

A SIMULATION MODEL FOR PREDICTING PESTICIDE CONCENTRATIONS IN PADDY WATER AND SURFACE SOIL. I. MODEL DEVELOPMENT

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ABSTRACT

A simulation model for predicting pesticide concentrations in paddy water and surface soil (PCPF-1) was developed. The PCPF-1 model simulates the fate and transport of pesticide in paddy water and 1cm deep oxidative paddy surface soil layer, or the pesticide source layer (PSL). The model considers the pesticide fate and transport processes in paddy water such as dissolution of pesticide in paddy water compartment, pesticide transfer by desorption from the PSL, dilution by precipitation and irrigation, concentration from evaporation and transpiration, and dissipation by biochemical and photochemical degradation. In the PSL compartment, adsorption in soil, pesticide transport through percolation of paddy water, and pesticide dissipation by biochemical degradation are considered. The model program was coded using Visual Basic for Applications as a Macro in Microsoft Excel that includes data sheets of daily water balance and daily UV-B radiation received on paddy water. The model behavior and sensitivity analysis was conducted by using field data of daily water balance and UV-B radiation obtained at the experimental paddy rice field at National Institute of Agro-Environmental Sciences (NIAES), Ibaraki, Japan in 1988. Simulated pesticide concentrations in paddy water and PSL decreased exponentially with time. PCPF-1 successfully simulated oscillating pesticide concentrations in paddy water that affected by abrupt dilution from irrigation and precipitation and pesticide transfer from PSL. PCPF-1 indicated potentials to be a tool for investigating the pesticide fate and transport processes. The model validation using experimental data will be discussed in the concurrent paper.

Keywords: Simulation model, paddy field, pesticide, kinetics, microsoft excel

INTRODUCTION

Paddy rice farming has been very well sustainable and the production of paddy rice in submerged soils has been practiced continuously for over 4 000 years [1]. However, extensive use of fertilizers and pesticides and their improper field management appear to have adverse effects on the healthy aquatic ecosystem [2] and possibly on drinking water. Monitoring studies for pesticide concentrations in river systems in Japan indicated that several herbicides commonly used in paddy fields have been detected [3-7]. Japan Environmental Agency listed about 70 chemicals as suspected endocrine disrupter substances. Among them, about 40 chemicals are pesticides and about a half of them are currently registered [8]. Therefore, public concern for the surface water quality affected by pesticides is becoming eminent. A simulation using pesticide fate and transport models is relatively inexpensive and less time consuming than field monitoring and laboratory experiments. Simulation models can be used as tools for analyzing the mechanisms of the pesticide transport phenomena and for evaluating the best management practices in controlling pesticide discharges from paddy fields. Also, they can be used as an educational

tool for the extension of the best management practices and environmental ethics for farmers and consumers. However, only a few models for the pesticide fate and transport in paddy fields have been reported [9-11].

RICEWQ was developed to evaluate the dissipation and runoff of agrochemicals from their use on aquatic crop such as rice production [9]. RICEWQ, which is developed in part from the lake water-quality model contained within SWRRBWQ [12], is a process oriented lumped parameter model requires over 40 input parameters. The model consists of water balance algorithms including precipitation, evaporation, seepage, irrigation, releases and overflow. The algorithm for the pesticide application considers multiple applications, pesticide drift and interception by foliage and water. The crop algorithm includes crop growth, associated pesticide washoff, degradation and its post harvest field deposition. The water quality algorithm considers dilution, volatilization, soil adsorption, decay in the field and re-suspension from bottom sediments [9].

Inao and Kitamura [10] developed a model, PADDY, predicting pesticide concentrations in water and soil in paddy fields. The model accounts for pesticide mass balance in both paddy water and 5mm thick surface soil. It also simulates

pesticide transport below the paddy surface soil. The pesticide model simulates the dissolution, volatilization and degradation of the pesticide in paddy water, adsorption/desorption and degradation in paddy soil layer. The PADDY model has been validated and applied for a number of cases in Japan [10, 13]. However, the PADDY model did not consider the daily fluctuation of paddy water depth and photochemical degradation process. The daily fluctuation of the paddy water depth associated with hydrological and management conditions such as precipitation, irrigation and drainage is an important factor in accounting for the pesticide mass balance and water balance. Also, the photochemical degradation in paddy water can be important for the dissipation of pesticides susceptible to the photochemical degradation [14]. Incorporating the variable paddy water depth and photochemical degradation may improve the model predictability and expand the application of the model simulation to various management practices.

Other practical importance for the simulation model is simplicity and easiness of the simulation procedures including input data preparation, model execution, and output data processing. Many pesticide transport simulation models are still executed on DOS. Those programs are difficult to use and time consuming especially for users who are new to simulation studies. However, some of newly developed model programs such as HYDRUS 1D, HYDRUS 2D, SWRRBWQ are Windows based in order to increase the user friendliness [15-17]. The PADDY model is also executed using Microsoft® Visual Basic® based on Windows [10]. On the other hand, simple simulation can be practised in a popular spreadsheet programs. Moreover, macro programming using Visual Basic for Application in Microsoft Excel makes it possible to perform simulations using complex numerical procedures in popular spreadsheet software.

We developed a new model for predicting pesticide

concentrations in paddy water and surface soil (PCPF-1) using Visual Basic for Application in Microsoft Excel. In this paper, we discussed the development of governing equations, numerical procedures and the model behavior and sensitivity analyses. The sister paper will discuss the parameter estimation and the model validation using experimental data.

