PSL}$ (1/day) is the first–order rate constant of the biochemical degradation of pesticide, and the subscript PSL refers to the paddy surface–soil layer. The model program was coded using Visual Basic® for Applications in Microsoft Excel®.

**Behavior of rice pesticide in a paddy block – PCPF–B model**

For a block of paddy plots, the PCPF–B model was developed. The paddy block can comprise a dozen paddy plots of different areas. Because it is rarely the case when one single pesticide is applied to the whole block, the block is divided into treated and untreated areas with the total area equal to the block size. Different pesticide application scenarios (application dates and areas) can be simulated by the PCPF–B model–i.e., pesticide application schedule in the paddy block can follow the normal distribution or uniform distribution within an application period or they can be fed for each individual date by users (**Fig. 2**). It should be noted that the PCPF–B model will consider those plots receiving pesticide application in the same day as one plot ($A(i)$). This imaginary plot has the size equal to the total area of those individual plots applied on that day. Although the assumption of simultaneous pesticide application was used in rice pesticide fate and transport simulation to represent a worst–case scenario by Karpouza and Capri (2006), this method of data input is not realistic. Inao *et al*. (2003) assumed normal distribution to represent pesticide application schedule for a large (55 ha) paddy watershed; this method, however, may not be suitable for model simulation, especially in the case of a small watershed where this assumption is not valid.

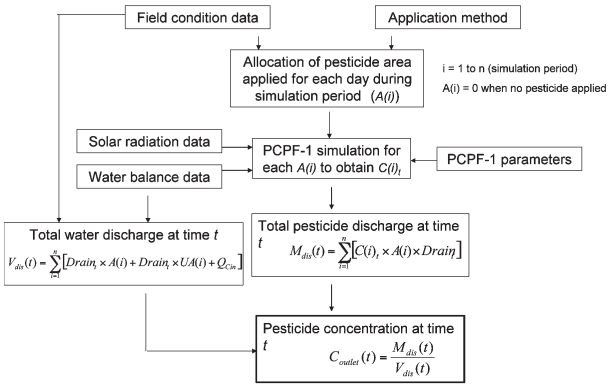


**Fig. 2.** Algorithm of PCPF–B model for predicting pesticide concentration at the outlet of a paddy block.

Once the pesticide is applied, the PCPF–B model simulates the pesticide concentration at time t, $C(i)_t$, in the corresponding applied paddy area $A(i)$ from multiple (or single) paddy plots according to the input data based on the PCPF–1 algorithm. The concentration of pesticide in runoff water from the paddy plot is considered equal to that in paddy water because of the completely mixed reactor assumption. PCPF–B combines all pesticide discharges from individual plots to calculate the pesticide concentration at the outlet of the paddy block. Total pesticide discharge at time t, $M_{dis}(t)$, is then given by

$$M_{dis}(t) = \sum_{i=1}^{n} \left[ C(i)_t \times A(i) \times Drain_t \right] \quad (4)$$

PCPF–B takes into account the dilution effect of the water drained from other plots in the block, which are not treated with the pesticide in question (untreated area, denoted as $UA(i)$ in **Fig. 2**), and the water that directly flows into the canal (denoted as $Q_{Cin}$ in **Fig. 2**). The total water discharge at the canal outlet of the block at time t, $V_{dis}(t)$, is calculated as

$$V_{dis}(t) = \sum_{i=1}^{n} \left[ Drain_t \times A(i) + Drain_t \times UA(i) + Q_{Cin} \right]$$

or

$$V_{dis}(t) = \sum_{i=1}^{n} \left[ Drain_t \times (A(i) + UA(i) + Q_{Cin} \right] \quad (5)$$

where $Drain_t$ is the drainage rate at time t.

In the PCPF–B model, paddy water is considered directly released into major canals/tributaries and the length of the canals within the block is relatively short (about a few hundred meters for a block of less than 10 ha), the pesticide residence time in the canal or the time needed for transporting pesticide from paddy plots to the outlet of the block is short. Hence, it is assumed that the process of pesticide dissipation in canal water can be neglected in the model. Therefore, the pesticide concentrations at the canal outlet of the block, $C_{outlet}(t)$, can be finally calculated as

$$C_{outlet}(t) = \frac{M_{dis}(t)}{V_{dis}(t)} \quad (6)$$

The PCPF–B model's program calculating the above equations is also coded using Visual Basic for Applications in Microsoft Excel as for the PCPF–1 model. The Excel file includes a Macro program of PCPF–B, datasheets for input parameters, and daily water balance and daily UV–B radiation received on paddy water.

