

A SIMULATION MODEL FOR PREDICTING PESTICIDE CONCENTRATIONS IN PADDY WATER AND SURFACE SOIL II. MODEL VALIDATION AND APPLICATION

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ABSTRACT

A simulation model for predicting pesticide concentrations in paddy water and surface soil (PCPF-1) was validated with the result of field monitoring data of pretilachlor dissipation in experimental paddy rice field at National Institute of Agro-Environmental Sciences (NIAES), Ibaraki, Japan in 1998. Parameter values were determined from laboratory and field experiments. Environmental conditions and pesticide concentrations in experimental rice paddy plot at NIAES were monitored after the herbicide application for 52 days in 1998. Pesticide concentrations in paddy water and 1cm deep surface paddy soil sampled at 1, 3, 7, 14, 21, 28, 35 (water only), 42 and 49 days after the herbicide application were measured using gas chromatography with nitrogen/phosphorus detector (NPD-GC). The PCPF-1 model successfully simulated the drastic decline of pretilachlor concentrations in paddy water during the first week. Although the prediction of pesticide concentrations in paddy water during the mid-period of the simulation was over estimated, PCPF-1 prediction had good agreement with observed data of pretilachlor concentrations both in paddy water and surface soil for the first 10 days and last 20 days of simulation. For the pretilachlor dissipation in paddy field, pesticide desorption from paddy soil to paddy water was the key process controlling the rate of the pesticide dissipation. PCPF-1 has potential to be a beneficial tool for investigating the pesticide fate and transport processes as well as for controlling pesticide transport from the paddy field that affecting the both surface and ground water.

Key words: Simulation model, paddy field, pretilachlor, dissipation, monitoring

INTRODUCTION

Our previous paper [1] discussed the development of a simulation model for predicting pesticide concentrations in paddy water and surface soil (PCPF-1). The PCPF-1 model simulates the fate and transport of pesticide applied as granule formation in paddy water and paddy surface soil layer or pesticide source layer (PSL). Paddy water compartment has variable depths depending on the irrigation management and hydrological condition. The PSL has a constant depth of 1.0 cm except during the initial pesticide percolation period. Both the compartments are assumed to be a completely mixed reactor having uniform and unsteady chemical concentrations.

In the paddy water compartment, the model considers pesticide fate and transport processes such as dissolution of pesticide, 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, pesticide adsorption in soil, its transport through percolation of paddy water, and the dissipation by biochemical degradation are considered. The first order kinetic model was applied to simulate the dissolution of pesticide in paddy water, the desorption from PSL to paddy water, and the biochemical degradation in paddy water and PSL. The simulation of pesticide desorption and biochemical

degradation in soil can be selected as either single phase, or biphasic first order kinetics. The modified first order kinetic model using UV-B radiation on paddy water was employed for the simulation of pesticide dissipation due to photochemical degradation.

The model program was coded using Visual Basic for Applications in Microsoft Excel. The input data consist of 21 measured parameters, the daily water balance data and the daily UV-B radiation received on paddy water. Upon execution of the Macro program, the Macro performs the model calculations and automatically creates output data and figures in a Microsoft Excel file. PCPF-1 successfully simulated pesticide concentrations in paddy water and PSL using arbitrarily determined parameter values and observed data [1].

This paper validates the PCPF-1 model using measured parameters and input variables obtained from the monitoring study investigating the fate of commonly used herbicides in rice paddy field. The pesticide used for the validation of PCPF-1 model was pretilachlor. Pretilachlor [2-chloro-2',6'-diethyl-N-(2-propoxyethyl) acetanilide for IUPAC, acetamide for C.A.], was introduced by Ciba-Geigy for selective control against main annual grasses, broad-leaved weeds and sedges in transplanted and seeded rice [2]. Pretilachlor is one of the 41 agrochemicals that have to meet the water quality standards for holding the registration in Japan, 1995 and its allowable maximum concentration in water is 0.4 mg l⁻¹ [3].

Physicochemical properties of pretilachlor are listed in Table 1.

A limited number of studies has been carried out for investigating the behavior of pretilachlor in paddy field [4-6]. According to Fajardo *et al.* [5], half-lives of pretilachlor under paddy field conditions were about 4 days and 10 days, respectively for paddy water and 0-1 cm surface paddy soil. Pretilachlor dissipation in paddy field conditions has been simulated using PADDY model [7] using parameters obtained in laboratory and from literature. PADDY successfully predicted pretilachlor concentrations in both paddy water and 0-1 cm surface soil [4].

MATERIALS AND METHODS

Model parameter estimation

A computer simulation of pretilachlor dissipation in the

experimental paddy field was carried out for 52 days after the herbicide application. Hydrologic and management condition used for the simulation was as same as those in the field monitoring of the pretilachlor dissipation in the experimental rice paddy in National Institute of Agro-Environmental Sciences (NIAES) in Ibaraki, Japan in 1998. Initial conditions of the pesticide concentrations in paddy water and surface paddy soil were assumed to be 0.0 mg l⁻¹ and 0.0 mg kg⁻¹, respectively. Model options for the kinetic processes were set to be biphasic first order for desorption and single-phase first order for biochemical degradation in soil, respectively.

Table 2 shows 21 model input parameters and their values obtained from the experiments conducted in NIAES. Particle density, bulk density and saturated volumetric water content of 0-1 cm paddy surface soil were measured in the laboratory. Parameter values of dissolution rate and biochemical degradation rate in water for pretilachlor were

Table 1. Physico-chemical properties of pretilachlor [2].