THEORY AND GOVERNING EQUATIONS

The PCPF-1 model simulates the pesticide fate and transport in two compartments, paddy water and paddy surface soil layer or the pesticide source layer (PSL here after). The paddy water compartment is assumed to be a completely mixed reactor having variable water depths. The PSL compartment is also assumed to be a completely mixed reactor, but with a constant depth of 1.0 cm. Both the compartments are assumed homogeneous having uniform, unsteady chemical concentrations. The PSL is defined as a 1.0 cm thick conceptual surface paddy soil layer governing the pesticide dissipation and transport processes under oxidative flooded condition. According to Takagi *et al.*, submerged 1cm layer paddy soil is aerobic such that the pesticide adsorption/desorption and microbial degradation occurs under oxidative conditions [13]. Inao and Kitamura [10] reported that soil thickness more than 5 mm had no influence on the pesticide desorption. Theoretically thinking, the magnitude of the influence of the pesticide desorption may be continuous and a function of depth. However, surface soil sampling for the pesticide residues in paddy soil is commonly done at initial 1cm layer [13, 18, 19]. From the practical point of view, we set the thickness of PSL to be 1.0cm for the PCPF-1 model development. Considering the paddy field environment, the conceptual pesticide fate scenario used in the model development is shown in the Figure 1.

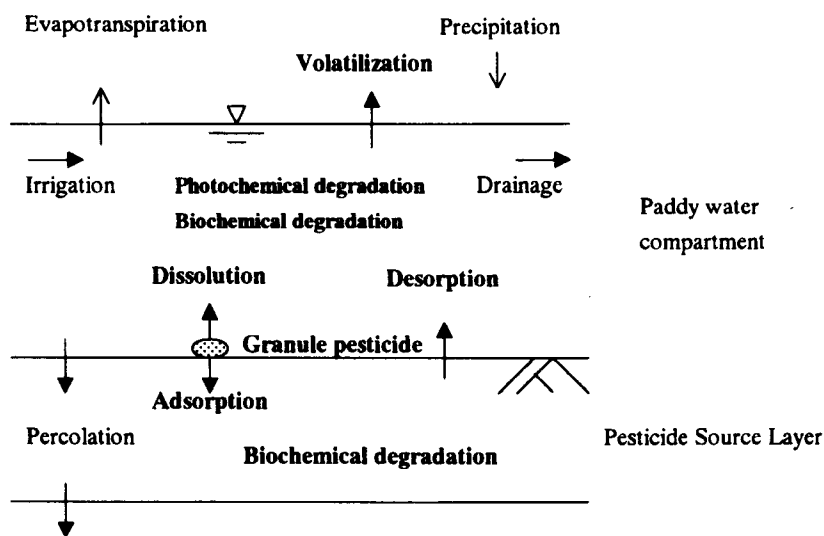


Figure 1. Conceptual pesticide fate and transport in paddy rice field.

Upon application of the granule pesticide, its dissolution in the paddy water proceeds according to the dissolution rate of the pesticide. As the paddy water percolate through the PSL, dissolved pesticide is transported from paddy water into PSL. The pesticide in PSL is assumed to partition between dissolved and adsorbed phase according to the equilibrium soil/water partitioning or adsorption coefficient of given pesticide. The pesticide transport from paddy water into paddy soil during the initial period was assumed such that the thickness of the PSL increases with the rate of daily percolation from zero until it reaches the maximum thickness of 1.0 cm. After cumulative percolation front exceeding 1.0 cm, the pesticide in the soil water leaches out from the PSL to the subsurface soil matrix with the concentration following the equilibrium adsorption coefficient of the pesticide. During the simulation, the pesticide concentration in the paddy water is affected by the pesticide transfer by desorption from the PSL, dilution of the dissolved pesticide by precipitation and irrigation, concentration from evaporation and transpiration, and the pesticide dissipation by volatilization, and biochemical and photochemical degradation. In the PSL compartment, the pesticide concentration is affected by the pesticide desorption into paddy water, percolating pesticide from paddy water, equilibrium adsorption on to PSL soil, leaching to the subsurface soil below PSL and biochemical degradation. Each of the pesticide fate and transport processes was mathematically expressed using optimum assumptions. The development of the governing equations considering pesticide mass balances in both paddy water and PSL compartment was discussed below.

Water balance in paddy water

The daily water balance within paddy water compartment was considered with precipitation, irrigation, drainage, percolation and evapotranspiration as given below.

$$A \frac{dh_{PW}}{dt} = A * [RAIN + IRR - DRAIN - PERC - ET] \quad (i)$$

where h_{PW} is the depth of water in paddy field (L), t is time (T), A is the area of the paddy field (L^2). $RAIN$ is the average rainfall rate during dt ($L T^{-1}$), IRR is the rate of irrigation water supply ($L T^{-1}$), $DRAIN$ is the surface drainage or overflow rate ($L T^{-1}$), $PERC$ is the rate of percolation ($L T^{-1}$), ET is the rate of evapotranspiration ($L T^{-1}$). In Equation (i), precipitation, percolation and evapotranspiration were assumed homogeneous over the paddy area and the seepage through levee was not considered in the model.