**Execution of PCPF–B model**

As in the PCPF–1 model, the PCPF–B model was executed with measured and observed data. Pesticide properties data were derived from the literature as shown in **Table 1**. Although the estimation of some parameters such as volatilization coefficient and photolysis rate were not conducted in Japan, those experiments were conducted under standard laboratory conditions and were expected to be suitable for modeling application. The application rate was taken from the product label. Water balance data were obtained from monitoring studies as described in the next section. Measured daily data of

**Table 1.** Input parameters for PCPF–B model simulation

| | Unit | Value | Comment |
|---|---|---|---|
| *General information* | | | |
| Area of block | $m^2$ | 50600 | Field survey |
| Pesticide treated area | $m^2$ | 19600 | Field survey |
| Date to start simulation | | 2004/05/01 | |
| Simulation period | d | 30 | |
| Inclusion of seepage | | Yes/No | Using water balance data |
| Water holding period | d | 4 | Product label recommendation |
| *Input data for plot simulation* | | | |
| Water compartment | | | |
| Application rate | $g/m^2$ | 0.005 | Product information |
| Solubility of the pesticide | mg/L | 80 | Tomlin (2003) |
| Dissolution rate | 1/d | 0.239 | Watanabe and Takagi (2000b) |
| Desorption rate | 1/d | 0.2256 | Cavanna *et al*. (1998) |
| Volatilization coefficient | m/d | $5.82\times10^{-13}$ | Makay and Leinonen (1975) |
| Photolysis rate | 1/d | 0.0028 | FAO (2002) |
| Biochemical degradation rate | 1/d | 0.1584 | Ambrust *et al*. (1999) |
| Factor of light attenuation by crop | 1/d | 0.0162 | Watanabe and Takagi (2000b) |
| Fraction of UVB over Rs | | 0.001232 | Watanabe and Takagi (2000b) |
| Soil compartment | | | |
| Bulk density | $g/cm^3$ | 0.937 | Watanabe and Takagi (2000b) |
| Saturated water content | $cm^3/cm^3$ | 0.603 | Watanabe and Takagi (2000b) |
| Partitioning coefficient | L/kg | 9.92 | Ambrust *et al*. (1999) |
| Degradation rate const. | 1/d | 0.0103 | Ambrust *et al*. (1999) |
| *On application date & amount* | | | |
| Detailed information | Application date | Application area | |
| | See Fig. 4 | See Fig. 4 | |

precipitation, irrigation, drainage, lateral seepage, percolation, and paddy water levels (cm) of 30 days were fed to a data worksheet. Also, solar radiation ($MJ/m^2$) data from a local meteorological station closest to the monitoring site were obtained from the national meteorological agency (JMA, 2009). Data on pesticide application (date and area), which were obtained by means of questionnaires to farmers during a field survey, were also fed into the worksheet. The parameters for PCPF–1 execution are presented in **Table 1**.

Bensulfuron–methyl was selected as a target for the simulation. The selection of this sulfonylurea herbicide is due to its popularity in the study region as well as the availability of data.

**Field–data collection for model validation**

For evaluating the PCPF–B model, water balance and pesticide concentration data were collected from field monitoring studies. For single–plot simulation, data from a monitoring study conducted in Tokyo, Japan, in 2003 were used (Watanabe *et al*., 2006a). A pesticide product containing bensulfuron–methyl was applied to two plots with two different water management systems. One was the intermittent irrigation practice (AI scenario) and the other was the continuous irrigation and drainage practice (CI scenario). Pesticide concentrations and water balance in each plot were monitored for a period of 21 days. Details of this study can be found in Watanabe *et al*. (2006a).

For paddy block simulation, data from a paddy watershed study conducted in Sakura river basin, Ibaraki Prefecture, 50 km northwest of Tokyo, Japan, in 2004 were used. In this study, a detailed field monitoring was carried out in a paddy block, which is a part of a 97–ha watershed. The paddy block consisted of 17 paddy plots and an upland plot and a secondary drainage canal. The total area of paddy plots in the paddy block is about 5.06 ha (**Fig. 3**). Water balance in one representative plot was monitored together with the inflow and outflow of the canal section. The secondary drainage canal is 0.5 m wide and 320 m long, bordered by concrete walls. The estimated retention time of water was less than 2 h in the canal. These conditions satisfy the assumption made for the model: that no interaction with pesticides occurs during transport through the drainage canal.