Molecular formula	C ₁₇ H ₂₆ ClNO ₂
Molecular weight	311.9
Boiling pressure	135 °C/0.001 mm Hg
Vapor pressure	0.133 m Pa (20 °C)
K _{OW}	12020
Solubility	50 mg l ⁻¹
DT ₅₀ in soil	20-50 days
LC ₅₀ (96h)	0.9 mg l ⁻¹ (rainbow trout), 2.3 mg l ⁻¹ (carp)

Table 2. Input parameters for PCPF-1 model simulation.

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	0.1142
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

obtained using the methods described in Takagi *et al.*, [4]. The equilibrium soil adsorption coefficient was also obtained with the same manner described in Takagi *et al.*, [4] for Freundlich exponent of 1.0. Water solubility of the pretilachlor was obtained from the literature [2]. The mass transfer coefficient of pesticide volatilization was calculated according to Equation (xiii) of our previous paper [1] and physicochemical data of pretilachlor [2].

Desorption of neutral organic compounds from soil is generally biphasic [8] and often exhibit a significant fraction of chemicals by slow release following a comparatively rapid release [9]. Many early soil column studies of pesticide transport reported a retarded peak and pronounced tail in their breakthrough curves [10, 11], indicating that instantaneous and time dependent sorption/desorption processes occurred simultaneously [12]. The effect of the slow process or the rate limited process of pesticide desorption at especially low range concentrations may be under estimated by the single phase first order desorption kinetic model. In this project, we assumed that the pretilachlor desorption process in the PSL follow a biphasic first order kinetics. Input parameters required for the biphasic first order desorption process consist of rate constants for the initial and second phase process and the pesticide concentration in PSL at intercept of two phases. Takagi *et al.*, [4] obtained the parameter value for the desorption rate constant based on a laboratory model experiment that pretilachlor concentrations in the soil ranging from 5.3 mg kg⁻¹ to 2.9 mg kg⁻¹ during six days. However, the observed pretilachlor concentrations in the 0-1 cm surface paddy soil during the field experiment ranged from 2.5 mg kg⁻¹ to 0.064 mg kg⁻¹ (see Figure 7). Therefore, we assumed that the desorption rate constant obtained by Takagi *et al.*, [4] is appropriate for the initial phase desorption rate constant.

For the second phase, the rate constant was estimated from the field monitoring data of the pretilachlor concentrations in the experimental paddy field. The data set

used for the parameter value determination was from monitoring of pesticide concentrations in paddy water for a 5 day period (from 3 June to 8 June 1998) starting from 21 days after the pesticide application (Figure 1). The sampling and analytical procedures were the same as described in the following section. In Figure 1, the pesticide concentration fluctuated daily as a result of dilution by irrigation and concentration by desorbed pesticide from surface soil. Decline of pesticide concentrations in paddy water and soil over the 5 days period resulted from the mixed effects of dissipation processes including runoff, percolation, and degradation. However, the decline of the concentration in the surface paddy soil only due to desorption process can be estimated by taking the mass balance and calculating the amount of desorbed pesticide from the surface paddy soil into the paddy water.

At first, the pesticide concentration in 0-1cm surface soil on the 21 days after the herbicide application (DAHA) as an initial condition was estimated from the result of the linear regression analysis ($r^2 = 0.982$) of data on 14, 22 and 28 DAHA. For the estimation of the amount of desorbed herbicide from paddy surface soil, the differential value of herbicide concentration in paddy water between the minimum pesticide concentration after the irrigation and the maximum pesticide concentration before the next irrigation was obtained each day. Then, those differential pesticide concentrations in paddy water were multiplied by the average paddy water volume, which is equivalent of paddy water depth at 3.0 cm, in order to obtain the daily desorbed pesticide mass. Estimated pesticide concentrations in PSL during 5 day-period due to desorption were obtained by sequentially subtracting the daily amount of desorbed pesticide mass from the initial pesticide mass. Then data were fit to the first order kinetic model and its rate constant was obtained to be 0.0027 day⁻¹ with r^2 of 0.975 (Figure 2). Finally, this rate constant was used for the simulation of second phase desorption process.

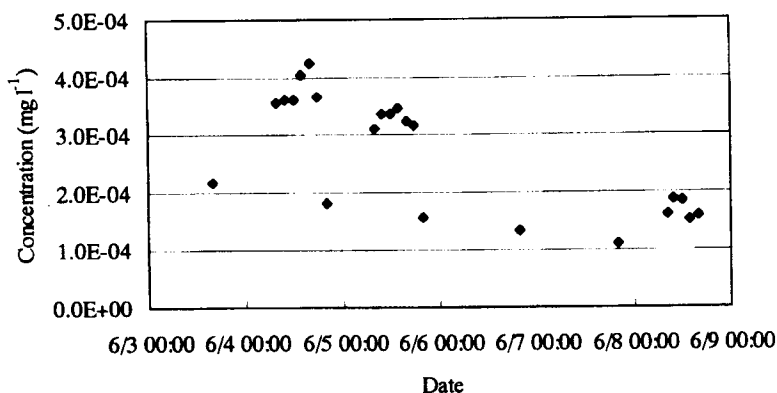


Figure 1. Pretilachlor concentrations in paddy water during the 5 day period from 3 June through 8 June in 1998.

