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# Report 263:

# Review and Evaluation of Pesticide Modeling Approaches in Rice Paddies

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## 1 Disclaimers

1) The model evaluation is based on the latest version of the models at the time of this study (RICEWQ v1.73, PCPF v3.01, and PFAM v0.5) available at the time of study. All models, including executable files and/or source codes, were obtained from the model developers. The results of model evaluation in this study may not be appropriate for the updated model versions in the future. For example, the newly released versions of RICEWQ v1.90 (Williams et al., 2011) and PFAM v0.65 (Young, 2011a) have been improved according to the identified modeling issues in this report.
2) In this report, modifications on the RICEWQ source codes and recompilation of the program are for model evaluation only.
3) Standalone PCPF was developed based on the original version in Excel application, and integrated into an integrated modeling platform in this study. The developed codes and applications are for model evaluation only.
4) Two external modules, for paddy water management and multiple pesticide applications, are developed to enable the PCPF applications with available field data. The development and implementation of the two modules did not change the original simulation algorithms and numerical methods in PCPF. The improvement of PCPF is only developed for model evaluation in this study. In addition, the module of multiple applications may not be appropriate for general modeling applications of PCPF, especially with bi-phasic processes simulated.

## 2 Overview

This is part two of a two-part study that reviews and evaluates models for pesticide risk assessment in rice paddies. Part one of the study is a comprehensive review of publically available models for rice pesticide simulations. The review is based on documented theoretical considerations and mathematical implementations of the models and is published as a peer-reviewed book chapter (Luo et al., 2011).

The current report (part two) evaluates the capabilities of three higher-tier models to simulate pesticide fate and distribution in rice paddies: "the Rice Water Quality Model (RICEWQ)", "simulation model for pesticide concentrations in paddy field (PCPF)", and "pesticide in flooded application model (PFAM)". This is one of the first studies on the application of rice pesticide models under California field conditions. It provides information on model selection, data acquisition, parameterization, and application for future studies. Relevant model improvements are suggested for better model performance.

Models are first evaluated by using a simplified paddy scenario in which both degradation and pesticide mass flow into and out of the paddy is disabled. This simplified scenario is designed to examine the modeling capability in simulating pesticide partitioning and mass transfer between the paddy water and sediment. The results indicate that RICEWQ overestimates the pesticide mass in sediment because of an error in calculating diffusion flux. For PCPF, pesticide distribution is highly sensitivity to pesticide dissolution rate constants and the development of the active sediment layer. A second evaluation compares model predictions under the field conditions that represent typical operations in rice production. All models predicted similar results of pesticide masses in water for pesticide applications to flooded paddies, and generally captured the dynamics measured in the field experiments. In sediment, RICEWQ and PFAM generated better results than the PCPF simulations with prescribed percolation and dissolution rate constants. For simulations involving pesticide applications to dry paddies, results indicate that RICEWQ version 1.7.3 underestimates concentrations in water after flooding, while the revised RICEWQ, by correcting the diffusion flux calculation, gives predictions comparable to PFAM.

Model improvements on performance are suggested based on the evaluation results. Major suggestions include

1) RICEWQ: to correct the formulation of pesticide diffusion;
2) PCPF: to improve the algorithm for water-sediment pesticide transfer after the development of the active sediment layer, and include modeling capability for dry-paddy applications;
3) PFAM: to introduce an option for explicit simulation of slow release.

## 3 Introduction

According to Crop Production 2008 Estimates by National Agricultural Statistics Service (USDA, 2008), California is the second largest U.S. rice-growing state with 519 thousand acres for rice production. About 90% of California rice is grown in the Sacramento Valley. Pesticides continue to be a critical and growing component of California rice technology. According to the Pesticide Use Reporting maintained by Department of Pesticide Regulation, statewide use of pesticides in rice fields was 1.9 million kg in 2008 (DPR, 2008). Pesticides regularly used in the Sacramento Valley for rice production include propanil, copper sulfate, and thiobencarb. Pesticide use has a potential to cause aquatic toxicity since flooded rice fields dominate the landscape of the Sacramento Valley and the agricultural drains in the rice-producing regions are tributaries of the Sacramento River. In late 1970s and early 1980s, fish kills were reported in the Colusa Basin agricultural drains receiving rice discharge water contaminated with thiocarbamate herbicides (SWRCB, 1990; Bennett et al., 1998). In 1983 an off taste in the municipal drinking water of the City of Sacramento was attributed to thiobencarb sulfoxide (Cornacchia et al., 1984).

As a result, monitoring program of pesticides from rice discharge water was developed since 1980. In 1990, the Central Valley Regional Water Quality Control Board set performance goals for pesticides used in rice production, as target concentrations not to be exceeded in water both in the agricultural drains and in drinking water sources. To meet the performance goals, Department of Pesticide Regulation instituted a variety of measures, primarily the holding of pesticides on fields or closed water system for sufficient degradation before water release. The compliance with performance goals is mainly verified by monitoring data from sampling sites located on major streams and water treatment plant intakes. Submitted monitoring data are usually associated with low resolutions in both space and time, and thus insufficient to characterize the spatial distribution and the main sources of pesticide residues. Therefore, mathematic models are needed to characterize effects of pesticide use, management practices, and environmental factors on pesticide fate and distribution. In addition, the regulatory program has evolved currently to consider negative impacts of pesticides on aquatic organisms. Detailed information for pesticide residues, such as the magnitude, timing and frequency of peak concentrations, are required to examine the ecosystem exposure by the use of pesticides in rice paddies. While the monitoring data is usually not available for the required information, continuous modeling at field scale could provide reasonable estimates for a decision making process toward meeting regulatory requirements and improving management practices.

Rice pesticide modeling can be utilized to analyze the mechanisms of pesticide fate and transport processes, and evaluate management practices in controlling pesticide discharge from paddy fields. Successful simulation of rice pesticide fate and transport is based on accurate mathematical description of pesticide behaviors in various components and construction of the relational model that would adequately represent the governing processes in the rice field condition. Therefore, mathematic models are required to handle flood-related pesticide simulations such as pesticide volatilization, partitioning, degradation, and discharge. Currently, a number of simulation models for pesticides used in paddy rice production are available (Luo et al., 2011); however, only a few of them have been applied in California rice fields. Rice production in California presents a unique adaptation of rice culture to California's weather, land, and water conditions. Therefore, models developed and calibrated in other regions could not be directly applied to evaluate pesticide fate and transport in rice fields of California. In this study, popular models for rice pesticide simulation will be assessed theoretically and practically for their capability to simulate pesticide fate and distribution under California field conditions. The results of this study are anticipated to provide guidance for model selection and model improvement for their use in pesticide registration processes.

## 4 Objectives

This study is mainly designed to evaluate the capability and limitations of existing models in simulating pesticide fate and transport in rice paddies. Specific objectives include: [1] to review previous studies for pesticide fate processes in rice paddies and their modeling implementations; [2] to collect and format available field monitoring datasets for model evaluation; [3] to compare equations and algorithms of selected models for rice pesticides, and apply them to the field conditions of California rice culture; and [4] to identify model capability and limitations in simulating pesticide dissipation and distribution, and [5] provide recommendations for rice pesticide evaluation for registration purposes in California.

## 5 Methods and materials

### 5.1 Model selection

Three higher-tier rice pesticide models were selected for model evaluation. RICEWQ (Rice Water Quality Model) was developed by Waterborne Environmental Inc. in 1991, the version tested (version of 1.7.3) was released in 2008 (Williams et al., 2008). It's developed and compiled with FORTRAN 95 to run under MS-DOS. A Windows-based GUI is available with built-in scenarios representing predominant rice production practices in California, the Mississippi Delta, and the Gulf Coastal Plain of the United States. The second model is PCPF (Simulation Model for Pesticide Concentrations in Paddy Field), initially developed at the Tokyo University of Agricultural and Technology in 2000 (Watanabe and Takagi, 2000a, b). It is a lumped parameter model that simulates the fate and transport of pesticides in the two compartments of paddy water and paddy soil. Some model improvements have been incorporated into the tested version of 3.01 in 2006 (Watanabe et al., 2006). The model program was coded using Visual Basic for Application in Microsoft Excel. Finally, PFAM (Pesticide in Flooded Agriculture Model) is under development by the USEPA Office of Pesticide Programs (Young, 2011b). It's designed specifically for use in a regulatory setting responding to the data available during a regulatory assessment. The model version 0.50 was evaluated in this study. The mathematics for this model is coded with FORTRAN 95/2003, and also supplied with graphic user interface written in Visual Basic. Further information on these rice pesticide models are available in Luo et al. (2011).

### 5.2 Model evaluation

Two tests, an equilibrium test and a field test, were conducted for model evaluation:

**Equilibrium test** (Section 6). The equilibrium test utilized a simplified scenario for environmental configuration and chemical properties. By disabling advection and degradation processes, the scenario was designed to test the modeling capability in simulating mass transfer between the paddy water and sediment. Pesticide distribution at equilibrium provides a basis for quick evaluations for the model performance of the essential components, including water management (automatic irrigation), general mass balance, mass transfer between the paddy water and sediment, and stability of simulation algorithms.

**Field test** (Section 7). Field measurements for rice pesticides in California were collected from the literature. Environmental conditions (rice paddy dimension, soil properties, weather etc.), management practices, and measured data were retrieved from digital or printed versions of the papers and reports. All data were reorganized into a uniform format, consistent with the general requirements of model data inputs (Luo, 2010).

In the field test, models were evaluated for their capability to simulate pesticide fate and distribution under California field conditions. Model predictions were compared to monitoring data from selected studies that represent typical operations in rice production including irrigation, draining, and water holding times, multiple pesticide applications, and both wet-paddy and dry-paddy pesticide applications. Un-calibrated modeling results were compared with the field measurements of pesticide mass and concentration in the paddy water and sediment.

## 6 Equilibrium test

### 6.1 Scenario development for the equilibrium test

A simplified scenario was designed to test the model performance in establishing pesticide equilibrium between the paddy water and sediment, and associated processes including automatic irrigation, initial pesticide distribution, and water-sediment mass transfer. Different from field conditions, the simplified scenario disabled advection and degradation processes of pesticide in a rice paddy. While pesticide mass losses via advection and degradation do not affect chemical equilibrium, they delay the establishment of equilibrium by generating pesticide concentration differences between the paddy water and sediment. In addition to the common assumptions of rice pesticide models, the following additional assumptions were applied in the equilibrium test.