It was assumed that farmers in this block performed similar water management practices; thus, water balance in the other plots was the same as that in the representative one. To obtain data on pesticide application (product, application date, and application area), question-

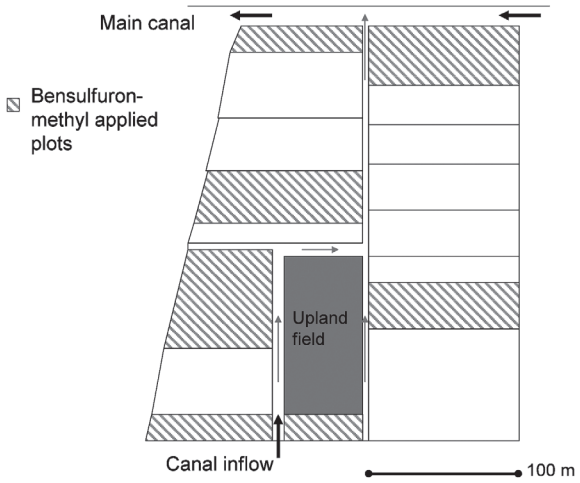


**Fig. 3.** Description of the studied paddy block.

naires were sent to farmers who cultivated in the block and these were then collected for analysis.

To monitor the concentrations of bensulfuron–methyl at the block outlet, water samples were periodically taken starting on April 26, 2004. On sampling days, about 2000 ml water samples were taken at the outlet. The concentrations in the water samples of bensulfuron–methyl were analyzed using a liquid chromatography–tandem mass spectrometer (LC/MS/MS) method. Details about water sampling and chemical analysis can be found in Vu *et al*. (2006).

### Statistical analysis

Model performance was objectively assessed by comparing the graphical agreement between predicted and observed concentrations of bensulfuron–methyl in paddy water. In addition, the performance was also assessed by statistical indices, including root mean square error (RMSE) and modeling efficiency (EF) in equations (7) and (8):

$$RMSE = \frac{100}{\bar{O}} \sqrt{\frac{\sum_{i=1}^{n} (P_i - O_i)^2}{n}} \quad (7)$$

$$EF = \frac{\sum (O_i - \bar{O})^2 - \sum (P_i - O_i)^2}{\sum (O_i - \bar{O})^2} \quad (8)$$

where $P_i$ and $O_i$ are the predicted and observed values, respectively, $\bar{O}$ is the average of the observed values and n is the number of observations. In general, the lower the RMSE, the higher is the agreement between the measured and the predicted data. In contrast, the optimal value for EF is 1; thus, the closer to 1 the values of EF, the greater is the correspondence between measured and predicted data (Loague and Green, 1991).

## RESULTS AND DISCUSSION

### Pesticide concentration in an individual plot within the paddy block

To evaluate the performance of PCPF–B in simulating pesticide concentration in an individual plot within the block, the model was run with data from single–plot monitoring. The water balance data from the plot–monitoring study (Watanabe *et al*., 2006a) were fed into the worksheet of PCPF–B as water balance of the block. Single pesticide application in one plot was simulated and the predicted concentrations of bensulfuron–methyl in the paddy plot were compared with the observed data. There was a close agreement between measured and predicted concentrations of bensulfuron–methyl in paddy water as shown in **Fig. 4**. For both water management scenarios, the PCPF–B model predicted well the behavior of bensulfuron–methyl in paddy water of an individual plot. The high accuracy was also reflected by the low RMSE value and the EF value close to 1 (**Table 2**). The ability of PCPF–1 to simulate bensulfuron–methyl behavior was proven in the case when precise water balance data are available.