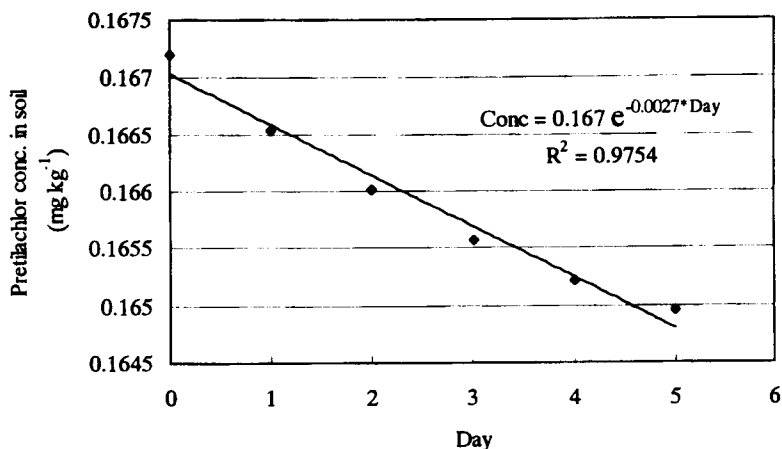


Figure 2. Estimated pretilachlor concentrations in 0-1cm surface paddy soil due to the desorption after 21 DAHA.

For the desorption process, the phase interceptions between two phases are depending upon the amount of fractions of rapid and slow desorption. Pignatello and Xing, [9] presented detailed reviews on the mechanisms of slow sorption and desorption processes. The slow desorption and its rate may be specific to chemical, soil and its constituents such as organic matter and minerals, as well as contact time for soil and chemicals [9]. Therefore, specific experiments may be required to determine the actual phase interception. Since there was no available data, the pesticide concentration in the PSL for the phase interception was estimated to be 0.2 mg kg⁻¹ by considering the observed pesticide concentration in surface paddy soil (see Figure 7).

For photochemical degradation of the pesticide, the first order rate constant with respect to the cumulative UV-B radiation was determined by conducting the newly developed experiment in ambient paddy field condition. Dissipation of four dissolved pesticides, mefenaset, pretilachlor, bensulfuronmethyl, and imazosulfuron was monitored under natural ambient sunlight condition. Three liter of each pesticide solution having a concentration of 1.0 mg l⁻¹ was prepared with autoclaved paddy water that sampled from the pesticide-free paddy block. Each pesticide solution was divided into two glass containers of 24 cm diameter and 7cm high. A set of four containers corresponding to each of four pesticide solutions was covered by a glass lid and wrapped with aluminum foil to cutoff the sunlight entering the solution. The other set was covered by quartz glass plate in order to minimize the UV light attenuation by the glass plate it self. The quartz glass plate used for the experiment was SG grade having 26 cm diameter with 2 mm thickness that passes more than 90% of light having wavelength from 280 nm to 2000 nm (Fujiwara Seisakusho co. Ltd). Those containers were placed about 90 cm above ground next to the experimental rice paddy under ambient conditions. UV-B radiation over the rice canopy in the experimental field was also monitored by MS-210w UV-B sensor (EKO Instruments Trading co., ltd.) during

the experiment. Forty ml of sample was taken from each container every week for 42 days. Each sample was conditioned for pH of about 6.5. Pesticides were extracted using Sep-Pac C18 and eluted with acetone. Then samples were analyzed by using gas chromatography equipped with nitrogen/phosphorus detector (NPD-GC) [4, 6].

It was assumed that pesticide dissipation observed in the container for dark conditions was due to the hydrolysis of the pesticide, and that for natural sunlight conditions was due to combination of hydrolysis and photochemical degradation including direct and indirect photolysis. Therefore, pesticide concentration solely due to photochemical degradation was obtained by subtracting the concentration obtained in dark condition from that in natural sunlight condition. Then, natural log of adjusted pesticide concentrations, ln [Conc.], versus cumulative UV-B radiation in kJ m⁻² for corresponding sampling date were plotted. The first order rate constant of photochemical degradation as a function of the cumulative UV-B radiation, k_{PHOTO} in Equation (xv) in our previous paper [1], was obtained from the regression analysis (Figure 3). The k_{PHOTO} value for the pretilachlor was determined to be 0.00083 m² kJ⁻² with an r² of 0.96.

Field monitoring and daily input data

Environmental conditions and pesticide concentrations in rice paddy were monitored for 52 days after the herbicide application at experimental rice paddy plot at NIAES in 1998. A commercial preparation of granule herbicide, Hayate[®] containing 1.5% of pretilachlor (0.6 kg a.i. ha⁻¹), 5% of daimuron, 0.3% of imazosulfuron, and 0.2% of dimethametryn as weight composition was applied on 9 m x 9 m paddy plot on May 13, after 6 days after the rice nursery (var. Nihonbale) transplanting. General procedure for the monitoring experiment is described in detail by Takagi *et al.*, [4]. Physical and chemical properties of the paddy soil (0-1 cm) used for the experiment are listed in Table 3.