#### *6.1.1 Environmental characteristics*

A "static environment" was defined to mimic a rice paddy during a water-holding period. The most important assumption in the static environment is that pesticide losses via advective water flows (drainage, overflow, lateral and vertical seepages, and any other spillage) were disabled. Mathematically, the simulated rice paddy is a closed system with a fixed water depth maintained by automatic irrigation (or manually prescribed irrigation and evapotranspiration in PCPF.). Daily precipitation in the weather input file is set as zero to avoid overflow. For PCPF, percolation is allowed during the initial period of simulation for the establishment of the active sediment layer. This process only redistributes pesticide between the paddy water and sediment, without mass loss to the external environment.

In the equilibrium test, environmental characteristics were adapted from the default scenario for *California Rice* presented in the Windows platform of RICEWQ model version 1.7.3 (Williams et al., 2008). Detailed information on the base scenario and parameter adjustments for the simplified scenario are summarized in Table 1. The default scenario is used to represent typical field conditions and management practices in California rice production. Since the equilibrium test was designed to evaluate model predictions for the relative magnitude of pesticide distribution between the paddy water and sediment, the selection of a base scenario would only minimally affect the test results, if at all.

#### *6.1.2 Chemical properties*

The pesticides in the equilibrium test were assumed to be *extremely persistent*. Mathematically, all degradation rate constants, including those for volatilization, hydrolysis, photolysis, biochemical degradation etc., are set to zero. $K_{OC}$ is the main property differentiating the "persistent pesticides" used in the equilibrium test. Typical rice herbicides molinate and thiobencarb were used as test agents, with $K_{OC}$ values of 120 and 1000 L $kg^{-1}$[OC], respectively. Other chemical properties, such as molecular weight and water solubility were retrieved from the FOOTPRINT and USDA pesticide property database (USDA, 2001; FOOTPRINT, 2017) (Table 6).

To simplify the model parameterization, interfacial transport processes between the paddy water and sediment, e.g., pesticide settling, resuspension, direct partitioning, and desorption, are aggregated using an overall water-sediment mass transfer coefficient (MTC). This approach was applied in the development of PFAM (Young, 2011b). More details on the derivation of the MTC are provided in Section 6.3.

In summary, the equilibrium test was based on a static environment and persistent pesticides as defined above. The computational convergence, or a "steady state", of model simulation was assumed to be reached for pesticide masses in the paddy water and sediment at the end of the rice growing season. The assumption was evaluated by calculating the relative changes of moving average of daily predicted pesticides masses. A relative change of less than 0.1% was considered as the evidence for the steady state of pesticide distribution.

Table 1. California Rice Scenario in RICEWQ and parameter adjustments for the equilibrium test

| *Variable* | *Suggested in RICEWQ* | *Adjusted for equilibrium test* |
|---|---|---|
| Operation schedule for rice production | Emergence, 05/16 (JD136)<br>Maturation, 10/01, (JD274)<br>Harvest, 10/08 (JD281) | No change |
| Maximum aerial coverage of crop | 0.8 | No change |
| Water management | Five events (irrigation and drainage), with typical water depth of 10.2 cm | Fixed water depth of 10.2 cm |
| Irrigation rate (cm $day^{-1}$) | 5 | No change |
| Surface area of paddy (ha) | 10 | No change |
| Infiltration rate (cm $day^{-1}$) | 0.2 | 0 (RICEWQ and PFAM)<br>0.1 (PCPF) [1] |
| Depth of active sediment layer (cm) | 5 | 1 [2] |
| Field capacity (cm $cm^{-1}$) | 0.37 | No change |
| Wilting point (cm $cm^{-1}$) | 0.21 | No change |
| Initial soil moisture (cm $cm^{-1}$) | 0.37 | No change |
| Bulk density of bed sediment (kg $L^{-1}$) | 1.43 (particle density of 2.65 indicates a porosity of 0.46) | No change |
| Suspended solid concentration (mg $L^{-1}$) | 20 | 0 [3] |
| Organic carbon for both suspended solids and bed sediment (%) | 1.16 | No change |
| Application data | Applied on 05/06, 1.12 kg $ha^{-1}$ | Assume 100% application efficiency |
| Slow release | Disabled | Disabled (RICEWQ and PFAM)<br>Dissolution rate constant ($day^{-1}$) = 1, 0.1, 0.01, 0.001, and 0.0002 (PCPF) |
| Weather data | Sacramento (W23232) (USEPA, 2007) | Rainfall is set as zero to avoid overflow. |

Notes: JD = Julian day

[1] PCPF requires percolation for the development of the active sediment layer after pesticide application. Percolation rates at field conditions typically range from 0.1 to 0.2 cm $day^{-1}$. For PCPF, a percolation rate of 0.1 cm $day^{-1}$ was assumed for the first 5DDA (days after application). The percolation approximately generate 1.0 cm of the active sediment layer as required by PCPF, based on the sediment porosity of 0.46 (Table 1). Rate of 0.1 cm $day^{-1}$ was selected to represent a clay soil type (MED-Rice, 2003).

[2] RICEWQ and PFAM can be applied with any values of sediment depth, while PCPF is developed based on an active sediment depth of 1 cm (although the PCPF program does accept other values as depth). Therefore, a sediment layer of 1 cm was used for all models just for the convenience of model comparison in the equilibrium test. In the field test, default values, i.e., 5 cm for RICEWQ and PFAM and 1 cm for PCPF, were applied.

[3] PCPF does not simulate pesticide adsorbed in suspended solids (SS). Zero SS concentration was assumed for model comparison in the equilibrium test. In addition, sub-compartments of DOC and biomass, as in the environmental description of PFAM, were not considered in the equilibrium test.

## 6.2 Expected pesticide distribution at equilibrium

The fate and behavior of a pesticide in the equilibrium test could be described as follows. Once applied to the paddy water, the released and dissolved portion of the applied pesticide is distributed into the paddy water and sediment according to the corresponding modeling algorithms. Chemical equilibrium is established by the simulated water-sediment mass transfer processes. Minor fluctuations of water depth may be observed because of the separately simulated processes of water loss (evaporation) and gain (irrigation). This also results in minor variations on pesticide mass, concentration, and diffusion flux in the rice paddy. *Pesticide distribution*, defined as the ratio of pesticide masses in the paddy water and in the sediment at equilibrium, may be derived using the thermodynamic criterion for equilibrium as described using fugacity.

$$\frac{M_w}{Z_w V_w} = \frac{M_d}{Z_d V_d} = \frac{M_{ww}}{Z_{water} V_{ww}} = \frac{M_{wp}}{Z_{particle} V_{wp}} = \frac{M_{dw}}{Z_{water} V_{dw}} = \frac{M_{dp}}{Z_{particle} V_{dp}} = \cdots \tag{1}$$

where $M$ (kg) is the pesticide mass, $Z$ (mol m$^{-3}$ Pa$^{-1}$) is the fugacity capacity, and $V$ (L) is the volume, respectively. Variables and subscripts used in this subsection are summarized in Table 2.

Table 2. Key variables and subscripts for pesticide distributions in rice paddies

| ***Symbol*** | ***Unit*** | ***Description*** |
|---|---|---|
| | | |
| Variables: | | |
| $M$ | kg | Pesticide mass in a (sub-) compartment |
| $Z$ | mol $m^{-3}$ $Pa^{-1}$ | Fugacity capacity of pesticide in a (sub-) compartment |
| $V$ | L | Volume of a (sub-) compartment |
| $C$ | kg $L^{-1}$ | Aqueous concentration of pesticide, $C_{ww}$ and $C_{dw}$ |
| | kg $kg^{-1}$ [particle] | Adsorbed concentration of pesticide, $C_{wp}$ and $C_{dp}$ |
| $v$ | dimensionless | Volume fraction of a sub-compartment in a compartment |
| $H$ | Pa $m^3$ $mol^{-1}$ | Henry's law constant |
| $K_d$ | L $kg^{-1}$ | Adsorption coefficient |
| $\theta$ | dimensionless | Porosity of paddy sediment (= $v_{dw}$) |
| $c_{SS}$ | kg $L^{-1}$ | Concentration of suspended solids (SS) |
| $f_{OC}$ | dimensionless | Organic carbon (OC) content in particles |
| $K_{OC}$ | L $kg^{-1}$[OC] | OC-normalized adsorption coefficient |
| | | |
| Subscripts: | | |
| $w$ | | Water compartment (including pure water, SS, and other sub-compartments such as DOC, biomass, etc.) |
| $ww$ | | Pure water in the water compartment |
| $wp$ | | SS in the water compartment |
| $d$ | | Sediment compartment (including sediment particles, pore water, and other sub-compartments such as DOC, biomass, etc) |
| $dw$ | | Pore water in the sediment compartment |
| $dp$ | | Particles in the sediment compartment |

Note: symbols listed above are used to formulate pesticide distribution between the paddy water and sediment. Different variables and subscripts may be used in the original model documentations.