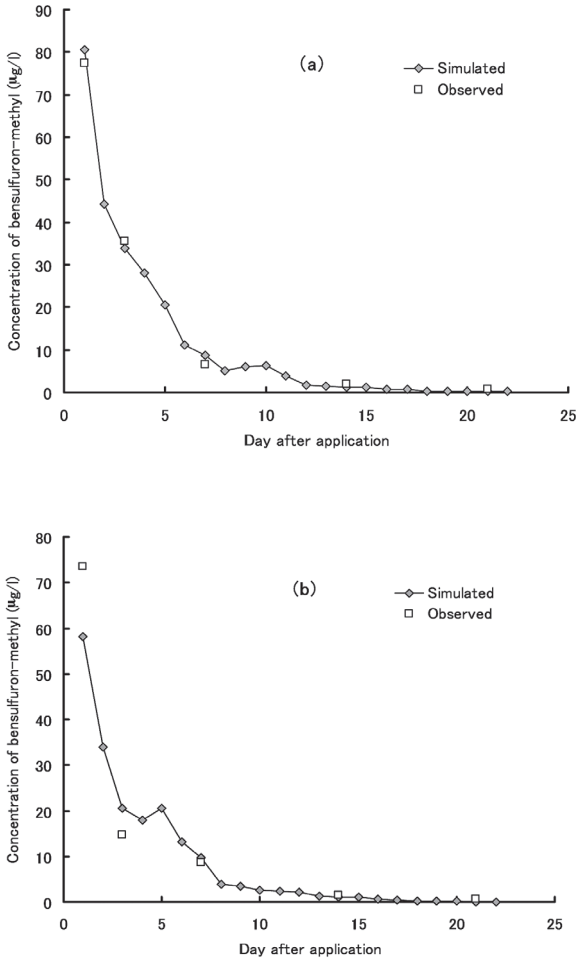


**Fig. 4.** Measured and predicted concentrations in paddy water of bensulfuron–methyl in (a) intermittent irrigation applied plot and (b) continuous irrigation and drainage applied plot.

**Table 2.** Statistical analysis of the model performance in different scenarios

| | RMSE | EF |
|---|---|---|
| Single plot (AI scenario) | 7.2 | 0.99 |
| Single plot (CI scenario) | 34.2 | 0.93 |
| Paddy block outlet (without WHP and seepage) | 481.9 | –61.12 |
| Paddy block outlet (with WHP only) | 238.5 | –12.5 |
| Paddy block outlet (with WHP and seepage) | 450.8 | –47.3 |

WHP: Water Holding Period

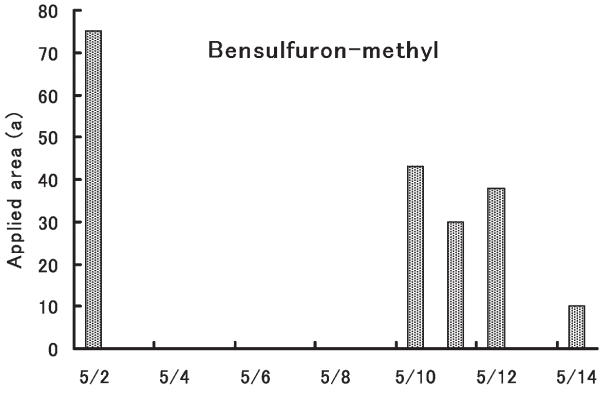


**Fig. 5.** Actual distribution of pesticide application in the studied paddy block.

### Pesticide concentration at the outlet of the drainage canal of the paddy block

With good performance in the individual–plot simulation, the PCPF–B model was set to run for a paddy block with data from the paddy block study. According to the field survey, bensulfuron–methyl was applied on seven plots in the monitored paddy block (**Fig. 3**) on different days during the monitoring period. **Fig. 5** shows the temporal distribution of applied bensulfuron–methyl mass and it is clear that the normal distribution assumption will not be reasonable in this study. **Fig. 6** shows all water balance components in the paddy compartment of the monitored block in 2004. Daily runoff/drainage from the paddy fields was estimated from the daily water balance in the receiving canal. Daily irrigation was calculated using the daily water balance in the paddy compartment from the estimated percolation, seepage, evapotranspiration, and paddy water depth. Note that water depth was assumed to be constant at 5 cm during the monitoring period. A significant drainage occurred during large rainfall events (**Fig. 6**). During the early period of May, the increasing surface drainage may be because farmers released paddy water during transplanting to have an optimum paddy water depth.