Pesticide mass balance in paddy water compartment

Pesticide fate and transport processes affecting

pesticide concentrations in the paddy water compartment include: (1) dissolution of the granule pesticide in paddy water after the pesticide application, (2) desorption of the adsorbed pesticide from the PSL into paddy water, (3) pesticide inflow with irrigation water when its pesticide load is significant, (4) offsite pesticide discharge by surface drainage, (5) pesticide transport below paddy water compartment with percolation, (6) pesticide volatilization from paddy water to atmosphere, and (7) pesticide dissipation by photochemical and biochemical degradation. Each process is assumed to occur independently and their effects on the pesticide concentration were assumed to be additive without any interaction. The pesticide mass balance in the paddy water compartment is expressed considering above processes as given below,

$$\frac{dM_{PW}}{dt} = \dot{M}_{PW-DISS} + \dot{M}_{PW-DES} + \dot{M}_{IRR} + \dot{M}_{OF} + \dot{M}_{PW-PERC} + \dot{M}_{VOL} + \dot{M}_{PW-DEG} \quad (ii)$$

where, M_{PW} is the total pesticide mass in paddy water (M), $\dot{M}_{PW-DISS}$ is the mass rate of pesticide dissolution of applied granule pesticide in paddy water ($M T^{-1}$), \dot{M}_{PW-DES} is the mass rate of pesticide desorption from the PSL into paddy water ($M T^{-1}$), \dot{M}_{IRR} is the mass rate of pesticide inflow with irrigation ($M T^{-1}$), \dot{M}_{OF} is the mass rate of pesticide outflow by drainage and overflow ($M T^{-1}$), $\dot{M}_{PW-PERC}$ is the mass rate of pesticide transport below paddy water compartment with percolation ($M T^{-1}$), \dot{M}_{VOL} is the mass rate of pesticide volatilization from paddy water to atmosphere ($M T^{-1}$), and \dot{M}_{PW-DEG} is the mass rate of pesticide dissipation by photochemical and biochemical degradation ($M T^{-1}$).

The change of pesticide mass in paddy water, which is the left side of Equation (ii), can be rewritten with the paddy water depth and the pesticide concentration in the paddy water as below. Since both the depth of paddy water and the pesticide concentration in the paddy water are variables,

$$\frac{dM_{PW}}{dt} = A \frac{d(h_{PW} C_{PW})}{dt} \quad (iii)$$

where C_{PW} is pesticide concentration in paddy water ($M L^{-3}$).

Pesticide dissolution from applied pesticide granule

The rate of dissolution of pesticide mass is rewritten by applying product rule on the differential term as below,

$$\begin{aligned} \dot{M}_{PW-DISS} &= A \left[\frac{d h_{PW} C_{PW}}{dt} \right]_{DISS} \\ &= A \left[h_{PW} \frac{dC_{PW}}{dt} + C_{PW} \frac{d h_{PW}}{dt} \right]_{DISS} \end{aligned} \quad (iv)$$

The dissolution of applied granule pesticide into paddy water is assumed to follow the first order kinetics. The change of the pesticide concentration in paddy water due to pesticide dissolution is given by,

$$\left[\frac{dC_{PW}}{dt} \right]_{DISS} = k_{DISS} (C_{SLB} - C_{PW}) \quad (v)$$

where k_{DISS} is the first order rate constant of pesticide dissolution in water (T^{-1}), C_{SLB} is the solubility of pesticide in water ($M L^{-3}$). The expression of the first order kinetics equation takes the same form as given in the PADDY model [10]. The change of the pesticide concentration in paddy water depends on the rate constant and the concentration differential between its solubility value and ambient pesticide concentration in paddy water. Substituting Equation (v) into (iv), the expression of the rate of mass transfer by pesticide dissolution is given by,

$$\dot{M}_{PW-DISS} = A h_{PW} k_{DISS} (C_{SLB} - C_{PW}) + A \left[C_{PW} \frac{d h_{PW}}{dt} \right]_{DISS} \quad (vi)$$

The pesticide dissolution process described with above equation is terminated when the total dissolved pesticide mass exceeds the mass of applied pesticide.

Pesticide desorption from the pesticide source layer

The pesticide desorption process is also assumed to occur following the first order rate law. The change of the pesticide concentration in the PSL due to pesticide desorption is given by,

$$\left[\frac{dC_{S-PSL}}{dt} \right]_{DES} = -k_{DES} C_{S-PSL} \quad (vii)$$

where C_{S-PSL} is the pesticide concentration in the soil for the PSL ($M m^{-1}$ dry soil basis), k_{DES} is the first order rate constant for the pesticide desorption from the PSL (T^{-1}). Neglecting the effect of the initial variation of the PSL depth, the rate of pesticide mass transfer from the PSL into paddy water is now expressed as;

$$\begin{aligned} \dot{M}_{PW-DES} &= -A d_{PSL} r_{b-PSL} \left[\frac{dC_{S-PSL}}{dt} \right]_{DES} = A d_{PSL} r_{b-PSL} k_{DES} C_{S-PSL} \end{aligned} \quad (viii)$$

where d_{PSL} is the depth of the PSL (L) and ρ_{b-PSL} is the bulk density of PSL ($M L^{-3}$).

In most cases, the uptake or release of organics by natural particles is bimodal in that it occurs in fast and slow stages [20]. Slow fraction of some pesticides was found to increase with contact time in the environment [21]. Many different mechanisms have been proposed to explain the observance of rate-limited or slowly reversible sorption-desorption process [22-25]. In this model, we included options for biphasic first order kinetic model for simulating the processes of pesticide desorption and biochemical degradation in soil. The biphasic first order kinetic model keeps the same process as in Equation (viii), however its rate changes at the certain threshold concentration on the intercept of two phases. The model simulation for the biphasic first order kinetic can be performed by setting the first and second phase rate constants and the phase intercept concentration where slow process is assumed to begin. For the case of the single-phase first order kinetic model, the second phase rate constant has the same value as the first phase rate constant.