The fugacity capacity of a compartment is the volume-weighted average of the fugacity capacities of all enclosed sub-compartments. For example, two sub-compartments of pure water (*ww*) and suspended solid (*wp*) are generally considered in the paddy water, and $Z_w$ is expressed as

$$Z_w = v_{ww} Z_{water} + v_{wp} Z_{particle} \tag{2}$$

where $v$ (dimensionless) is the volume fraction of the sub-compartment, and $Z_{water}$ and $Z_{particle}$ (mol $m^{-3}$ $Pa^{-1}$) are the fugacity capacities for pure water and particles, respectively,

$$Z_{water} = \frac{1}{H} \tag{3}$$

$$Z_{particle} = \rho_{particle} K_d Z_{water} \tag{4}$$

where $H$ (Pa m$^3$ mol$^{-1}$) is the Henry's law constant, $K_d$ (L kg$^{-1}$) is the adsorption coefficient, and $\rho_{particle}$ (kg L$^{-1}$[particle]) is the density of particle grains. The volume of SS, which is related to the concentration of SS ($c_{SS}$, kg L$^{-1}$[water]), is negligible relative to the water volume. The fugacity capacity of the water compartment is

$$\begin{aligned} Z_w &= v_{ww} Z_{water} + v_{wp} Z_{particle} \\ &= (1 - v_{wp}) Z_{water} + v_{wp} \rho_{particle} K_d Z_{water} \\ &\cong Z_{water} + c_{SS} K_d Z_{water} \end{aligned} \tag{5}$$

By including SS, the above equations provide general formulation for the fugacity capacity in the water compartment. Similarly, two sub-compartments of pore water and sediment particles are considered for the paddy sediment. The fugacity capacity for the sediment compartment is

$$\begin{aligned} Z_d &= v_{dw} Z_{water} + v_{dp} Z_{particle} \\ &= \theta \cdot Z_{water} + (1 - \theta) \rho_{particle} K_d Z_{water} \\ &= \theta \cdot Z_{water} + \rho_b K_d Z_{water} \end{aligned} \tag{6}$$

with $\rho_b$ (kg L$^{-1}$) for bulk density of the paddy sediment. With the formulations of fugacity capacities in Eqs. (5) and (6), the ratio of $M_w/M_d$ in Eq. (1) is finalized as

$$\frac{M_w}{M_d} = \frac{Z_w V_w}{Z_d V_d} = \frac{d_w (c_{SS} K_d + 1)}{d_d (\rho_b K_d + \theta)} \tag{7}$$

where $d_w$ and $d_d$ (cm) are depths of the paddy water and sediment, respectively. In PFAM, users are allowed to specify different values of OC contents in suspended ($f_{OCwp}$) and sediment particles ($f_{OCdp}$). Eq. (7) can be generalized using $K_{OC}$,

$$\frac{M_w}{M_d} = \frac{Z_w V_w}{Z_d V_d} = \frac{d_w (c_{SS} K_{OC} f_{OCwp} + 1)}{d_d (\rho_b K_{OC} f_{OCdp} + \theta)} \tag{8}$$

The above equations define the predicted pesticide distribution between the paddy water and sediment at chemical equilibrium. Model computational integrity was tested by comparing predicted $M_w$ and $M_d$ at the steady state with above equations. Further investigations were conducted for observed deviations from the expected distribution. Based on the environmental parameters (Table 1) for the equilibrium test and $K_{OC}$ for molinate and thiobencarb, the expected pesticide distribution at chemical equilibrium can be predicted as

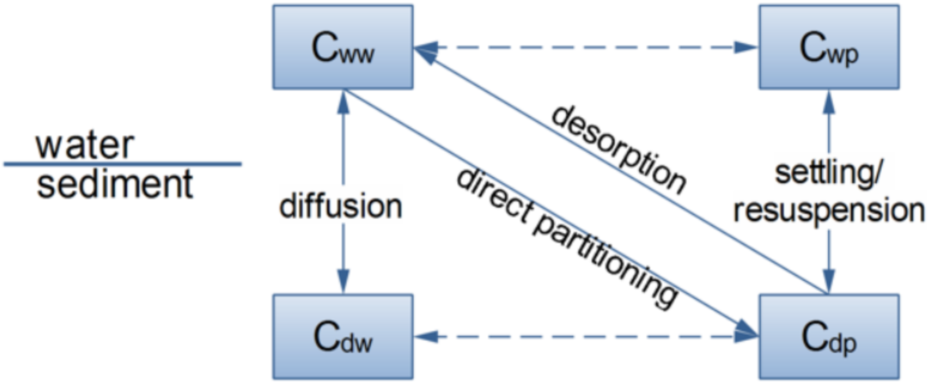
$$\frac{M_w}{M_d} = \frac{10.2 \times (0 \times K_{OC} + 1)}{1.0 \times (1.43 \times 1.16\% \times K_{OC} + 0.46)} = \frac{614.9}{K_{OC} + 27.7} \tag{9}$$

For molinate ($K_{OC} = 120$), $M_w/M_d = 4.163$

For thiobencarb ($K_{OC} = 1000$), $M_w/M_d = 0.598$

### 6.3 Overall mass transfer coefficient between water and sediment

Interfacial transport processes between water and sediment (Figure 1) are governing transfer mechanisms for pesticide fate and distribution in a rice paddy. However, the associated mass transfer coefficients (MTCs) for the individual processes, such as mixing (diffusion) velocity, settling velocity, resuspension velocity, and mixing depth for direct partitioning, are generally not provided in registration submissions. To simplify model parameterization and generate comparable model inputs and outputs, the concept of *overall water-sediment transfer* was adopted in this study. The overall MTC is an integrated measure of all pesticide transfer mechanisms between the paddy water and sediment. The documentation of PFAM indicated that "*it is unnecessary to explicitly model the individual exchange mechanisms since all phases of pesticide within a compartment are at equilibrium and therefore the concentration of pesticide in any given form (aqueous or sorbed) dictates the concentration of the other forms of the pesticide*" (Young, 2011b).



| | ***RICEWQ*** | ***PCPF*** | ***PFAM*** |
|---|---|---|---|
| Simulated processes | Diffusion<br>Settling<br>Resuspension<br>Direct partitioning | Desorption | Overall water-sediment transfer |

Notes:

1) In addition to the interfacial transport processes, percolation is also simulated by all models as an advective process transferring pesticide from the paddy sediment to water.
2) The process of "direct partitioning" is used in RICEWQ to allow chemical adsorption to paddy sediment from direct contact of the water column with sediment (Williams et al., 2008).

Figure 1. Simulated interfacial transport processes between the paddy water and sediment

Development of the overall MTC was started with the general formulation of water-sediment transfer flux. In RICEWQ and PFAM, the flux is proportional to the aqueous concentration difference between water and sediment,

$$F_{dw} = -\omega(C_{ww} - C_{dw}) \tag{10}$$

where $F_{dw}$ (kg s$^{-1}$) is the mass flux with positive direction from sediment to water, $\omega$ (m$^3$ s$^{-1}$) is the 1st order water-to-sediment MTC, and $C_{ww}$ and $C_{dw}$ (kg m$^{-3}$) are the aqueous concentrations in water and in sediment, respectively. The parameter $\omega$ could be formulated as an overall coefficient that includes all means of pesticide exchange between the paddy water and sediment.

The effective mass flux from sediment to water ($F_{dw}$) is the difference between mass flux from sediment to water and that from water to sediment:

$$F_{dw} = \vec{F}_{dw} - \vec{F}_{wd} = M_d\vec{K}_{dw} - M_w\vec{K}_{wd} \tag{11}$$

where $K_{ij}$ (s$^{-1}$) is transfer rate constant from $i$ to $j$. By considering typical interfacial transport processes of diffusion, settling, and resuspension, the $K_{ij}$ can be expressed as (Luo et al., 2007):

$$\begin{aligned} \vec{K}_{dw} &= \frac{D_{Dwd} + A\,v_{dp}u_{resus}Z_{particle}}{Z_d V_d} \\ \vec{K}_{wd} &= \frac{D_{Dwd} + A\,v_{wp}u_{settl}Z_{particle}}{Z_w V_w} \end{aligned} \tag{12}$$

where $u_{resus}$ and $u_{settl}$ (m s$^{-1}$) are velocities of particle resuspension and settling, respectively, $D_{Dwd}$ (kg Pa$^{-1}$ s$^{-1}$) is Mackay-type D value for water-sediment diffusion (Mackay, 2001). By putting Eq. (12) in to (11), the final equation for $F_{dw}$ is:

$$\begin{aligned}
F_{dw} &= \frac{M_d}{Z_d V_d}(D_{Dwd} + A v_{dp} u_{resus} Z_{particle}) - \frac{M_w}{Z_w V_w}(D_{Dwd} + A v_{wp} u_{settl} Z_{particle}) \\
&= \frac{M_{dw}}{Z_{water} V_{dw}}(D_{Dwd} + A v_{dp} u_{resus} Z_{particle}) - \frac{M_{ww}}{Z_{water} V_{ww}}(D_{Dwd} + A v_{wp} u_{settl} Z_{particle}) \\
&= \frac{C_{dw}}{Z_{water}}(D_{Dwd} + A v_{dp} u_{resus} Z_{particle}) - \frac{C_{ww}}{Z_{water}}(D_{Dwd} + A v_{wp} u_{settl} Z_{particle}) \\
&= \frac{D_{Dwd}}{Z_{water}}(C_{dw} - C_{ww}) + \frac{A Z_{particle}}{Z_{water}}(C_{dw} v_{dp} u_{resus} - C_{ww} v_{wp} u_{settl}) \\
&= \frac{D_{Dwd}}{Z_{water}}(C_{dw} - C_{ww}) + A K_d \rho_{particle}(C_{dw} v_{dp} u_{resus} - C_{ww} v_{wp} u_{settl}) \\
&= \frac{D_{Dwd}}{Z_{water}}(C_{dw} - C_{ww}) + A K_d (C_{dw} \rho_b u_{resus} - C_{ww} c_{SS} u_{settl})
\end{aligned} \tag{13}$$

In the water quality modeling for ponds and lakes, it's common to assume that $\rho_b u_{resus} = c_{SS} u_{settl}$, so that there is a dynamic equilibrium between the mass of suspended solid and that of bed sediment.

$$F_{dw} = (\frac{D_{Dwd}}{Z_{water}} + A K_d \rho_b u_{resus})(C_{dw} - C_{ww}) \tag{14}$$

Compared to Eq. (10), $\omega$ can be written as:

$$\omega = \frac{D_{Dwd}}{Z_{water}} + A K_d \rho_b u_{resus} \tag{15}$$

The D value of the interfacial diffusion was formulated based on the two-film theory as a function of contact area, boundary layer depths ($\delta$, m), fugacity capacities, and chemical diffusivities ($D_t$, m$^2$ s$^{-1}$) (Luo et al., 2007):

$$D_{Dwd} = A\theta(\frac{\delta_{dw\_d}}{Z_d D_{td}} + \frac{\delta_{dw\_w}}{Z_w D_{tw}})^{-1} \tag{16}$$

Therefore, Eq. (15) is rewritten as:

$$\omega = A\theta(\frac{\delta_{dw\_d}}{Z_d D_{td}} + \frac{\delta_{dw\_w}}{Z_w D_{tw}})^{-1} Z_{water}^{-1} + A K_d \rho_b u_{resus} \tag{17}$$