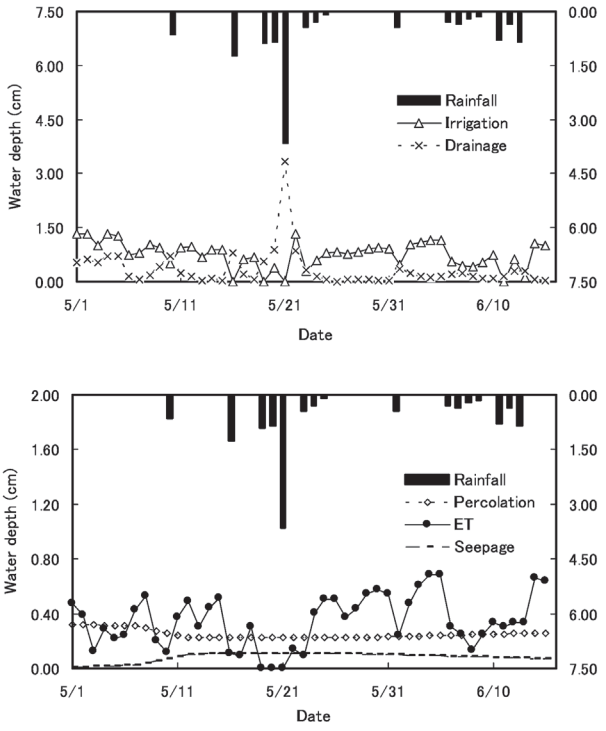


**Fig. 6.** Daily water balance components in the paddy block during the monitoring period.

Using the described input data, the PCPF–B model predicted the concentrations of bensulfuron–methyl in individual plots (**Fig. 7**) and at the block outlet (**Fig. 8**). As shown in **Fig. 7**, dissipation of bensulfuron–methyl in individual plots was similar to that described in the previous section. The concentration of bensulfuron–methyl peaked at 1 day after pesticide application in each plot and decreased exponentially. The variation of pesticide concentration among the plots is due to the variation in water balance components from day to day. These simulated concentrations are comparable with observed data in Japanese paddy fields reported in the literature (Okamoto *et al.*, 1998; Watanabe *et al.*, 2006a).

The simulated curve of bensulfuron–methyl concentration at the block outlet greatly overestimates the observed data, although both simulated and observed data have two main concentration peaks corresponding to two major application periods in the block (**Fig. 8**). Other peaks were due to the fluctuation of canal inflow, causing a different dilution factor from day to day. However, for the paddy block scale, the performance of the model was not satisfactory with very high RSME and negative EF values (**Table 2**). These overestimations are proba-

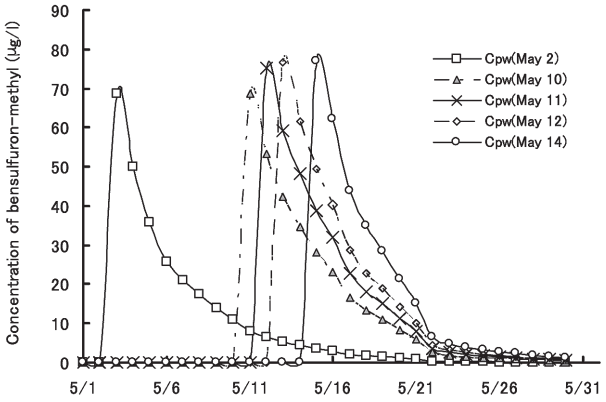


**Fig. 7.** Simulated concentrations of bensulfuron-methyl in individual paddy plots in the block.

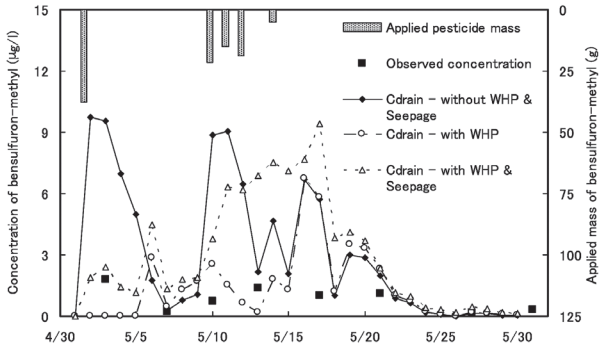


**Fig.8.** Simulated and observed (■) concentrations of bensulfuron-methyl at the block outlet.

bly due to the better–than–expected water management in the studied block, which resulted in less pesticide runoff amount from treated plots than what was estimated in our water balance calculation. Farmers managing some of these plots may, to some extent, have practiced water holding after pesticide application to prevent pesticide runoff, although bensulfuron–methyl was detected in the canal water on the application date, meaning that runoff still occurred on that day.