Pesticide transport by irrigation, drainage and percolation

When the pesticide concentration in irrigation water is significant, the rate of pesticide inflow through irrigation water is calculated with the pesticide concentration in the irrigation water and the rate of irrigation as,

$$\dot{M}_{IRR} = A IRR C_{W-IRR} \quad (ix)$$

where C_{W-IRR} is the pesticide concentration in irrigation water. Similarly, the rate of pesticide discharge by drainage water is calculated with the pesticide concentration in the paddy water and the rate of drainage as,

$$\dot{M}_{OF} = -A DRAIN C_{PW} \quad (x)$$

Also, the rate of the pesticide transport by percolation from the paddy water into the paddy soil is expressed with the pesticide concentration in the paddy water and the rate of percolation as,

$$\dot{M}_{PW-PERC} = -A PERCC_{PW} \quad (xi)$$

Pesticide volatilization from paddy water to atmosphere

The volatilization of the pesticide from paddy water to atmosphere is simulated by the pesticide mass transfer

coefficient, which is also used in the PADDY model [10].

$$\dot{M}_{VOL} = -Ak_{L-A}C_{PW} \quad (xii)$$

where k_{L-A} is the pesticide mass transfer coefficient from paddy water to atmosphere ($L T^{-1}$). The method developed by Mackay and Leinonen [26] was used to estimate k_{L-A} , and it is given as,

$$k_{L-A} = \left[\left(K_L^{CO_2} \sqrt{\frac{M_{CO_2}}{M}} \right)^{-1} + \left(H K_G^{H_2O} \sqrt{\frac{M_{H_2O}}{M}} \right)^{-1} \right]^{-1} \quad (xiii)$$

where M is the relative molecular mass of the pesticide, M_{CO_2} and M_{H_2O} are the relative molecular masses of CO_2 and H_2O , $K_L^{CO_2}$ (4.75 m d^{-1}) is the mass transfer coefficient of the CO_2 in water, $K_G^{H_2O}$ (720 m d^{-1}) is the mass transfer coefficient of H_2O in air and H is the Henry's constant of the pesticide [27] and $H=16.04 M VP / C_{SLB}T$, where VP is the vapor pressure of the pesticide (mm Hg), C_{SLB} is the water solubility of the pesticide ($M L^{-3}$), and T is the ambient temperature (K).

Pesticide dissipation by degradation processes:

Pesticide dissipation processes in paddy water included in the model are photochemical degradation and biotic and abiotic degradation. For the biotic and abiotic degradation processes, it is difficult to offer a general estimate of the relative importance of either process under conditions that enable both biotic and abiotic transformations to occur [28]. In this model, they were considered together as one process and is called biochemical degradation hereafter. The rate of pesticide dissipation by two dissipation pathways were assumed to be additive. Considering the variation of the paddy water depth, the rate of pesticide dissipation by

$$\dot{M}_{PW-DEG} = A \left(\left[\frac{dh_{PW} C_{PW}}{dt} \right]_{PW-PHOTO} + \left[\frac{dh_{PW} C_{PW}}{dt} \right]_{PW-BIOCHEM} \right)$$

$$\text{where } \left[\frac{dh_{PW} C_{PW}}{dt} \right]_{PW=PHOTO} \quad \text{and} \quad \left[\frac{dh_{PW} C_{PW}}{dt} \right]_{PW=BIOCHEM} \quad (xiv)$$

photochemical and biochemical are the changes of the pesticide masses during dt in the paddy water due to photochemical and biochemical degradation, respectively. Pesticide degradation by photochemical reactions is very

complex phenomena. It comprises direct and indirect photolysis that depends upon the characteristics and the structure of given pesticide, its amount and the spectrum of the irradiation, types and characteristics of the solvent and constituents in the solvent and etc. [29]. However, in order to keep the simplicity of the model expression for complex reactions, the change of pesticide concentration due to photochemical degradation was assumed to be a function of the UV radiation received on the solute or paddy water. UV is a common light source of irradiation for the photochemical degradation studies and applicable for the experiments obtaining the required parameters. The rate of metolachlor photolysis was depend on the duration of UV irradiation and followed the first order kinetics [30, 31]. It is also advantageous to consider the photochemical degradation with respect to the amount of radiation instead of the time since the radiation from the sunlight is transient and depending on the whether conditions in the field. Although Schwarzenbach *et al.* [29] suggested that the whole spectrum of the irradiation must be known for the quantification of photochemical processes, we focused on UV-B region (wavelength of 280-320 nm) where, in general, exhibit intensive light adsorption by many chemical compounds. Loss of light in crossing the air-water interface can be usually neglected since it is only a few percent for solar elevations above 20 degrees [32]. We also neglected the light adsorption by paddy water since it is difficult to evaluate wavelength-dependent underwater light field that depends on the highly variable absorption properties of water [32]. Applying the first order rate law, the change of the pesticide concentration as a function of the cumulative UV-B radiation energy is given as below (xv),

$$\frac{dC_{PW}}{dE_{UVB-C}} = -k_{PHOTO} C_{PW} \quad (xv)$$

where E_{UVB-C} (kJ m^{-2}) is the cumulative UV-B radiation received on the solution body and k_{PHOTO} ($\text{m}^2 \text{kJ}^{-1}$) is the first order rate coefficient of photochemical degradation with respect to the cumulative UV-B radiation. Then, the change of the pesticide concentration in paddy water as a function of time is obtained with the derivative of the cumulative UV-B radiation as a function of time by applying chain rule as,

$$\frac{dC_{PW}}{dt} = \frac{dC_{PW}}{dE_{UVB-C}} \frac{dE_{UVB-C}}{dt} \quad (xvi)$$

Applying the product rule and substituting Equation (xvi), now the change of the pesticide mass in paddy water due to photochemical degradation as a function of time becomes as

shown in Equation (xvii).