It's assumed that the mass transfer velocities for diffusion, resuspension, and settling are in the same order of magnitudes. The above equation can be simplified as:

$$\omega = k_{xfer} A(\theta + \rho_b K_d) \tag{18}$$

with $k_{xfer}$ (m $s^{-1}$) for the empirical coefficient of overall water-sediment mass transfer. In addition to particles, other adsorbing media (e.g., biomass, DOC) can be also considered in the sediment, and a general formulation of $\omega$ is given by:

$$\omega = k_{xfer} A[\theta + \frac{\sum(m_d K_d / 1000)}{V_d}] \tag{19}$$

where $\Sigma(m_d K_d/1000)$ ($m^3$) is the sum of the products of mass and associated partitioning coefficient for each adsorbing medium in the sediment. The formulation of $\omega$ is identical to those derived by others (USEPA, 2004; Young, 2011b). It's noteworthy that the term $m_d$ is for the mass of adsorbing medium (particle, DOC, biomass) in the sediment, not for the mass of pesticide. For example, $m_{dp}$ (kg) is for the mass of sediment particles, not the mass of pesticide adsorbed in sediment particles ($M_{dp}$). The parameter $k_{xfer}$ is on the order of $10^{-8}$ m $s^{-1}$ for lakes, ponds, and other standing water bodies (Vanderborght and Wollast, 1977; Shwarzenbach et al., 1993; Mackay et al., 2006; Young, 2011b), and set as $1\times10^{-8}$ m $s^{-1}$ for model initialization in this study.

Compared with the equation for diffusion flux in RICEWQ, Eq. (18) in page 6 of the RICEWQ user's manual, the overall water-sediment MTC for RICEWQ ($K_{difus}$, m $day^{-1}$) is formulated as

$$K_{difus} = \frac{\omega}{A} \cdot 86400 = k_{xfer}(\theta + \rho_b K_d) \cdot 86400 \tag{20}$$

As discussed before, $K_{difus}$ from the above formulation covers all means of pesticide exchange between the paddy water and sediment. Therefore, other MTCs for other water-sediment transfer processes in RICEWQ, i.e., settling velocity ($K_{setl}$) and mixing depth to allow direct partitioning to bed ($K_{bed}$) should be set to zero.

In PCPF, the process of pesticide desorption (DES) from the paddy sediment to water is assumed to occur following the first order rate law,

$$\left.\frac{dC_{dp}}{dt}\right|_{DES} = -k_{DES} C_{dp} = -k_{DES} K_d C_{dw} \tag{21}$$

with $k_{DES}$ ($day^{-1}$) as the rate constant for the pesticide desorption. Compared to the interfacial process formulated in Eq. (10), the PCPF algorithm implies that desorption process is not affected by the pesticide concentration in water. For model comparison, it's assumed that the overall MTC derived previously could be applied for estimating the desorption flux in PCPF,

$$\begin{aligned} k_{DES} K_d &= \omega \cdot 86400 \\ k_{DES} &= k_{xfer} \frac{(\theta + \rho_b K_d)}{K_d} \cdot 86400 \end{aligned} \tag{22}$$

## 6.4 Results of the equilibrium test

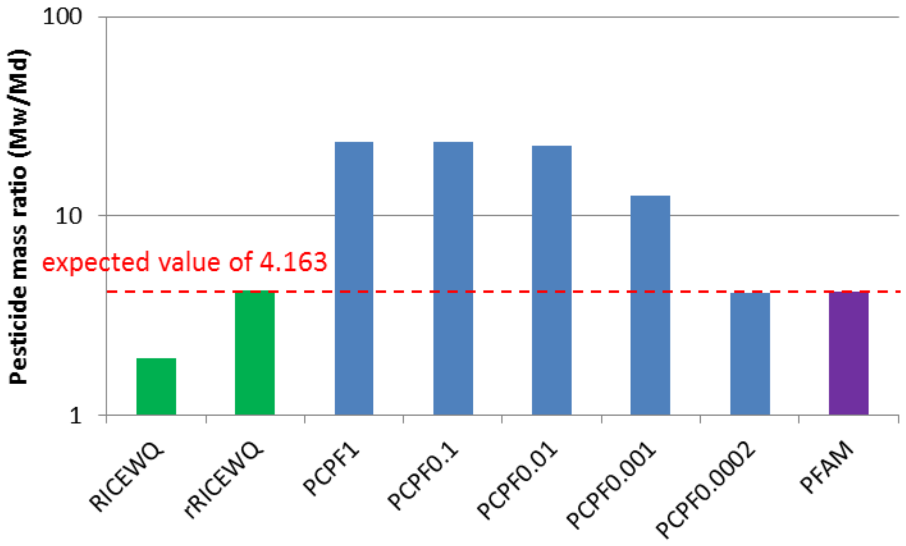


Figure 2. Equilibrium test results (data and illustration) for “persistent molinate”

Table 3. Data for Figure 2

| ***Model*** | $k_{dissolution}$ ($d^{-1}$) | $M_w$ | $M_d$ | ***Modeled*** $M_w/M_d$ | ***Expected*** $M_w/M_d$***, Eq. (7)*** |
|---|---|---|---|---|---|
| RICEWQ | - | 7.390 | 3.810 | 1.940 | 4.163 |
| Revised RICEWQ | - | 9.050 | 2.150 | 4.209 | 4.163 |
| PCPF | 1 | 11.807 | 0.502 | 23.520 | 4.163 |
| PCPF | 0.1 | 10.529 | 0.448 | 23.502 | 4.163 |
| PCPF | 0.01 | 11.293 | 0.504 | 22.407 | 4.163 |
| PCPF | 0.001 | 9.989 | 0.789 | 12.660 | 4.163 |
| PCPF | 0.0002 | 8.939 | 2.184 | 4.093 | 4.163 |
| PFAM | - | 9.010 | 2.164 | 4.164 | 4.163 |

Note: development and results of revised RICEWQ will be discussed in Section 7.1.

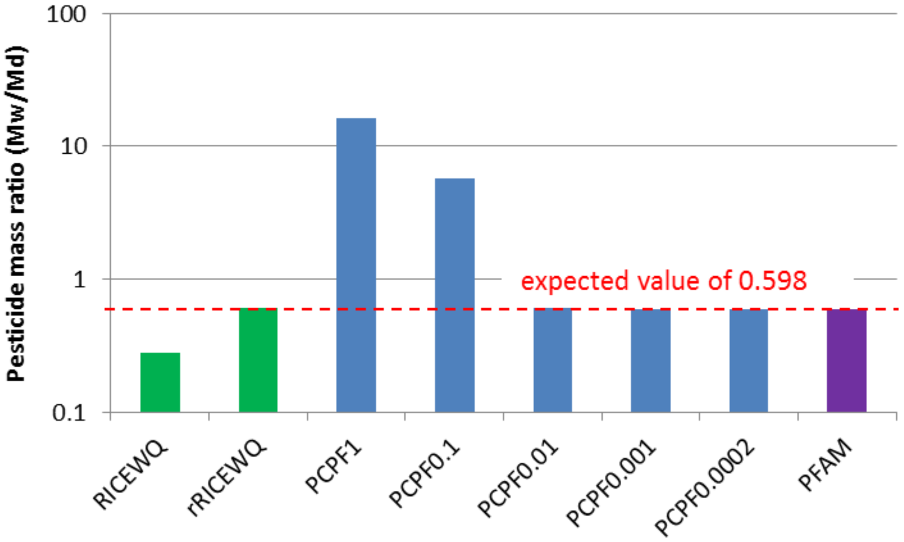


Figure 3. Equilibrium test results (data and illustration) for “persistent thiobencarb”

Table 4. Data for Figure 3

| ***Model*** | $k_{dissolution}$ ($d^{-1}$) | ***$M_w$*** | ***$M_d$*** | ***Modeled $M_w/M_d$*** | ***Expected $M_w/M_d$, Eq. (7)*** |
|---|---|---|---|---|---|
| RICEWQ | - | 2.450 | 8.750 | 0.280 | 0.598 |
| Revised RICEWQ | - | 4.230 | 6.970 | 0.607 | 0.598 |
| PCPF | 1 | 10.439 | 0.648 | 16.101 | 0.598 |
| PCPF | 0.1 | 9.326 | 1.613 | 5.781 | 0.598 |
| PCPF | 0.01 | 5.905 | 5.015 | 1.177 | 0.598 |
| PCPF | 0.001 | 4.174 | 7.015 | 0.595 | 0.598 |
| PCPF | 0.0002 | 4.189 | 7.010 | 0.598 | 0.598 |
| PFAM | - | 4.186 | 6.988 | 0.599 | 0.598 |

Note: development and results of revised RICEWQ will be discussed in Section 7.1.

## 6.5 Discussion on equilibrium test results

### *6.5.1 General description*

*RICEWQ overestimates pesticide mass in the paddy sediment*. Results of the equilibrium test showed that the ratio of modeled $M_w/M_d$ and expected $M_w/M_d$ is approximately equal to the porosity of 0.46 (Figure 2 and Figure 3). Since water-sediment mass transfer is the only process in determining the pesticide distribution, further investigation should focus on the code segment of diffusion calculation and porosity-associated variables in the model.

For the PCPF results in the equilibrium test, pesticide distribution was dependent on the values of dissolution rate constant and percolation rate. Generally, expected chemical equilibrium could be approached with slow dissolution rate constant. In this case, majority of the applied pesticide would be released after the accumulation of the PSL. Otherwise*, PCPF overestimates pesticide mass in the paddy water*.

PFAM generates pesticide distribution comparable to the expected values under the equilibrium test.