Meanwhile, if normal distribution were used to allocate the pesticide application area/mass, the simulated curve also has some concentration peaks, but the occurrence of the peaks did not correspond with the actual application periods in the block (data not shown). Therefore, the inclusion of a discrete application algorithm has enhanced the possibility of PCPF–B simulating the pesticide concentration at the paddy block outlet.

**Effect of water management on paddy block simulation results**

The PCPF–B provides some options for considering different water management approaches in the block, such as the application of water–holding period and the inclusion of seepage as pesticide loss to drainage canal (**Table 1**).

The application of a water–holding period (4 days as recommended in the pesticide label) as a management practice for the whole block remarkably increased the model performance as shown in **Table 2** and **Fig. 8**. The cause of this improvement is that, during the water–holding period, drainage was completely stopped from treated plots and pesticide was allowed to be dissipated inside the paddy plot. Consequently, water–holding practice helped reduce significantly the concentrations of bensulfuron–methyl in drainage water. Therefore, the overestimation mentioned in the previous section will be reduced with the application of a water–holding period. However, since management depends on the farmers, more detailed monitoring data are required for a better evaluation of the model.

Seepage was also optionally taken into consideration during the simulation. When the option for seepage inclusion was chosen (as Yes in **Table 1**), equation (4) and (5) will become

$$M_{dis}(t) = \sum_{i=1}^{n} \left[C(i)_t \times A(i) + (Drain_t + Seep_t)\right] \quad (9)$$

$$V_{dis}(t) = \sum_{i=1}^{n} \left[(Drain_t + Seep_t) \times (A(i) + UA(i)) + Q_{Cin}\right] \quad (10)$$

where $Seep_t$ is the seepage rate at time t.

However, the improvement in model performance was limited when seepage was included into pesticide loss to drainage canal (**Table 2**). This is because, at this stage, PCPF–B considers pesticide loss through seepage similar to pesticide loss though surface drainage without any interaction with the levee soil. The seepage loss was also not subjected to the application of water–holding practice. Therefore, seepage loss to drainage canal would increase the pesticide concentration in the canal water and consequently would increase the overestimation factor and reduce the model performance.

Seepage may contribute significantly to pesticide loss from paddy fields to the drainage canal and eventually to the river. The new guidelines for pesticide registration in Japan by the Ministry of Agriculture, Forestry, and Fisheries (MAFF, 2009) also recommend the inclusion of seepage in its standard river scenario for PEC derivation. However, other popular rice pesticide models such as PADDY (Inao *et al*., 2003) and RIVWQ (Karpouza and Capri, 2006) do not consider the load of pesticide through seepage to their river compartment. More research on this aspect should be conducted in the future to collect sufficient data for deriving and validating the seepage process in paddy fields.

The results of simulations in the case of water–holding practice and seepage inclusion again indicate the strong effect of water management uncertainty in large–scale paddy area simulation. Later, a probabilistic risk assessment approach may be necessary to cover all the uncertainties and produce a more comprehensive assessment of pesticide flow in paddy fields.

## CONCLUSION

A simulation model, PCPF–B, was developed based on the PCPF–1 model to predict pesticide concentrations in water of a paddy block outlet. The PCPF–B model simulated with high accuracy the behavior of bensulfuron–methyl in individual paddy plots. At the paddy block scale, the general trend of pesticide transport at the block outlet was predicted, but overestimation occurred for most of the observed points, which badly affected model performance. Improvement in the pesticide application algorithm enhanced predictability, but uncertainty in water balance strongly affected the performance of the model. More studies are required to find an appropriate approach to minimize the effect of water balance on model performance in the case of a large paddy area.