For the change of the pesticide concentration in paddy water due to biochemical degradation, the reaction was assumed to follow the first order kinetics. Similar to the above equation, the change of the pesticide mass in the paddy water due to biochemical degradation is given in Equation xviii, where $k_{BIOCHEM-PW}$ (T^{-1}) is the first order rate constant of biochemical degradation in paddy water. Replacing Equations (xvii) and (xviii) into Equation (xiv) gives Equation (xix). The last two terms in Equation xix are the pesticide mass

contribution through variable paddy water depth due to photochemical and biochemical degradation processes. These terms are difficult to estimate since all the reactions in the paddy water occur simultaneously. However, the contribution from these two processes to the changes of the pesticide concentrations in paddy water seemed not to be significant, as found in the sensitivity analysis. Therefore, we assumed that the last two terms in Equation (xix) could be neglected. Finally, the governing equation for the pesticide mass balance in paddy water is given by Equation xx

$$\left[\frac{d h_{PW} C_{PW}}{dt} \right]_{PW-PHOTO} = -h_{PW} k_{PHOTO} C_{PW} \frac{dE_{UVB-C}}{dt} + \left[C_{PW} \frac{d h_{PW}}{dt} \right]_{PW-PHOTO} \quad (xvii)$$

$$\left[\frac{d h_{PW} C_{PW}}{dt} \right]_{PW-BIOCHEM} = -h_{PW} k_{BIOCHEM-PW} C_{PW} + \left[C_{PW} \frac{d h_{PW}}{dt} \right]_{PW-BIOCHEM} \quad (xviii)$$

$$\begin{aligned} \dot{M}_{PW-DEG} &= A h_{PW} \left(-k_{PHOTO} \frac{dE_{UVB-C}}{dt} - k_{BIOCHEM-PW} \right) C_{PW} \\ &+ A \left[C_{PW} \frac{d h_{PW}}{dt} \right]_{PW-PHOTO} + A \left[C_{PW} \frac{d h_{PW}}{dt} \right]_{PW-BIOCHEM} \end{aligned} \quad (xix)$$

$$\begin{aligned} &A \frac{d(h_{PW} C_{PW})}{dt} \\ &= A h_{PW} k_{DISS} (C_{SLB} - C_{PW}) + A \left[C_{PW} \frac{d h_{PW}}{dt} \right]_{DISS} \\ &+ A d_{PSL} \rho_{b-PSL} k_{DES} C_{S-PSL} \\ &+ A IRR C_{W-IRR} - A DRAIN C_{PW} - A PERC C_{PW} - A k_{L-A} C_{PW} \\ &+ A h_{PW} \left(-k_{PHOTO} \frac{dE_{UVB-C}}{dt} - k_{BIOCHEM-PW} \right) C_{PW} \end{aligned} \quad (xx)$$

Pesticide mass balance in pesticide source layer

The pesticide fate and transport processes affecting the pesticide concentration in the PSL considered in the model

were: 1) pesticide adsorption in soil and subsequent partitioning in soil water in the PSL upon dissolution of applied pesticide, 2) pesticide transport into and out of PSL through percolation of paddy water, 3) biochemical

degradation in the PSL, and 4) pesticide desorption from the PSL into paddy water. Similar to the paddy water compartment, it is assumed that each process is independent and that their effects on the pesticide concentration in PSL are additive without any interaction. The pesticide mass balance in the PSL is expressed as (xxi)

$$\frac{dM_{PSL}}{dt} = \dot{M}_{PSL-DISS} + \dot{M}_{PSL-PERC} + \dot{M}_{PSL-DEG} + \dot{M}_{PSL-DES} \quad (xxi)$$

where M_{PSL} is the total pesticide mass in the PSL, $\dot{M}_{PSL-DISS}$ is the rate of pesticide mass transfer into the PSL upon pesticide dissolution process, $\dot{M}_{PSL-PERC}$ is the rate of pesticide mass transport into and out of PSL through percolation, $\dot{M}_{PSL-DEG}$ is the rate of pesticide mass dissipation by biochemical degradation process in the PSL, and $\dot{M}_{PSL-DES}$ is the rate of pesticide mass transfer by pesticide desorption process from the PSL into paddy water.

When dissolution of the pesticide begins, the depth of the PSL increases following the piston type movement of the percolation front until the maximum depth of 1.0cm. At the same time, the pesticide is partitioned into solid and liquid phase according to the soil adsorption coefficient of given pesticide. Therefore, the change in pesticide mass in PSL is described as below,

$$\frac{dM_{PSL}}{dt} = A \left(\frac{\theta_{Sat-PSL}}{k_{d-PSL}} + \rho_{b-PSL} \right) \frac{d(d_{PSL} C_{S-PSL})}{dt} \quad (xxii)$$

$$\dot{M}_{PSL-DISS} = A \theta_{Sat-PSL} \left[\frac{d d_{PSL} C_{W-PSL}}{dt} \right]_{PSL-DISS} + A \rho_{b-PDL} \left[\frac{d d_{PSL} C_{S-PSL}}{dt} \right]_{PSL-DISS} \quad (xxiii)$$