### *6.5.2 Pesticide diffusion in RICEWQ*

According to the RICEWQ manual, diffusion is a function of concentration difference between the water column and bed sediments (Williams et al., 2008),

$$M_{diffus} = K_{diffus} \times SA \times (F_{DS}C_d - F_{DW}C_w) \tag{23}$$

where $M_{diffus}$ (mg day$^{-1}$) is the mass of diffusion, $K_{diffus}$ (m day$^{-1}$) is the rate of diffusion, $SA$ (m$^2$) is the paddy surface area, $C_d$ (mg m$^{-3}$) is the total pesticide concentration in sediment, $F_{DS}$ (dimensionless) is the fraction of total sediment pesticide in dissolved form, $C_w$ (mg m$^{-3}$) is the concentration of pesticide in the paddy water, $F_{DW}$ (dimensionless) is the fraction of total water-column pesticide in dissolved form. It's expected that Eq. (23) is equivalent to the general formulation of diffusion flux in Eq. (10). According to the source codes (line 964), $C_d$ (or "CPS" in the source code) is derived as

FORTRAN code: CPS(J1)=PS(J1)/(DS*SA) (24)

where PS (mg) is total pesticide in sediment. The above equation can be expressed in algebra formulas,

$$\begin{aligned} C_d &= \frac{M_{dw} + M_{dp}}{d_d \times SA} \\ &= C_{dw}\theta + C_{dp}\rho_b \end{aligned} \tag{25}$$

Chemical equilibrium is assumed between the pore water and sediment particles ($C_{dp} = K_dC_{dw}$),

$$C_d = C_{dw}(\theta + K_d\rho_b) \tag{26}$$

$F_{DS}$ is defined as (Williams et al., 2008),

$$F_{DS} = \frac{\theta}{\theta + K_d\rho_b} \tag{27}$$

Substituting $C_d$ and $F_{DS}$ into Eq. (23),

$$M_{diffus} = K_{diffus} \times SA \times (\theta \cdot C_{dw} - C_{ww}) \tag{28}$$

Compared to the expected formulation in Eq. (10), *porosity is incorrectly included in calculating diffusion flux*. With above diffusion equation in RICEWQ, the chemical equilibrium will be established with $\theta C_{dw} = C_{ww}$. Since porosity is between (0, 1), this error in diffusion formulation will overestimate the pesticide concentration and mass in the sediment. The diffusion equation was taken directly from the Simulator for Water Resources in Rural Basins – Water Quality (SWRRBWQ) (Arnold et al., 1991), and the same issue may exist in other water quality models that share the algorithm.

The effect of including porosity in the calculating diffusion flux could be quantified by comparing with the theoretical mass ratio at equilibrium in Eq. (7),

$$\left.\frac{M_w}{M_d}\right|_{\text{RICEWQ}} = \frac{C_{ww} d_w (c_{SS} K_d + 1)}{C_{dw} d_d (\rho_b K_d + \theta)} = \frac{C_{ww}}{C_{dw}} \cdot \left.\frac{M_w}{M_d}\right|_{@\,equilibirum} = \theta \cdot \left.\frac{M_w}{M_d}\right|_{\text{expected}} \tag{29}$$

### *6.5.3 Initial distribution of pesticides in PCPF*

PCPF may overestimate pesticide mass in the water compartment, and the predicted pesticide distribution will approach the expected pattern with smaller dissolution rate constant (Figure 2 and Figure 3). This issue is related to the following facts in the model development:

1) Adsorption, which is the main process in PCPF for pesticide transport to the sediment, only occurs during the pesticide dissolution;
2) The paddy sediment layer (PSL) is also accumulated, by percolation flux, during the early period of simulation. Therefore, the pesticide dissolution rate constant and percolation rate are governing parameters in determining the distribution pattern of applied pesticides;
3) Diffusion process is not simulated in PCPF.

In addition to those reported in Figure 2 and Figure 3, various combinations of dissolution rate constants and percolation rates are applied in the equilibrium test of PCPF. Based on the test results, the following comments and suggestions for PCPF model application are derived.

1) The dissolution rate constant and percolation rate (especially that during the development of PSL) should be carefully investigated before and during the applications of PCPF. The dissolution rate constant has significant effects on the model capability in capturing the peak concentrations in the water column.
2) In PCPF, the percolation rate is associated with both pesticide distribution (mass transfer from the water to sediment) and dissipation (mass loss to the subsurface soil). This may bring difficulties in the model calibration and application. The inclusion of a diffusion process is suggested for the further improvement of PCPF, so that pesticide distribution could be simulated based on the concentration differences between the paddy water and sediment.
3) Mass balance calculations in PCPF are associated with <1% errors due to the numerical analysis in solving the differential equations. It's noteworthy that such error is not observed in PFAM, which is based on analytical solutions of differential equations, or in RICEWQ, where in-series calculations are applied.

4) Further investigation on PCPF indicated that, unrealistic high values of the dissolution rate constant (e.g., 100 $d^{-1}$) may cause unstable numerical analysis on the differential equations in PCPF, and generate negative concentrations. PCPF won't report this problem, but simply replaces the negative results with zeros (*source codes, line 348*). The replacement results in significant underestimation of pesticide mass in the paddy water, which is also the signal for a too-high value of the dissolution rate constant. A maximum value of dissolution rate constant may be set to warn model users when feeding input parameters.

PCPF differs markedly from RICEWQ and PFAM in the modeling approach for pesticide transfer dynamics between sediment and water. PCPF considers pesticide fate and distribution in two environmental compartments: [1] the paddy water; and [2] the paddy sediment layer (PSL). The depth of water column is determined by influent and effluent water fluxes. For sediment, the initial depth of the paddy sediment ($d_d$) is zero and it keeps "growing" after pesticide application by percolation fluxes until establishing the maximum depth ($d_{PSL}$) of 1 cm. This is similar to the environmental settings in the adsorption/dilution model (Johnson, 1991). This is also the reason why PCPF requires a non-zero percolation rate at least for the early period of simulation. The actual $d_d$ in the simulation is set as the minimal value between accumulative percolation and $d_{PSL}$ depth (Figure 4),

$$d_d(t) = \min(\int \frac{PERC}{\theta} \cdot t, d_{PSL}) \tag{30}$$

where PERC (cm $hr^{-1}$) is the percolation rate (the rate is provided in the unit of cm $day^{-1}$, and converted into hourly value by PCPF).

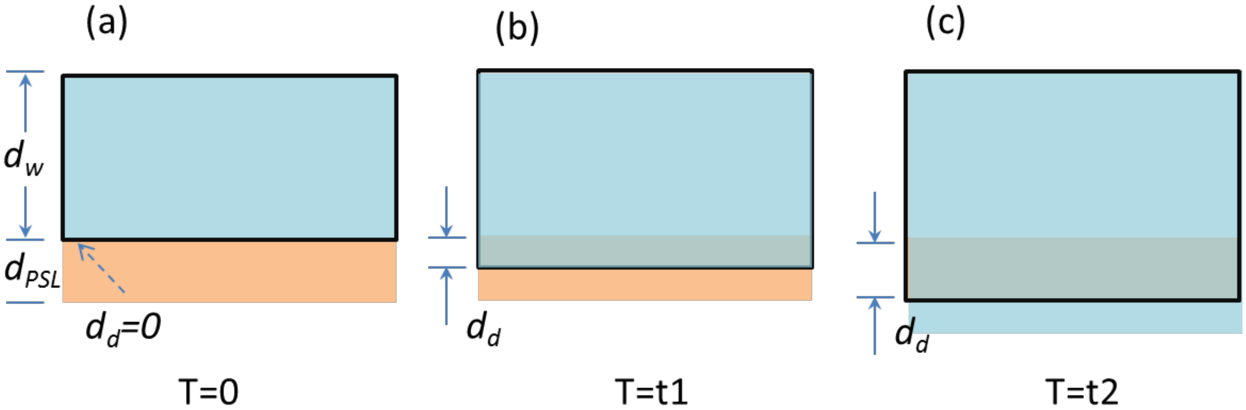


Figure 4. Development of the "paddy soil layer" ($d_d$) in PCPF.

Notes: The solid black box defines the simulation domain, while the contaminated area is colored in blue. At the beginning of PCPF simulations, penetration depth in the sediment is zero (a). The depth is "growing" with percolation flux (b), and the dissolved pesticides during a stimulation time step will be distributed between the paddy water and penetrated PSL by assuming chemical equilibrium between the two compartments. The penetration depth has a maximum value ($d_{PSL}$) of 1.0 cm as suggested by the model developer (PCPF program has the option for user-defined $d_{PSL}$). Once $d_{PSL}$ is reached, further percolation will result in net loss of pesticide out of the simulation domain by leaching to the lower soil layers (c). In the equilibrium test, therefore, percolation is disabled once the $d_{PSL}$ is reached to minimize this loss (Table 1).

Unlike other models, PCPF does not simulate pesticide diffusion. Mass transfers between the water and sediment are simulated by initial distribution (adsorption) and two unidirectional processes of percolation (from bulk water to pore water) and desorption (from sediment particle to bulk water). Adsorption of applied pesticide on PSL occurs only during the pesticide dissolution period. At each time step of that period, PCPF calculates the amount of pesticide dissolved into the paddy, and distributes it into water and sediment compartments according to the adsorption coefficient. Since the PSL is zero at the beginning of simulation and gradually developed by percolation flux, this algorithm would generally overestimate pesticide mass in the paddy water.

The dissolution rate constant is the governing factor on the initial distribution of pesticide in PCPF. For pesticides with a large dissolution rate constant, dissolution processes may be completed within the first several hours after application while the PSL depth is still very small. In this case, the majority of the released pesticide will be distributed into the paddy water. With small dissolution rate, a significant portion of the applied pesticide may still be available for adsorption after the PSL has been fully developed. Therefore, a small dissolution rate constant in PCPF may generate similar results of pesticide distribution as expected in Eq. (7).

Percolation rate during the dissolution period significantly affects the pesticide distribution in the following two processes: [1] the percolation rate directly relates to the development of PSL, Eq. (30); and [2] the percolation flux transports dissolved pesticides from the paddy water to sediment. As discussed previously, PCPF tends to overestimate pesticide mass in the paddy water. Percolation processes may help smooth the concentration differences between the water and sediment. However, percolation rate is usually small in rice paddies and removes a relatively small amount of pesticide from the water into the sediment (Takagi et al., 2011).

# 7 Field test

## 7.1 Developments of computer tools for model evaluation in field conditions

### *7.1.1 Modification of RICEWQ*

The modification of RICEWQ focused on the correction of the diffusion calculation. As discussed previously, RICEWQ incorrectly formulates the concentration differences between bulk water and pore water by calculating dissolved concentration in sediment using the total sediment volume as opposed to pore-water volume. The source code was revised accordingly and recompiled using Lahey-Fujitsu FORTRAN Compiler version 7.2. The newly developed program is referred as “revised RICEWQ” hereinafter.