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## REFERENCES

Armbrust, K. L., Y. Okamoto, J. Grochulska and A. C. Barefoot 1999 Predicting the dissipation of bensulfuron methyl and azimsulfuron in rice paddies using the computer model EXAMS2. *Journal of Pesticide Science*, **24**: 357–363

Cavanna, S., E. Garatti , E. Rastelli and Molinari GP 1998 Adsorption and desorption of bensulfuron– methyl on Italian paddy field soils. *Chemosphere*, **37**: 1547–1555

FAO (Food and Agriculture Organization) 2002 *FAO specifications and evaluations for plant protection products: Bensulfuron–methyl*. FAO, pp. 1–26

Inao, K. and Y. Kitamura 1999. Pesticide paddy field model (PADDY) for predicting pesticide concentrations in water and soil in paddy fields. *Pesticide Science*, **55**: 38–46

Inao, K., Y. Ishii, Y. Kobara and Y. Kitamura 2003 Landscape–scale simulation of pesticide behavior in river basin due to runoff from paddy fields using pesticide paddy field model (PADDY). *Journal of Pesticide Science*, **28**: 24–32

JMA (Japan Meteorological Agency) 2009 Past meteorological data retrieval. http://www.data.jma.go.jp/obd/stats/etrn/index.php (Last access 2009/02/24)

Karpouzas, D. G. and E. Capri 2006 Risk analysis of pesticides applied to rice paddies using RICEWQ 1.6.2v and RIVWQ 2.02. *Paddy Water Environment*, **4**: 29–38

Loague, K. and R. E. Green 1991. Statistical and graphical methods for evaluating solute transport models: Overview and application. *Journal of Contaminant Hydrology*, **7**: 51–73

MAFF 2009 Regarding data to be appended to applications for registration of agricultural chemicals (provisional translation). Available via http://www.acis.go.jp/eng/shinsei/13–3987.pdf. Access date April 30, 2009

Makay D. and Leinonen P. J. 1975 Rate of evaporation of low–solubility contaminants from water bodies to atmosphere. *Environmental Science & Technology*, **9**: 1178–1180

MED–Rice 2003 *Guidance document for environmental risk assessments of active substances used on rice in the EU for Annex I inclusion*. Document prepared by Working Group on MED–Rice, EU Document Reference SANCO/1090/2000 – rev.1, Brussels, pp. 108

Nguyen, N. V. and A. Ferrero 2006 Meeting the challenges of global rice production. *Paddy Water Environment*, **4**: 1–9

Okamoto, Y., R. I. Fisher, K. L. Armbrust and C. J. Peter 1998 Surface water monitoring survey for bensulfuron methyl applied in paddy fields. *Journal of Pesticide Science*, **23**: 235–240

Phong, T. K. 2008 *Investigation of fate and transport of granule and foliar sprayed pesticides in paddy fields*. Doctor dissertation. Tokyo University of Agriculture and Technology, Japan

Tomlin, C. (Ed) 2003 *The Pesticide Manual*. 13th edition. British Crop Protection Council, Farnham, UK

Vu, S. H., S. Ishihara and H. Watanabe 2006 Exposure risk assessment and evaluation of the best management practice for controlling pesticide runoff from paddy fields. Part 1: Paddy watershed monitoring. *Pest Management Science*, **62**: 1193–1206

Watanabe, H., K. Inao, S. H. Vu, T. K. Phong, S. Ishihara, K. Takagi and J. Tournebize 2008 Pesticide Exposure Assessment in Rice Paddy Areas: A Japanese Perspective. *In* "Pesticide risk assessment in rice paddies: Theory and practice" ed. by E. Capri and D. Karpouza, Elsevier, Amsterdam, pp. 167–211

Watanabe, H., H. T. M. Nguyen, S. Komany, S. H. Vu, Y. Asami, T. K. Phong and J. Tournebize 2006a Applicability of ELISA in pesticide monitoring to control runoff of bensulfuron–methyl and simetryn from paddy fields. *Journal of Pesticide Science*, **31**: 123–129

Watanabe, H. and Takagi K. 2000a A simulation model for predicting drug concentrations in pond water and surface soil I. Model development. *Environmental Technology*, **21**: 1379–1391

Watanabe, H. and Takagi K. 2000b A simulation model for predicting pesticide concentrations in paddy water and surface soil Ⅱ: Model validation and application. *Environmental Technology*, **21**: 1393–1404

Watanabe, H, K. Takagi and S. H. Vu 2006b Simulation of mefenacet concentrations in paddy fields by an improved PCPF–1 model. *Pest Management Science*, **62**: 20–29