$$\dot{M}_{PSL-DISS} = A d_{PSL} (\theta_{Sat-PSL} + \rho_{b-PSL} k_{d-PSL}) (k_{DISS} (C_{SLB} - C_{PW}) + \frac{C_{PW}}{d_{PSL}} \frac{d d_{PSL}}{dt}) \quad (xxiv)$$

from the PSL. Using the percolation rate and the equilibrium soil adsorption coefficient of the pesticide in the PSL, the rate of the pesticide transport through the percolation is given by,

where $\theta_{sat-PSL}$ is the volumetric saturated water content of the PSL ($L^3 L^{-3}$), k_{d-PSL} is the soil adsorption coefficient of the pesticide in the PSL ($L^3 M^{-1}$), and C_{S-PSL} is the concentration of the pesticide in soil in the PSL ($M M^{-1}$).

Pesticide mass transfer by partitioning of dissolved pesticide upon application

In the PSL as defined earlier, the applied pesticide in paddy water is assumed partitioned immediately upon its dissolution following the equilibrium soil adsorption coefficient. The rate of the pesticide mass transfer into PSL by the pesticide dissolution is expressed by considering the effects due to initial increase in PSL depth as, shown in Equation (xxii). Applying the first order kinetic equation as in the Equation (v) and rearranging, the rate of the pesticide mass transfer into the PSL by the pesticide dissolution becomes as shown in Equation (xxiv).

Pesticide transport by percolation

Percolation process in paddy soil with proper soil puddling upon field preparation is generally very slow. Average percolation rate in the experimental paddy field (except field edges) were 0.6 cm day^{-1} [33]. Many paddy fields recently reclaimed by heavy machineries have percolation rates less than 0.5 cm day^{-1} [34]. Adachi [35] reported that vertical percolation after the puddling ranged from 0.8 to 0.08 cm day^{-1} . In the model, the pesticide transport process in PSL through the percolation was assumed such that pesticide mass equivalent to that in the percolating paddy water enter, while the pesticide mass equivalent to that in the percolating soil water that equilibrates with adsorbed pesticide is leached

$$\dot{M}_{PSL-PERC} = A PERC \left(C_{PW} - \frac{1}{k_{d-PSL}} C_{S-PSL} \right) \quad (xxv)$$

Pesticide dissipation by biochemical degradation

Numerous transformations occur in the homogeneous phases, other transformations occur in the interface between phases [28]. Also, solute interactions of the pesticide concentration in water and soil phases are possible along with the non-equilibrium adsorption and desorption phenomena. Those reactions are simultaneous and interactive, and they are difficult to define or determine the absolute effect of the reaction. In order to simplify the model expression, the rate of the pesticide dissipation due to biochemical degradation in soil was considered with the change in the pesticide concentration in soil phase as given below,

$$\dot{M}_{PSL-DEG} = Ad_{PSL} \rho_{b-PSL} \left[\frac{dC_{S-PSL}}{dt} \right]_{BIOCHEM-PSL} \quad (xxvi)$$

The changes of the pesticide concentration in soil due to biochemical degradation was also assumed to occur by following the first order reaction similar to other rate constants discussed above, and the effects from the initial variations in PSL depth was assumed to be insignificant. Now, the equation for the pesticide degradation in PSL becomes,

$$\dot{M}_{PSL-DEG} = -Ad_{PSL} \rho_{b-PSL} k_{BIOCHEM-PSL} C_{S-PSL} \quad (xxvii)$$

where $k_{BIOCHEM-PSL} (T^{-1})$ is the first order rate constant of the pesticide biochemical degradation in the PSL. Similar to the pesticide desorption process, the option for the biphasic first order kinetic model was included for simulating the biochemical degradation process in soil. The option may be useful since bioremediation of soil often levels off after an initial rapid decline, which is believed to be mostly due to the decline of bioavailability for the microbial degradation [36]. Also, the aging appeared to reduce the bioavailability of the soil contaminant mixture [37].

Pesticide transfer by desorption

The desorption process from the PSL to paddy water was described in an earlier section. The rate of the pesticide transfer due to desorption from the PSL to paddy water is expressed as,

$$\dot{M}_{PSL-DES} = -Ad_{PSL} \rho_{b-PSL} k_{DES} C_{S-PSL} \quad (xxviii)$$

Finally, the governing equation for the pesticide mass balance in PSL becomes; Equation (xxix):

$$\begin{aligned} & A \left(\frac{\theta_{Sat-PSL}}{k_{d-PSL}} + \rho_{b-PSL} \right) \frac{d(d_{PSL} C_{S-PSL})}{dt} \\ & = Ad_{PSL} (\theta_{Sat-PSL} + \rho_{b-PSL} k_{d-PSL}) (k_{DISS} (C_{SLB} - C_{PW}) + \left[\frac{C_{PW}}{d_{PSL}} \frac{dd_{PSL}}{dt} \right]_{DISS}) \\ & + A PERC (C_{PW} - \frac{1}{k_{d-PSL}} C_{S-PSL}) \\ & - Ad_{PSL} \rho_{b-PSL} k_{BIOCHEM-PSL} C_{S-PSL} \\ & - Ad_{PSL} \rho_{b-PSL} k_{DES} C_{S-PSL} \end{aligned} \quad (xxix)$$

RESULTS AND DISCUSSION

Numerical procedure

Applying product rule on the differential term of

Equations (xx) and (xxix) and rearranging, governing equations (i), (xx) and (xxix) now form a non-homogeneous linear systems of ordinary differential equations as given by Equations (xxx), (xxxi) and (xxxii).

$$\frac{dh_{PW}}{dt} = RAIN + IRR - DRAIN - PERC - ET \quad (xxx)$$

The model program calculating above the equations was coded using Visual Basic for Applications in Microsoft Excel. The Excel file includes a Macro program of PCPF-1, datasheets for input parameters, daily water balance and daily UV-B radiation received on paddy water, model calculations and figures of predicted and observed daily pesticide concentrations. The datasheet for input parameters consist of names of macro program and pesticide, simulation period, and 21 measured parameters as indicated in Table 1.