The revised RICEWQ was also applied in the equilibrium test, and generated comparable results to the expected pesticide distribution (Figure 2 and Figure 3).

### *7.1.2 Standalone version of PCPF*

PCPF is originally developed in Visual Basic Application (VBA), and model simulations are performed within the Excel application. A standalone PCPF was developed by rewriting the source codes in Visual Basic (VB) in Microsoft Visual Studio 2010. The similarity in syntax and data structure between VBA and VB minimizes the incompatibility in the code migration.

### *7.1.3 Development of external modules for PCPF*

No changes were made in the PCPF core simulations, but two programs were developed as external modules to enable the application of PCPF in the field conditions.

Module #1: water management

In addition to daily weather data, PCPF requires daily water fluxes (irrigation, drainage, evapotranspiration, lateral seepage, percolation) and water depths, which are usually not reported in the field experiments. Therefore, a module was developed to simulate water balance and generate daily input data for PCPF, based on the similar approaches used in RICEWQ and PFAM. The main function was automatic irrigation with prescribed water depths and irrigation rates. Automatic irrigation is triggered when water depth is lower than the minimal depth, and the paddy is irrigated at the given rate until reaching the target water depth.

Module #2: multiple pesticide applications (for the same active ingredient)

PCPF is originally designed to allow only a single pesticide application. The module for multiple applications was developed as a post-processor: PCPF is run independently for each application and the simulation results (pesticide masses and concentrations) are saved as daily time series. Vector summation of the results from all individual applications is considered as the results of multiple applications. A known issue is that the PSL needs to be developed following each pesticide application.

### *7.1.4 Graphic user interface for rice pesticide models*

A graphic user interface (GUI) was developed as an integrated modeling platform to facilitate model comparison and application in field conditions. The GUI was implemented in Microsoft Visual Studio 2010 with the following functions,

1. To standardize input and output data for individual models.
2. To integrate rice pesticide models,
    2.1. For models with standalone programs (RICEWQ and PFAM), the GUI acts as a pre-processor to prepare input files according to the data acquisition and format; and a post-processor to read and save model outputs in a standard format.
    2.2. Models without standalone programs, such as PCPF in Excel or simple rice models with only equations, are programmed in Visual Basic by converting the original codes or implementing the equations, and integrated into the GUI.

## 7.2 Simulation design for the field test

RICEWQ (both the original and the revised version), PCPF, and PFAM are applied to field conditions in Colusa and Glenn counties of California. Detailed descriptions of the experiments are provided in the protocol of this study (Luo, 2010). Three case studies are selected in the field test to represent typical operations for rice production, including irrigation, drain, water holding, multiple pesticide application, wet-paddy application, and dry-paddy application (Table 5).

Table 5. Summary of field conditions for the field test

| | ***Case study #1*** | ***Case study #2*** | ***Case study #3*** |
|---|---|---|---|
| Reference | (Ross and Sava, 1986) | (Ross and Sava, 1986) | (Nicosia et al., 1991) |
| Pesticide | thiobencarb | molinate | carbofuran |
| Field size (ha) | 37 | 41 | 24 |
| Seeding date | 5/21/1983 (JD141) | 5/27/1983 (JD147) | 4/27/1988 (JD118) |
| Application dates and rates | 5/30/1983 (JD150): 4.48 kg $ha^{-1}$ | [1] 6/1/1983 (JD152): 4.48 kg $ha^{-1}$<br>[2] 6/6/1983 (JD157): 3.14 kg $ha^{-1}$ | 4/16/1988 (JD107): 0.233 kg $ha^{-1}$ |
| Water management | [1] before 6/7/1983: water depth 21-31 mm<br>[2] 6/7/1983 (8DDA): water depth 11-23 mm | [1] before 6/21/1983: water depth 12-24 mm<br>[2] 6/21/1983 (15DDA): drained completely<br>[3] 6/24/1983 (18DDA): water depth 4-16 mm | [1] 4/16/1988 (0DDA): dry paddy<br>[2] 4/26/1988 (10DDA): water depth 11 mm |
| Other data | | | Background concentration in soil: 0.02 mg $kg^{-1}$ |

Notes: JD = Julian day; DAA = days after (*the most recent*) application

Reported data in field experiments covered *management operations of crop, water, and pesticides*. In specific, the data included paddy location, dimension, water depth (irrigation, drainage, and water-holding operations), seeding date, pesticide application dates and rates. S*oil properties* were also partially available from the publications. Unreported soil properties were retrieved from the Soil Survey Geographic (SSURGO) database (USDA, 2011) according to the paddy locations. *Weather data* was retrieved from the nearest stations in USEPA meteorological data to support exposure modeling (USEPA, 2007). *Pesticide properties* were mainly taken from the FOOTPRINT and USDA pesticide property databases (USDA, 2001; FOOTPRINT, 2017) (Table 6). Water-sediment mass transfer was formulated with the *overall MTC* derived previously in this study (Section 6.3 for details). PFAM has a built-in function for *volatilization coefficient* from temperature, molecular weight, vapor pressure, and solubility. The same function was used, based on average temperature, to estimate volatilization coefficients for RICEWQ and PCPF. Actual daily water depths were not reported in the literature, but only summarized as mean water depth and variance during a certain period. In the field test, daily water depths were simulated by the automatic irrigation functions in the models based on the reported data.

Table 6. Chemical properties and associated uncertainty for molinate and thiobencarb

| ***Chemical properties*** | ***Carbofuran*** | ***Molinate*** | ***Thiobencarb*** |
|---|---|---|---|
| MW | 221.26 | 187.3 | 257.8 |
| Water solubility (ppm) | 322 | 1100 | 16.7 |
| KOC (L $kg^{-1}$[OC]) | 23.3 | 120 | 1000 |
| Vapor pressure (Pa) | $8.0\times10^{-5}$ | 0.5 | $2.39\times10^{-3}$ |
| Hydrolysis degradation HL (day) | 37 | 365 | Stable |
| Aqueous photolysis HL (day) | 71 | Stable | Stable |
| Degradation HL in unsaturated soil (day) | 29 | 28 | 21 |
| Aquatic dissipation HL (day) | 58 (sediment);<br>22 (water) [1] | 8.0 [2] | 8.7 [3] |

Notes: HL = half-life; data are taken from the FOOTPRINT and USDA pesticide property database (USDA, 2001; FOOTPRINT, 2017) unless otherwise noted,

[1] (Nicosia et al., 1991)

[2] (Ross and Sava, 1986)

[3] (Ceesay, 2000)

Other model input parameters which were not reported from the experiments, such as percolation rate, are taken from the California Rice Scenario (Table 1). The function for slow release in RICEWQ is disabled for comparable results to PCPF and PFAM. For PCPF, the dissolution rate constant is set as 0.03 $day^{-1}$. Based on the equilibrium test for thiobencarb, applied thiobencarb is fully dissolved within about 1 day with the dissolution rate constant of about 0.03 $day^{-1}$ (Figure 3). Here, 0.03 was selected as an arbitrary value for the initialization of un-calibrated simulation of PCPF.

## 7.3 Field test results and discussion

### *7.3.1 Case study #1: water management*

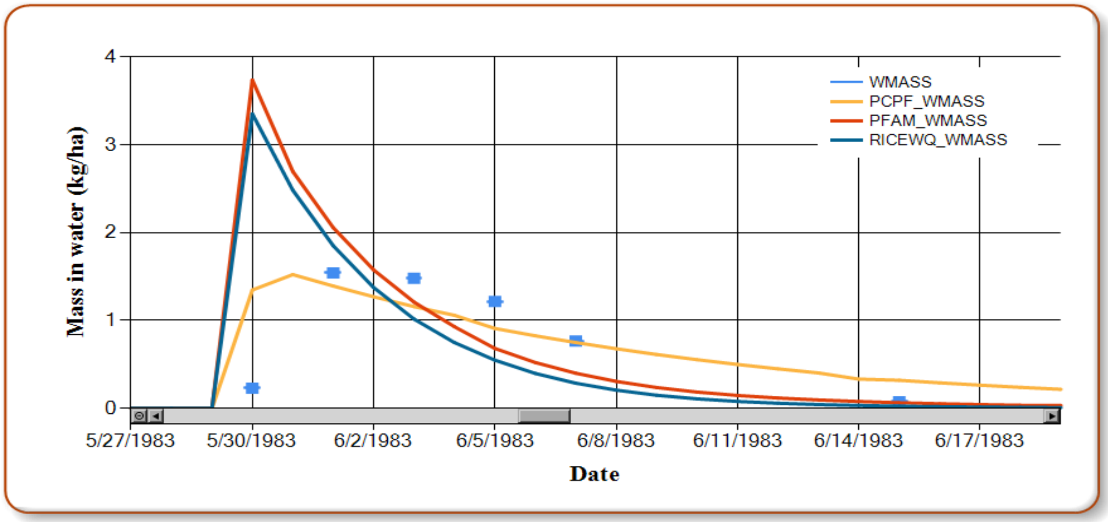
Case study #1 represents a granular application of thiobencarb to a flooded paddy of approximately 26 mm. Water levels were decreased to approximately 17 mm one week after application (Ross and Sava, 1986). Results of the simulations are presented in Figure 5. Pessticide mass in water is presented in the upper panel, concentration in wateris presented in the middle panel, and pesticide mass in sediment is shown in the lower panel.

Discussions on the results for case study #1:

1) RICEWQ and PFAM generated similar results for the dynamics of pesticide masses in water and sediment. The identified error in the diffusion formulation of RICEWQ has limited effects on the model predictions for wet-paddy applications. When a pesticide is

applied to a flooded paddy, effective diffusion flux is from water to sediment, and mainly determined by the pesticide concentration in the water.