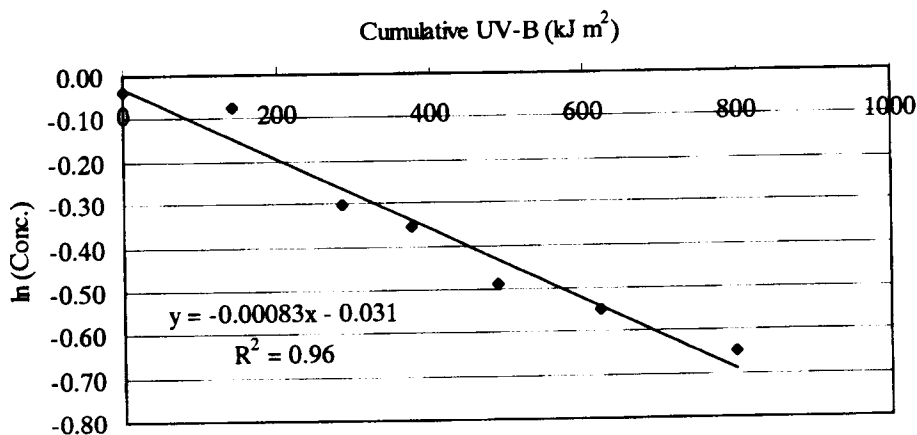


Figure 3. Pretilachlor dissipation due to photochemical degradation in paddy water.

Table 3. Physical and chemical characteristics of the surface paddy soil of experimental field.

Soil texture	pH (H ₂ O)	pH (KCl)	T-C (%)	T-N (%)	C/N ratio	Particle size distribution (%)		
						Sand	Silt	Clay
LiC	5.2	4.1	1.83	0.15	11.9	46.7	19.4	33.9

Paddy water and 1cm thick surface paddy soil were sampled at 1, 3, 7, 14, 21, 28, 35 (water only), 42 and 49 DAHA and their pesticide concentrations were measured by NPD-GC. Detailed description of procedures for sampling and pesticide analysis were also found in Takagi *et al.*, [4] and Fajardo *et al.*, [6].

For environmental variables, methods and measurement devices used for the monitoring are listed in Table 4. All the monitoring data were stored in a data logger (DIK-9420, Daiki Rikakogyo Co. Ltd.) installed in the field for further processing and analysis. The depth of precipitation, percolation and evapotranspiration were obtained as

Table 4. Environmental variables monitored for experimental paddy rice field.

Measured variable	Material and method
Paddy water depth	Water level sensor (LSP-100, UIJIN Co. Ltd, Tokyo). Time averaged data recorded every 10 minutes.
Evapotranspiration	Water level measured daily by hook gauge in lysimeter with four plants.
Percolation (spatial average)	Measured directly on 36 spots in experimental field by constant head-cylindrical permeameter method [13].
Rainfall	Hourly observation at NIAES weather station
Soil Eh (1 cm and 3cm)	Eh meter (D-13 HORIBA Co. Ltd. Tokyo). Time averaged data recorded every 10 minutes.
pH (paddy water, soil 1cm and 3cm)	pH meter (D-13 HORIBA Co. Ltd. Tokyo). Time averaged data recorded every 10 minutes.
Solar radiation above rice canopy	Hourly observation at NIAES weather station
Solar radiation below rice canopy	Solar radiation monitor (PCM-03, PREDE co., ltd. Tokyo). Time averaged data recorded every 10 minutes.
UV-B radiation above rice canopy	UV monitor (MS-210W, EKO instruments trading co., ltd. Tokyo). Time averaged data recorded every 10 minutes.
UV-B radiation below rice canopy	UV monitor (MS-210m, EKO instruments trading co., ltd. Tokyo). Time averaged data recorded every 10 minutes.

explained in Table 4. The depth of irrigation was estimated from the changes of the paddy water level recorded by water level sensor. The depth of the drainage was not measured and it was estimated from the daily water balance equation, Equation (i) in previous paper [1], and the monitoring data. From the result of the water balance calculations and field observation, it was presumed that there was significant amount of edge flow though the 1.5 meter long sheet piles that divide each field block. We assumed that the edge flow does not affect any reactions in surface paddy soil. Therefore in this project, we incorporated the edge flow into offsite drainage. The term *DRAIN* in Equation (i) is then the sum of overflow from the field drainage and edge flow through the sheet piles [1].

Daily data for precipitation, irrigation drainage, percolation, evapotranspiration, paddy water level and change of the paddy water level during 52 days were recorded as input variables for the daily water balance sheet in the Excel file for the model calculation. Also, daily UV-B radiation and cumulative UV-B radiation was calculated from the observed data and the data sheet was prepared in similar manner as the input variables for the calculation of photochemical degradation of the pesticide.

RESULTS AND DISCUSSION

Sensitivity analysis

The magnitude of influence to the model calculations by input parameters may be different depending on the simulating scenarios including the characteristics of the

pesticide and the environmental conditions such as weather, soil and water in the paddy field. Therefore in order to examine model behavior under actual simulation scenario, we also conducted the sensitivity analysis using real parameter values. They were initially set as original input parameter values as in Table 2. Daily water balance and UV-B radiation data during the field monitoring of the experimental rice paddy plot at NIAES in 1998 were used for all cases. Then similar to the sensitivity analysis in the previous paper [1], each value was changed $\pm 10\%$ from the original values. Table 5 lists means of relative difference (MRD) to the original calculated daily pesticide concentrations in paddy water and PSL when each parameter value was changed $\pm 10\%$.

MRD values were similar to the result of sensitivity analysis of previous paper except the biochemical degradation rate constant for soil since the input value was about one third of the value that used in the previous paper. The relative differences (RD) to the original calculated daily pesticide concentrations in paddy water and PSL also varied depending on the days during the simulation. Some RD values for the paddy water increased significantly near desorption phase intercept at 21 days after herbicide application (DAHA). However for the model users who are interested in relatively high pesticide concentrations during the early period, the effect of the model sensitivity to above parameters may not be significant. RD values for pesticide concentrations in paddy water during the first week after the pesticide application were mostly less than 0.1. Those in PSL exceeded 0.1 after 10 DAHA whereas pesticide concentrations in PSL decreased below 1.0 mg kg^{-1} .