The datasheet for the daily water balance consists of daily rainfall, irrigation, drainage, percolation, evapotranspiration, paddy water depth and its differential during the day in centimeter. Data were recorded from the

actual measurement in the field experiment or from the weather station if applicable and the daily water balance is taken so as to satisfy the Equation (xxx). Similarly, the datasheet for the daily UV-B radiation received on paddy water was recorded from the field observation. The determination of input parameter values and the method of data correction in the field experiment are discussed in detail in the concurrent paper.

Equations (xxxi) and (xxxii) were solved for C_{PW} and C_{S-PSL} , respectively, by using the fourth-order Runge-Kutta method [38] with given initial conditions. Since both equations depend each other, the numerical solutions of C_{PW} and C_{S-DL} were simultaneously obtained using an iterative procedure. The iteration was carried out until the solutions of both equations converge within the given criteria (less than 0.1% of relative error) at each time step. The time interval for the calculation of above equations was 1 day.

Table 1. The data sheet for input parameters for PCPF-1 model simulation.

Macro program	PCPF-1	
Pesticide	Pretilachlor	
Simulation period started from, and end on, year/month/day	1998/5/13	1998/7/4
Input parameters for paddy water		
Description	Unit	Value
Maximum simulation period.	day	52
Time interval	day	1
Application rate (pretilachlor)	g m ⁻²	0.06
Paddy field area	m ²	82.8
Solubility of the pesticide	mg l ⁻¹	50
1st order dissolution rate constant	day ⁻¹	0.063
1st order desorption rate constant (Phase 1)	day ⁻¹	0.114
Mass transfer coefficient. of pesticide volatilization	m day ⁻¹	6.00E-05
1st order photochemical degradation rate constant	m ² kJ ⁻¹	0.00083
1st order biochemical degradation rate constant	day ⁻¹	0.0714
Pesticide concentration in irrigation water	mg l ⁻¹	0
1st order desorption rate constant (Phase 2)	day ⁻¹	0.0030
Phase intercept concentration for desorption	mg l ⁻¹	0.2
Input parameters for Pesticide Source Layer		
Description	Unit	Value
Depth	cm	1.0
Particle density	g cm ⁻³	2.36
Bulk density	g cm ⁻³	0.937
Saturated volumetric water content	cm ³ cm ⁻³	0.603
1st order biochemical degradation rate constant (Phase1)	day ⁻¹	0.0368
Equilibrium soil adsorption coefficient	l kg ⁻¹	13.03
1st order biochemical degradation rate constant (Phase2)	day ⁻¹	0.0368
Phase intercept concentration for biochemical degradation	mg l ⁻¹	0.1

$$\begin{aligned}
& \frac{dC_{PW}}{dt} \\
& = k_{DISS} (C_{SLB} - C_{PW}) + \frac{1}{h_{PW}} \left[C_{PW} \frac{dh_{PW}}{dt} \right]_{DISS} \\
& + \frac{1}{h_{PW}} d_{PDL} \rho_{b-PDL} k_{DES} C_{S-PSL} \tag{xxxix} \\
& + \frac{1}{h_{PW}} IRR C_{W-IRR} - \frac{1}{h_{PW}} DRAIN C_{PW} - \frac{1}{h_{PW}} PERC C_{PW} - \frac{1}{h_{PW}} k_{L-A} C_{PW} \\
& + \left(-k_{PHOTO} \frac{dE_{UVB-C}}{dt} - k_{BIOCHEM-PW} \right) C_{PW} - \frac{1}{h_{PW}} \frac{dh_{PW}}{dt} C_{PW}
\end{aligned}$$

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

Upon execution of the Macro program, the Macro performs the model calculations and automatically creates output data and figures in a Microsoft Excel file. It is advantageous that PCPF-1 model was incorporated in a Microsoft Excel file. Data input procedure is simple and already familiar to many users, and the program is executed with four easy steps (click Tool, Macro, select the program and Run). Basic data processing is automatically done and further data analyses can be performed in the other sheets without opening other files. Furthermore, application of Macro makes it possible to link with other windows operating simulation models, and those separate models can be executed at once as if they are in one simulation package. This application is also useful to expand the investigation of the effect of the pesticide transport in paddy field on ground water systems or on surface water ecosystems or both. Also, the Microsoft Excel is the one of the most popular

spreadsheet softwares, which makes the extension of simulation techniques easier and faster.