2) By simulating the dissolution process, PCPF generated better results in the paddy water compared to other models, while all models overestimated pesticide mass in the paddy on the day of application. Slow release (including release from the product and dissolution into water) may be an important process for pesticide fate and distribution. In this case study, for example, field measurements indicated that the active ingredient may be not released or dissolved into the simulation domain immediately after application (Figure 5). RICEWQ has the option for simulating slow release. Model test results (not demonstrated in this report) suggested that, by introducing a 2-day slow release (RREAC = 0.346 $d^{-1}$), the RICEWQ performance could be significantly improved in this case study. PFAM does not have explicit functions for either slow release or dissolution, although manually delayed applications can be used to mimic those functions.
3) Water depths have significant effects on pesticide concentration, and should be carefully evaluated in the rice pesticide modeling. For example, RICEWQ and PFAM had similar results for pesticide mass in water on the day of application. However, PFAM-simulated concentrations were much higher than those simulated by RICEWQ (Figure 5) because of different predicted water depths.



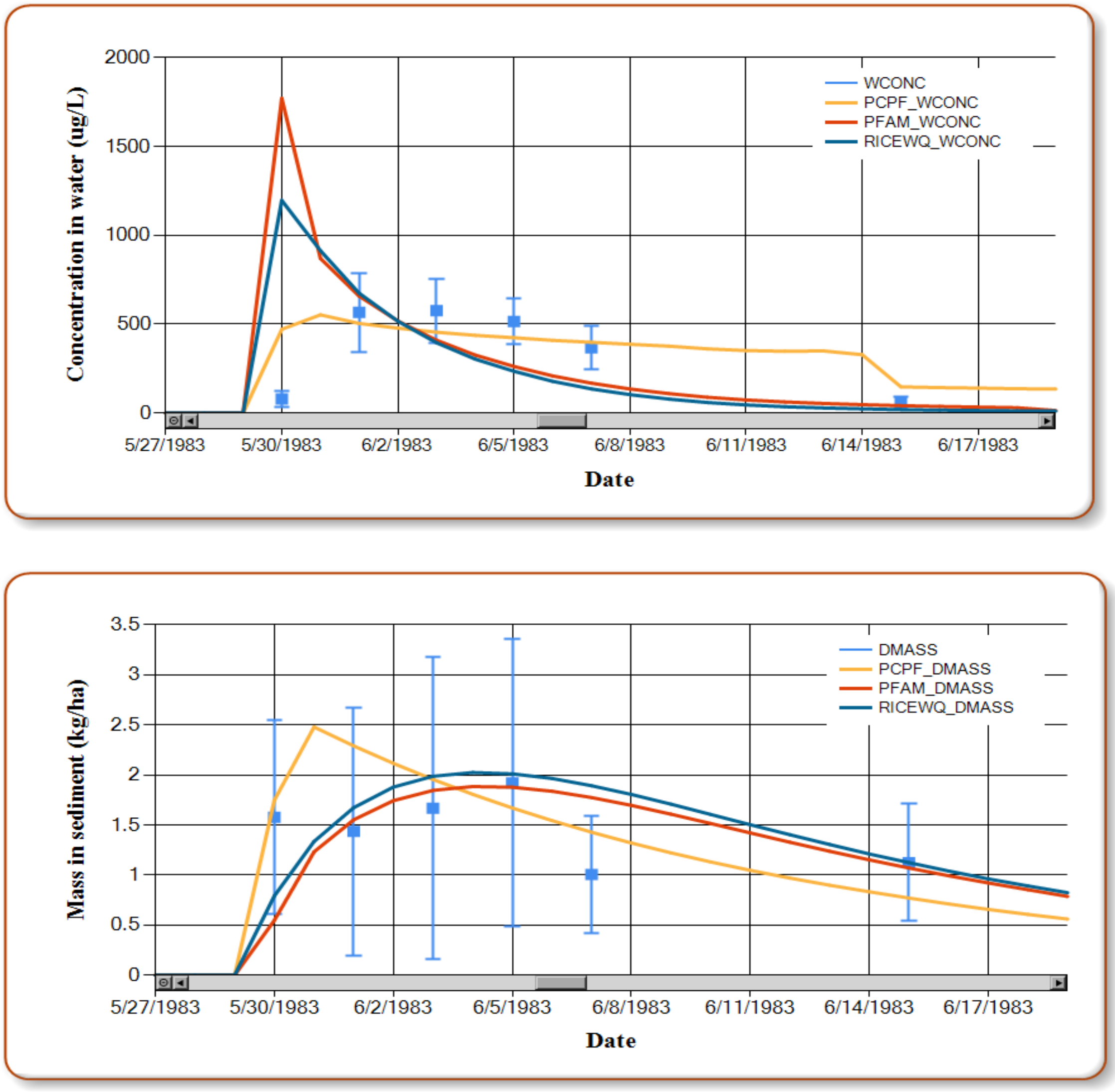


Figure 5. Model results for case study #1, reported as pesticide mass in water (upper panel), concentration in water (middle panel), and pesticide mass in sediment (lower panel)

### *7.3.2 Case study #2: multiple applications*

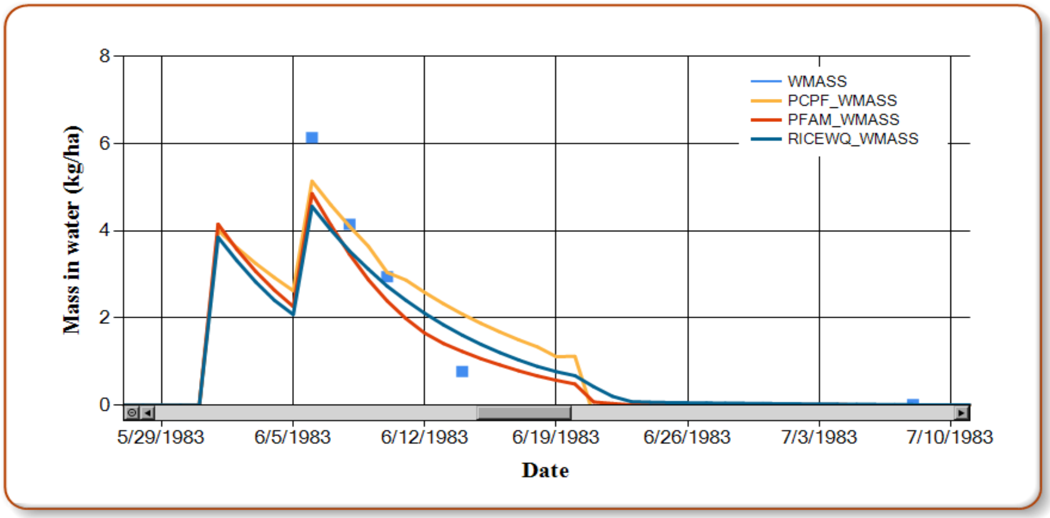
Case study #2 represents multiple applications of molinate to a flooded paddy of approximately 28 mm. The application interval was 5 days. The paddy was drained approximately three weeks after the first application (Ross and Sava, 1986). Results of the simulations are presented in Figure 6. Pessticide mass in water is presented in the upper panel, concentration in wateris presented in the middle panel, and pesticide mass in sediment is shown in the lower panel.

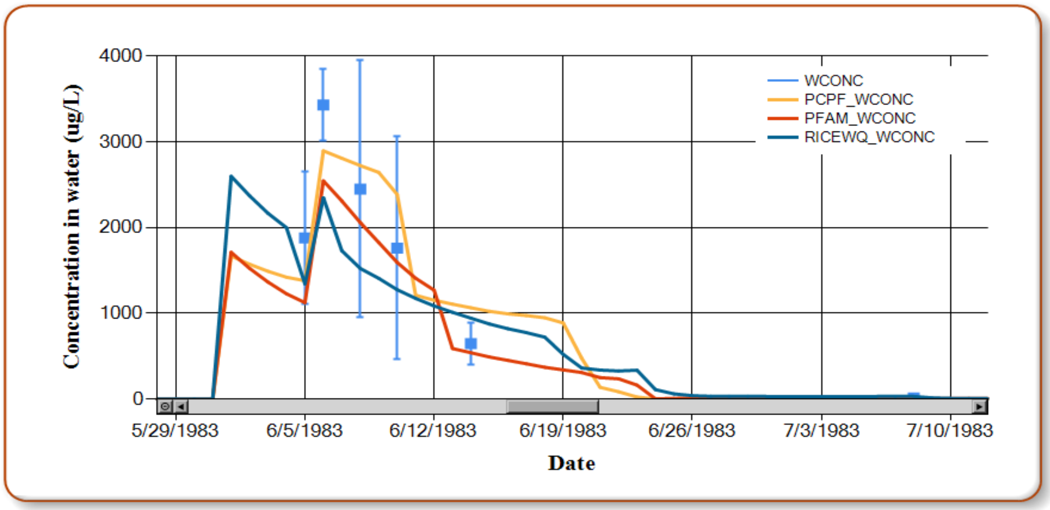
Discussions on the results for case study #2:

1) In the paddy water, all models reasonably captured the dynamics of pesticide mass and concentration from multiple applications. Un-calibrated models predicted aqueous

pesticide concentrations within the range of measured data, except for the peak concentration observed on the day of the second application;

2) With a prescribed dissolution rate constant of 0.03 day$^{-1}$, the PCPF predictions significantly underestimated the pesticide masses in sediment (Figure 6). As discussed previously, smaller dissolution rate constants are required to establish the expected chemical equilibrium (Figure 2 and Figure 3). Further model tests (not reported here) indicate that comparable mass in sediment to those by RICEWQ and PFAM can be generated using a dissolution rate constant of 0.001 day$^{-1}$). Compared to case study #1 with thiobencarb as the test agent, this study also indicated that pesticides with a lower KOC require even smaller dissolution rate constants in PCPF to generate comparable results to other models.