Table 5. The results of sensitivity analysis.

Input parameters	Difference to the original point (MRD)				
	+10%PW	+10%SL	-10%PW	-10%SL	Average
App	0.14	0.06	0.13	0.06	0.10
C_{SLB}	0.010	0.010	0.012	0.013	0.01
K_{DISS}	0.008	0.009	0.010	0.011	0.01
K_{DES1}	0.10	0.08	0.12	0.10	0.10
K_{L-A}	0.0009	0.0001	0.0009	0.0001	0.00
K_{PHOTO}	0.0051	0.0012	0.0052	0.0012	0.00
$K_{BIOCHEM-W}$	0.0353	0.0061	0.0382	0.0065	0.02
K_{DES2}	0.03	0.00	0.03	0.00	0.02
$C_{int-DES}$	0.06	0.05	0.06	0.05	0.06
ρ_{b-PSL}	0.09	0.05	0.05	0.05	0.06
$\theta_{sat-PSL}$	0.007	0.009	0.022	0.022	0.01
$K_{BIOCHEM-PSL1}$	0.08	0.03	0.07	0.08	0.07
K_{d-PSL}	0.04	0.05	0.05	0.06	0.05

App: Application rate, C_{SLB} : Solubility of the pesticide, K_{DISS} : Dissolution rate constant, K_{DES1} : 1st phase desorption rate constant, K_{L-A} : Mass transfer coefficient of pesticide volatilization, K_{PHOTO} : Photolysis rate constant (UV-B), $K_{BIOCHEM-W}$: Biochemical degradation rate constant for water, K_{DES2} : 2nd phase desorption rate constant, $C_{int-DES}$: Pesticide concentration in PSL for desorption phase intercept, ρ_{b-PSL} : Soil bulk density in pesticide desorption layer, $\theta_{sat-PSL}$: Saturated volumetric water content in pesticide desorption layer, $K_{BIOCHEM-PSL1}$: Biochemical deg. rate constant for soil, K_{d-PSL} : Equilibrium adsorption coefficient.

Model validation

The PCPF-1 model was validated using the results of the field monitoring for pretilachlor concentrations in the paddy water and 0-1 cm surface paddy soil. Input parameters (Table 2) and daily monitoring data described above were used to simulate the dissipation of pretilachlor in the NIAES experimental paddy field during the monitoring period from May 13 to July 4 in 1998.

The total depth (cm) of precipitation, irrigation, drainage, percolation and evapotranspiration during the monitoring period were 24.6, 50.2, 50.4, 10.4 and 14.8 cm, respectively. Corresponding daily averages were 0.47, 0.97, 0.97, 0.20 and 0.28 cm, respectively. Figure 4 shows daily precipitation, irrigation and paddy water depth during the monitoring period. Irrigation depths ranged about 1 to 2 cm and paddy water depth ranged within 2 to 4 cm reflecting to

the irrigation schedule. However, several large peaks of the water depth are observed following the periodical occurrence of major precipitations. Figure 5 shows daily UV-B radiation on the paddy water below the rice canopy. They ranged about 25 to 10 kJ m⁻² for the first 20 days depending on the weather condition whereas their range decreased to be about 10 to 5 kJ m⁻² towards the end of the monitoring period. After the 20 days, rice leaves started to grow over the UV-B sensor and the UV-B radiation on the paddy water is affected by the growth of the rice plant. Therefore using UV-B radiation below rice canopy is important especially for simulating the fate of pesticide susceptible to the photochemical degradation.

Figure 6 shows observed and simulated pretilachlor concentrations in paddy water and 0-1 cm surface paddy soil during the monitoring period. From the three year study (1995 to 1997) at NIAES experimental paddy field,

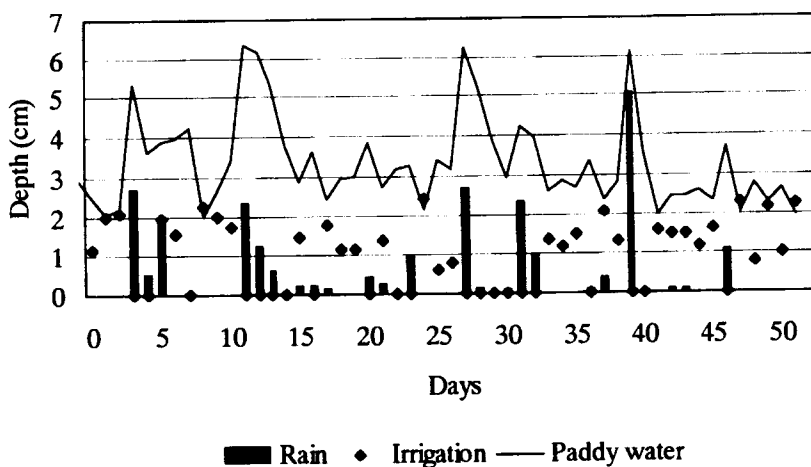


Figure 4. Daily precipitation, irrigation and paddy water depth (cm) during the monitoring.