Model behavior and sensitivity

Using arbitrarily determined parameter values, the model behavior and significant parameters were evaluated. For simulations performed for the sensitivity analysis, daily input data for water balance and UV-B radiation were used from actual daily monitoring data. They were obtained from a field experiment carried out at the experimental rice paddy of National Institute of Agro-Environmental Sciences (NIAES) in Ibaraki, Japan in 1998. The duration of the simulation was set to be 52 days. Parameter values for application rate, solubility in water and equilibrium adsorption coefficient were used in case of pretilachlor [13]. Those of bulk density and saturated volumetric water content for 1cm thick surface soil

were the same values as for the experimental paddy field in NIAES. Other parameters such as the rate constant for pesticide dissolution, the first phase rate constants for desorption, the rate constant of biochemical degradation in water, the first and second phase rate constants for biochemical degradation in soil were all set to be 0.1 day^{-1} . The second phase rate constant for desorption was set to be 0.01 day^{-1} in order to examine the effect of the biphasic first order kinetic process. For mass transfer coefficient of pesticide volatilization, parameter values were set to be 0.004 m day^{-1} by considering the average paddy water depth of 0.04 m in order to have the same magnitude as other rate coefficients (0.1 day^{-1}) (see Equation xxxi). Similarly for the photochemical degradation rate constant, parameter values were set to be $0.0086 \text{ m}^2 \text{ kJ}^{-1}$ by considering the average daily UV-B irradiation ($11.7 \text{ kJ m}^{-2} \text{ day}^{-1}$) during the monitoring period.

The result of the model simulation is shown in Figure 2. The simulated pesticide concentrations in paddy water and PSL both indicated exponential decrease with time as indicated in similar models for the paddy field application [9, 10, 14]. Simulated pesticide concentrations in paddy water behaved in a slightly oscillating manner responding to the dilution by irrigation and precipitation as well as to the concentration by the pesticide desorption from paddy soil. As indicated in Figure 2, the oscillation of simulated pesticide concentrations in paddy water corresponded to the changes in paddy water depth. However, predicted pesticide concentrations in paddy soil indicated smooth exponential decrease. The pesticide transport into/from PSL by steady and relatively small percolation rate was insignificant such

that only 6.6% of applied pesticide leached below PSL. Similar behavior is observed in the simulation using RICEWQ model [18].

The pesticide concentrations in PSL responded the slow desorption rate after the phase intercept concentration of 0.1 mg kg^{-1} . The smaller slope of the decline of pesticide concentration after the phase intercept indicates the slow pesticide release from the PSL. The behavior of the pesticide concentrations in paddy water was more sophisticated than that in PSL. Upon initiation of the slower desorption rate, the concentration in paddy water decreased rapidly as the result of less pesticide transfer from the PSL and corresponding dilution in the paddy water. However, the pesticide mass transfer from PSL is depending both on the rate coefficient and the pesticide concentration in PSL. Therefore, the pesticide concentration in paddy water achieved equilibrium with the pesticide mass transfer from PSL within about 10 days and afterward decline of the pesticide concentration in paddy water follow the same rate as that in PSL (Figure 2).

After the simulation using original parameter values, sensitivity analysis was performed by changing each one of the selected input parameters by $\pm 10\%$ of the original input value. Among the rate constants, those for the first phase desorption and biochemical degradation in soil had large influence to the model response. The relative differences from calculated concentrations in paddy water and PSL using original parameter values ranged about 14% to 20% following 2nd week after the pesticide application, however during the first week, errors were less than 5%.

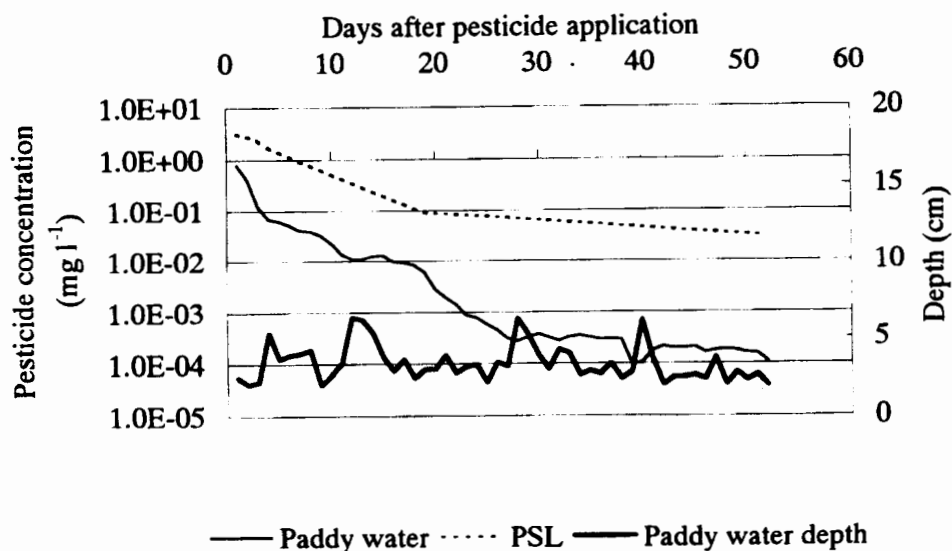


Figure 2. Simulated pesticide concentrations in paddy water and PSL and paddy water depths.

CONCLUSIONS

The following conclusions were obtained from this study. User friendliness and applicability of PCPF-1 may contribute to the development and the extension of the pesticide risk assessment and management in paddy rice production. PCPF-1 successfully simulated pesticide concentrations in paddy water and PSL using arbitrarily determined parameter values and observed data. Among the rate constants, those for the first phase desorption and biochemical degradation in soil were found to be sensitive parameters for the model response, however, their influence during the first week was insignificant. PCPF-1 indicated the potential for being beneficial tool for investigating the

pesticide transport problems resulting from paddy rice production. The model validation using experimental data will be discussed in the concurrent paper.

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