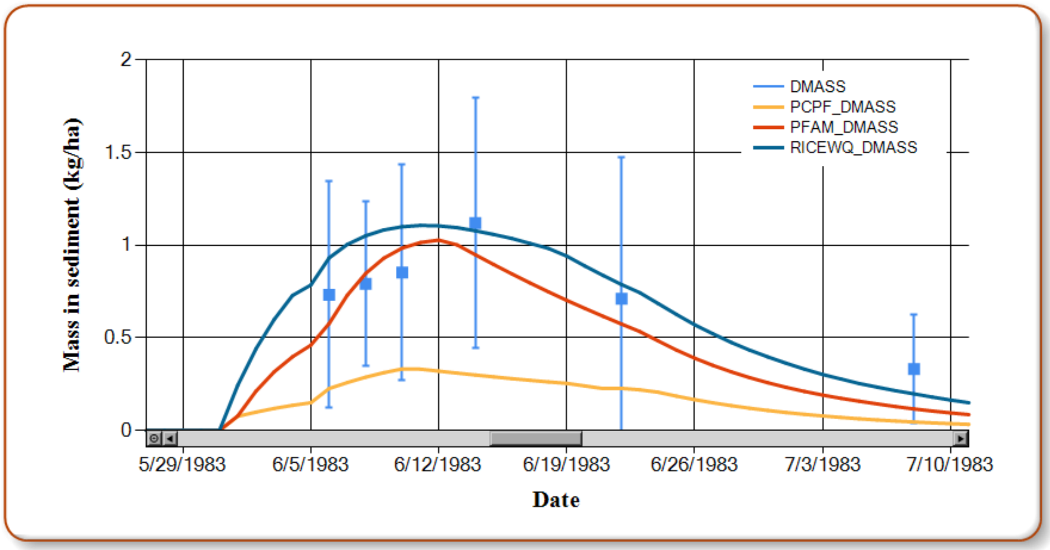


Figure 6. Model results for case study #2, reported as pesticide mass in water (upper panel), concentration in water (middle panel), and pesticide mass in sediment (lower panel)

### *7.3.3 Case study #3: dry-paddy application*

Case study #3 represents a granular application of carbofuran to a dry paddy. Carbofuran was incorporated to a depth of 7.8 cm in a section of the paddy. The paddy was flooded approximately 10 days after application and maintained at a depth of approximately 11 mm (Nicosia et al., 1991). Pessticide mass in water was estimated from reported concentrations in water. Simulation results are compared to field results in Figure 7 and Figure 8. Results for PCPF are not included because the model does not allow applications to dry paddies.

Discussions on the results for case study #3:

1) The error in formulating diffusion flux in RICEWQ had significant effects on model simulations for dry-paddy application. Pesticide mass and concentration in the paddy water were underestimated (Figure 7);
2) Revised RICEWQ, by correcting the diffusion calculation, generates comparable results as PFAM (Figure 8);
3) PFAM does not accept background concentrations as inputs. Therefore, reported background concentration in the sediment (when converted into kg ha$^{-1}$, it's smaller than the application rate by two orders of magnitudes) was not considered for both models.
4) PCPF does not have the capability for dry-paddy application.

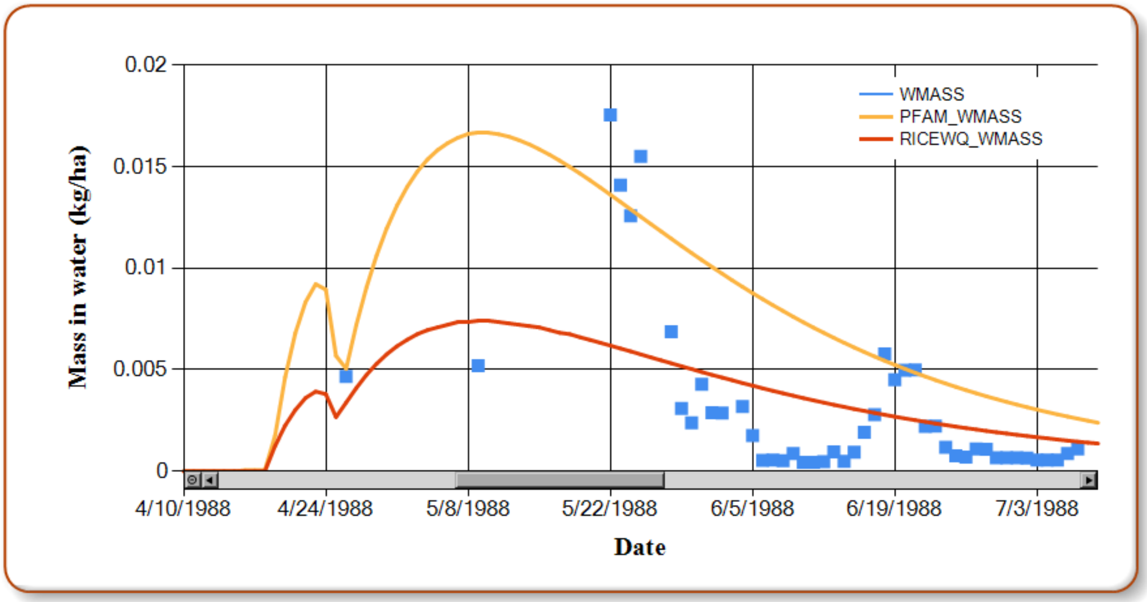


Figure 7. Model (original RICEWQ and PFAM) results for case study #3, reported as pesticide mass in water

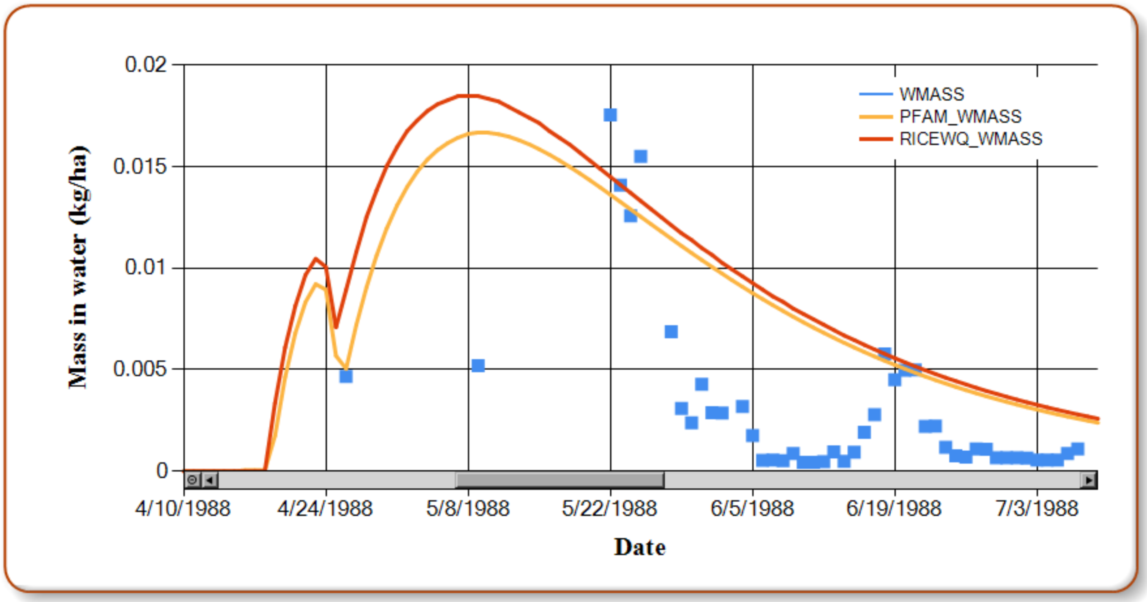


Figure 8. Model (revised RICEWQ and PFAM) results for case study #3, reported as pesticide mass in water

## 8 Conclusion

RICEWQ has the most comprehensive descriptions of pesticide transport and transformation pathways in rice paddies based on its ability to simulate foliar applications, slow release formulations, multiple transport pathways between water and sediment, degradation products, and bi-phase degradation. Activation of these features requires a larger dataset of model input parameters compared to other models. Some of those inputs, e.g., the rate and coefficients for washoff, diffusion, settling, and direct partitioning, may be not readily available from the registrant-submitted data, although guidelines for input parameter selection have been provided by the developer (Williams et al., 2008). These processes can be also deactivated by specifying zero for appropriate input parameters. Chemical transfer between water and sediment can be represented as it is in PFAM by specifying a single mass transfer coefficient in place of the diffusion coefficient.

An error in formulating diffusion flux in RICEWQ version 1.73 was identified during the model evaluation. Consequently, the model may overestimate pesticide mass and concentration in the sediment for simulations involving pesticide applications to dry paddies that are subsequently flooded. Mathematic procedures for quantifying the predicted deviation from the expected chemical equilibrium are provided. According to the field test results, this issue has negligible effects on the model predictions for wet-paddy applications. However, the model significantly underestimated pesticide mass in the paddy water in the case study of dry-paddy application. It is suggested that the equation of diffusion flux be modified to represent a reasonable concentration difference between the bulk water and pore water. A preliminary test was conducted by correcting the diffusion formulation, and the revised model generated reasonable results in comparison with expected pesticide distribution (Figure 2 and Figure 3) in the equilibrium test and with the PFAM predictions for dry-paddy application in the field test (Figure 8).

For PCPF, the pesticide distribution at equilibrium is sensitive to the selected values of dissolution rate constant and percolation rate. PCPF does not simulate diffusion processes, and percolation and desorption are the only process for mass transfer between water and sediment once the applied pesticide is fully dissolved. Therefore, simultaneous processes of pesticide dissolution and sediment-layer development during the first hours or days after application would generally determine the pesticide distribution in a rice paddy. Since the active sediment layer is developed from zero to 1 cm, the model may underestimate the pesticide mass in the sediment, especially for pesticides with lower KOC. Model improvement is suggested to reformulate pesticide transfer between the paddy water and sediment after the development of the active sediment layer. The improvement may also help develop the model capability for dry-paddy application.

No major issues are identified for PFAM in the equilibrium test. Results of the field test indicated that the lack of functions for slow release and initial concentration may limit model usefulness for simulating applications under field conditions. Mathematically, the effects of both slow release and initial concentration can be incorporated by manually adjusting the application amount and timing. However, explicit simulations of those effects are suggested if the model is to be used for pesticide registration purposes.

In addition, the model function of biphasic degradation is not tested in this study, because the function is not available for all models and the experimental data is not sufficient for parameterization and evaluation. Previous studies suggested the dissipation of some rice pesticides, such as methyl parathion (Kollman et al., 1992), followed biphasic first-order kinetics. Simulation for biphasic degradation is included in both RICEWQ and PCPF. A similar function and the ability to simulate slow release formulations are suggested for PFAM.

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