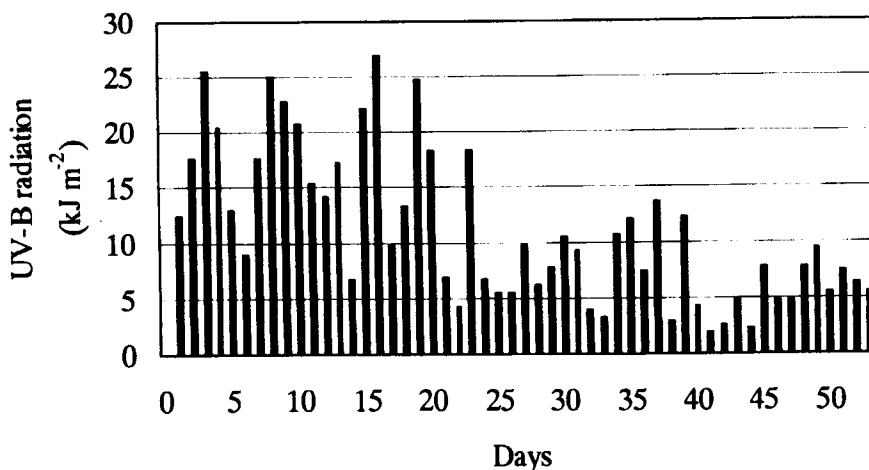


Figure 5. Daily UV-B radiation below rice canopy.

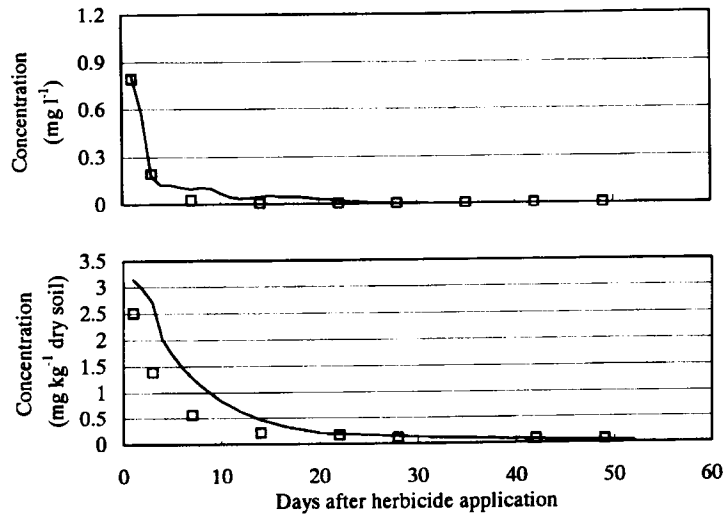


Figure 6. Simulated (—) and observed (□) pretilachlor concentrations in paddy water (above) and in 0-1 cm surface soil (below) during the monitoring period.

pretilachlor half-life obtained using first order kinetic model ranged from about 3.0 to 3.6 days and 6.9 to 9.9 days in the paddy water and 0-1cm surface soil, respectively [5, 6]. Observed pretilachlor dissipation in 1998 exhibited similar behavior. Observed pretilachlor concentrations in paddy water decreased rapidly after the herbicide application. Significant reduction of the pesticide concentration was mainly due to large precipitation occurred on 3rd (2.7 cm) and 5th (1.9 cm) day after the herbicide application (Figure 4). The model simulation of the drastic decline of pretilachlor concentrations in paddy water during the first week was excellent. The time to complete the dissolution of all applied herbicide was calculated to be 11.4 hour, and the observed and simulated pesticide concentrations on the first day were 0.79 and 0.82 mg l⁻¹, respectively. The relative errors of the

simulated pesticide concentrations to the observed values during the first week were 0.03, -0.07, and 2.8, respectively, for 1, 3 and 7 DAHA. The model also successfully predicted the pretilachlor concentration in 0-1 cm surface soil. Pretilachlor concentrations on the first day after the herbicide application were 2.51 and 3.28 mg kg⁻¹, respectively for the observed and predicted concentrations. The relative errors to observed pesticide concentrations during the first week were 0.31, 1.03, and 1.36 respectively for 1, 3 and 7 DAHA.

In order to evaluate the model performance in lower pesticide concentrations in the later part of the monitoring period, Figure 7 was presented as the natural log scale of Figure 6. For the model prediction of pesticide concentrations in paddy water, significant overestimation was occurred during second through fifth week. The largest relative errors

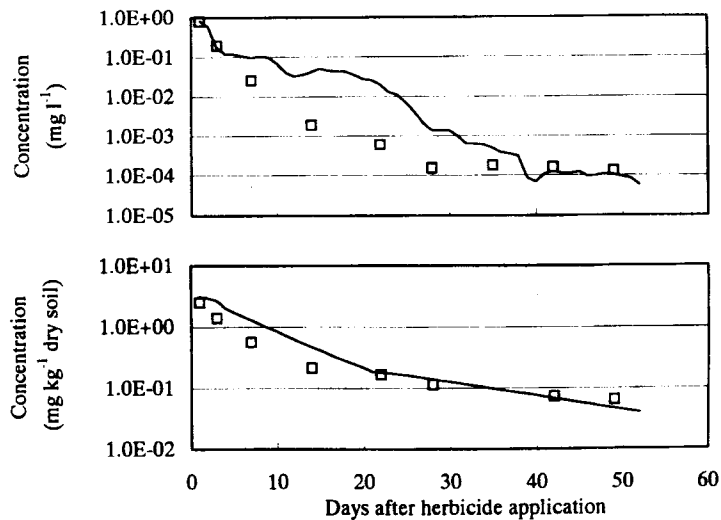


Figure 7. Natural log scale of simulated (—) and observed (□) pretilachlor concentrations in paddy water (above) and in 0-1 cm surface soil (below) during the monitoring period.

to the observation were 33 at 22 DAHA. However, during the last two weeks of simulation period, the model prediction was greatly improved. For the pretilachlor concentration in paddy soil, the predicted concentration decreased linearly during the first three weeks while observed data behaved more or less second order kinetics. After 20 DAHA when the pesticide concentration in PSL becomes below 0.2 mg kg^{-1} , the predicted pesticide concentration decreased following the first order kinetics with smaller rate constant. The model demonstrated the distinct effect of the biphasic first order kinetics for the desorption process and it is obvious that the model prediction for the pesticide concentrations in paddy surface soil were significantly improved after the initiation of second phase desorption. Also, the improvement on the prediction of pesticide concentrations in paddy water during the later period probably resulted from the accurate predictions for the pesticide concentration in paddy soil.

According to the simulation of pretilachlor monitoring experiment in 1998, major dissipation pathway was through the drainage (overflow and edge flow through sheet piles) and about 52% of applied pesticide was lost during the simulation period. Most of the pesticide loss (46% of applied mass) occurred within first 10 days. This phenomenon corresponds to the drastic decline of pesticide concentration during the initial period. Simulation of simetryn and molinate dissipation in paddy field by PADDY model indicated that 41% and 62% of applied mass was lost by runoff, respectively for the case of continuous irrigation-overflow drainage [7]. Pesticide losses through percolation below PSL was 6.4% of applied mass. Although the prediction of pesticide concentrations during mid period of the simulation was over estimated, PCPF-1 prediction had good agreements with observed data of pretilachlor concentrations both in paddy water and surface soil for the first 10 days and last 20 days of simulation. Here, we validated the PCPF-1 with the monitoring data obtained at NIAES experimental paddy rice field in 1998.

Model application and improvement

The sensitivity analysis indicated that some of parameters significantly affect the model calculations and they require accurate determination. Pesticide application rate influences the results with the same magnitude of the error in the input value except for the period near intercept of desorption process. Solubility and dissolution rate constant for the pretilachlor were not influential on the simulation results. However, they may be influential for the case of the pesticides that require longer dissolution time resulting from its slower dissolution rate or larger application rate. Mass transfer coefficient of the pesticide volatilization was the least influential among the parameters for the pretilachlor model simulation. Photochemical degradation of pretilachlor appeared to be the minor dissipation pathway in the paddy field environment. Sunlight photodegradation of metolachlor (acetamide herbicide) was also a relatively slow process [14].

However, the effects of photochemical degradation depend on the characteristics and simulation scenarios. The model did not consider the effect of suspended sediment [15, 16] or chemical and biological constituents in natural water [17]. Therefore it is important to ensure that the methods and photochemical condition for determining the photolysis parameter are applicable to the actual condition of the simulation. Armbrust *et al.*, [18] reported that the model predictions significantly over estimated the bensulfuron methyl and azimsulfuron concentrations in paddy water when indirect photolysis was neglected.

The most influential parameter for the simulation of the pretilachlor was desorption rate constant since the value was the largest among parameters. Pretilachlor desorption process appeared to follow the biphasic first order kinetics and three parameters were required for simulation of the process. The choice of application of the kinetic models is dependent on the characteristics of pesticide and the condition of the paddy field. Srivastava and Gupta, [19] applied the biphasic first order kinetic model to explain the dissipation of tralkoxydim in water-soil system. They attributed the slower dissipation of the pesticide in the second phase to the microbial degradation of gradually released pesticide that initially adsorbed on soil and organic matter. Lafleur *et al.*, [20] also applied the biphasic first order kinetic model to explain the dissipation of triflurain in soil. They concluded that first rapid stage of dissipation is due to free triflurain for ambient attack and the second slow stage is due to the dynamic equilibrium of sorbed/desorbed trifluralin.

The model response may significantly improve upon the application of appropriate model and parameter values. Figure 8 compares model responses for the application of three desorption processes with single phase first order kinetic model, original biphasic desorption parameters as in Table 2 and biphasic first order kinetic model using parameter values calibrated according to the observed pretilachlor concentrations. For the single phase first order desorption process, the desorption rate constant was 0.1142 day^{-1} , which is the same value as the original biphasic desorption rate constant of the first phase. For the calibrated biphasic first order desorption model, values of rate constants for the first and second phase and pesticide concentration at the phase intercept were calibrated in order to increase the fitness of the model calculation to the observed data. The calibrated parameter values of the rate constants for first and second phase and phase intercept pesticide concentration were 0.3 day^{-1} , 0.002 day^{-1} and 0.3 mg kg^{-1} , respectively. For the application of single phase desorption process, the model significantly underestimated the observed pesticide concentrations in paddy soil, and significantly overestimated those in paddy water after 20 DAHA. Compared to the simulation with the biphasic first order model using the original parameter values, greater pesticide desorption rate in the second phase decreased the pesticide concentration in the paddy soil and increased that of the paddy water. For the application using calibrated parameters, the model responded

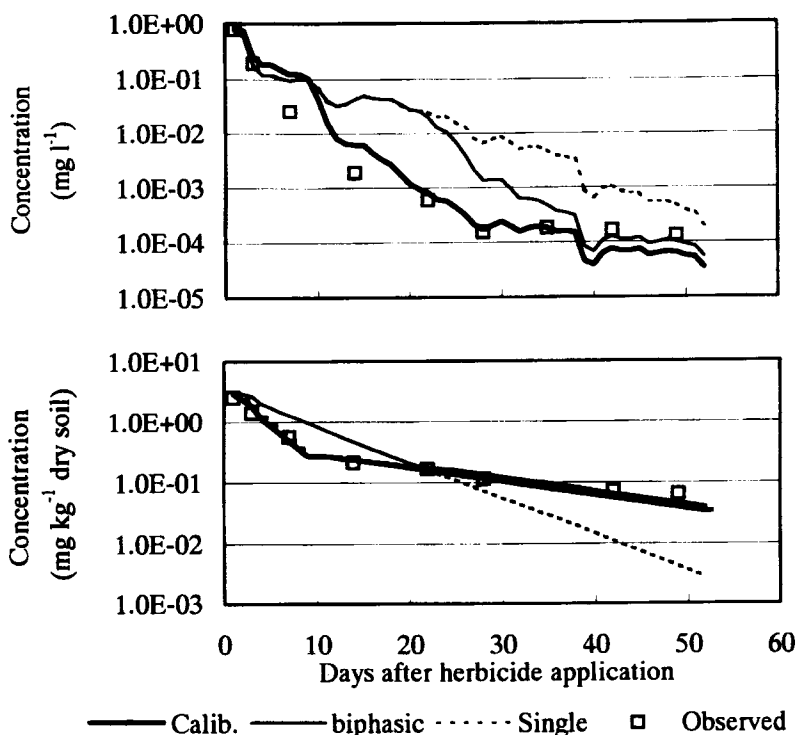


Figure 8. Simulated pretilachlor concentrations using calibrated biphasic desorption parameters, original biphasic desorption parameters, single phase desorption parameters and observed concentrations, for paddy water (above) and in 0-1 cm surface soil (below).

to the greater pesticide desorption during the first phase period by decreasing the pesticide concentration rapidly in the paddy soil compared with the simulation using original parameter values. Since the available pesticide for desorption was less and the pesticide desorption to the paddy water was small at the phase intercept on about 10 DAHA, the pesticide concentrations in paddy water was not increased significantly thereafter relative to other two simulations. Also, the second phase rate constant played an important role in maintaining the good fit to the observed data in paddy water towards the end of the simulation. For example, simulating the second phase with much smaller rate constant significantly decreased the pesticide concentration in paddy water while it did not affect those in paddy soil.

The sum of absolute relative error for the simulation using calibrated biphasic desorption parameters to the observed pesticide concentrations in paddy soil was 1.5 whereas those for the simulation using original biphasic desorption parameters and single phase desorption model were 4.3 and 5.8, respectively. Corresponding values for the observed pesticide concentrations in paddy water were 8.0, 67.0 and 142.5, respectively for the simulations using calibrated values of biphasic desorption parameters, original values of biphasic desorption parameters and single phase

first order desorption model. The above results imply that parameter calibration in order to increase the fitness of the pesticide concentration in paddy soil significantly improves the prediction of pesticide concentration in paddy water. For the prediction of pretilachlor dissipation in paddy field, it can be said that pesticide desorption from paddy soil to paddy water is the key process controlling the rate of the pesticide dissipation. Similar logic may be applied for the biochemical degradation in soil, since the pattern of decline in chemical concentration by biodegradation of persistent compounds shows also initial rapid decline followed by a phase with little or no fall in concentration [21].

Through the application of optimum model and parameter values, PCPF-1 demonstrated that the accurate prediction of pretilachlor concentrations in paddy water and surface paddy soil during entire simulation period is possible. With minor modification, the PCPF-1 can be used for the analytical purpose of more complicated pesticide fate and transport phenomena and also for the investigations such as strategic weed control using dose-response information.

Since the model assumption for paddy water was instantaneous completely mixed reactor, the effect of the diffusion and advective/convective mixing of the dissolved pesticide with irrigation water or rainwater within paddy

field was not considered. Therefore, simulated pesticide concentrations may not reflect those in actual paddy drainage especially for large paddy fields. Also, the model did not account for the edge flow or fast seepage through macropores along the levee and farm structure. For the application of the actual field condition, those edge flows and fast seepage should be included in the water balance and pesticide transport model since the percolation rate on that area exhibits as high as 10 cm day⁻¹ [22]. The improvement shall be necessary for application of the PCPF-1 model for the purpose of the water quality planning. However PCPF-1 can be an appropriate tool for the assessment and extension of the best management practices for controlling the pesticide runoff and leaching from the paddy field. The pesticide concentration during the earlier period after the pesticide application appeared to have the largest influence on the water quality from its runoff and leaching [23, 24] particularly for compounds having higher solubility values [25-27]. Since the model predictions of pesticide concentrations in paddy water and surface soil for that period were reliable, it can be used as a tool for the development and evaluation of surface drainage management and land preparation technique in order to reduce pesticide runoff and leaching from paddy field.

CONCLUSIONS

The PCPF-1 model was validated using the results of

the field monitoring for pretilachlor concentrations in the paddy water and 0-1 cm surface paddy soil. The model successfully simulated the drastic decline of pretilachlor concentrations in paddy water during the first week. For the prediction of pretilachlor dissipation in paddy field, pesticide desorption from paddy soil to paddy water was the key process controlling the rate of the pesticide dissipation. PCPF-1 also demonstrated the accurate prediction of the pretilachlor concentration during the entire simulation period with application of optimum model and parameter values. With minor modification, the PCPF-1 can be used for the analytical purpose of more complicated pesticide fate and transport phenomena. Therefore, PCPF-1 has potential to be a beneficial tool for investigating the pesticide fate and transport processes as well as for controlling pesticide transport from the paddy field that affecting the both surface and ground water.

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