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Pesticides in Flooded Applications Model (PFAM): Conceptualization, Development, Evaluation, and User Guide

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Abstract

The Pesticides in Flooded Applications Model (PFAM) was developed to facilitate risk assessments for pesticides used in flooded-agriculture applications such as rice paddies and cranberries bogs. PFAM was designed around the specific parameters that are typically available for a pesticide risk assessment, thereby simplifying the assessment process by allowing the user to concentrate on providing only relevant model inputs. The model considers the fate properties of pesticides and allows for the specifications of common management practices that are associated with flooded agriculture such as scheduled water releases and refills. It also allows for natural water level fluctuations resulting from precipitation and evapotranspiration. The purpose of this document is to describe the concepts used in the model. Because PFAM was designed for environmental protection regulatory purposes, the quality acceptance criteria specified that the model estimates should err on the high side of measured data, but it should not cause undue burden to stakeholders by being overly conservative. As evaluation results show, PFAM did tend to err on the high side of the data yet provided more realistic estimates than the currently used methods, which thereby reduced stakeholder burden. Thus, PFAM satisfactorily performed as a regulatory model. The code for the mathematics of the model is written in Fortran 95/2003, while the user interface code is in Visual Basic Dot Net. As is important for a regulatory model, PFAM is nonproprietary, with the model code and documentation being freely available.

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1. Introduction

Pesticide use on cranberries, rice, and other applications where a pesticide is used in conjunction with flooding presents unique issues to pesticide risk assessors trying to estimate relevant environmental concentrations. For these types of uses, assessors need a model with special flood-handling features to address issues such as whether the pesticide is applied post- or pre-flood, water levels that vary over the course of the crop, scheduled water releases and refills, and flow-through washouts. A relevant model for pesticide exposure assessments would consider these factors as well as the availability of specific fate parameters for a pesticide risk assessment.

The current U.S. Environmental Protection Agency (USEPA) model for flooded applications is similar in concept to the equilibrium model suggested by Johnson (1991) and delivers rough but protective concentration estimates. That model is an equation that determines the aqueous concentration of a pesticide that is at equilibrium with 10 cm of water and 1 cm of sediment (USEPA, 2007a). While simple and effective for environmental protection, it does not take full advantage of available information such as degradation, management practices such as flooding and draining, or long-term use of a pesticide. Such simple estimates may provide protective screening-level estimates, but if a pesticide fails the screen, there is no standard model to provide more pesticide- and application-specific concentrations for use in higher tier risk assessments.

The new Pesticides in Flooded Agriculture Model (PFAM) described here was designed specifically for use in a regulatory setting wherein model inputs and processes will correspond to the data available during a regulatory assessment. In a regulatory assessment, assessors have available only a few chemical fate parameters, such as those listed in Table 1-1. For this reason, an appropriate model would balance the complexity of the model with the available inputs (Crout et al., 2009; Freni et al., 2009; Ranatunga, et al., 2008). PFAM was designed around the specific chemical parameters given in Table 1-1, which are typically the only parameters available for a regulatory pesticide assessment. Thus, PFAM is only as complex as the available data allow. The balance of complexity with available data is consistent with good modeling practices as specified by the USEPA (USEPA, 2009a).

PFAM borrows heavily from the mathematical formulation of the processes used in the model EXAMS (Burns, 2000), which is a USEPA standard for modeling pesticide water quality for non-volume-varying bodies. Note that there are several models described in the literature that are aimed at determining water quality resulting from aquatic agriculture (e.g., Johnson, 1991; Jeon et al, 2007; Kim et al, 2008; Karpouzas and Etori, 2006; Tournebize et al., 2006; Yoshinaga, et al, 2004; Watanabe and Takagi, 2000), but none are specifically designed around the methods used for pesticide risk assessments, non-proprietary, and freely available for public inspections, as is desirable for USEPA regulatory models (NRC, 2007, USEPA 2009a).

Table 1-1. Typical Relevant Chemical Parameters Available for a Pesticide Exposure Assessment for Flooded Applications.

Parameter	Notes
Sorption Coefficient (Koc)	As typically defined.
Aerobic Metabolism Rate	Only whole system (solid and aqueous) degradation rate is available. Typically for 20 to 25°C.
Anaerobic Metabolism Rate	Only whole system (solid and aqueous) degradation rate is available. Typically for 20 to 25°C.
Vapor Pressure	Typically for 20 to 25°C.
Solubility	Typically for 20 to 25°C.
Aquatic Photodegradation Rate	Conducted on thin (mm) aqueous layer with artificial light.
Hydrolysis	Conducted at pH 5, 7, and 9.

2. PFAM Conceptual Development

2.1 Overview of the Processes in PFAM

PFAM is conceptualized in Figure 2-1 and includes both hydrological processes and chemical processes. The water body depth may change due to precipitation, refill, drainage, evaporation, and weir-height changes. The model consists of two regions: a water column and a benthic region. Each individual region is completely mixed and at equilibrium with all phases within the individual region, and equilibrium within each region follows a linear isotherm. The two regions are coupled by a first-order mass-transfer process. Chemical transformation processes (i.e., hydrolysis, bacterial metabolism, photolysis, and sorption) within each region are formulations that were heavily borrowed from the USEPA EXAMS model (Burns, 2000). Changes in water body conditions (temperature, water levels, wind speed, etc) and the resulting changes in degradation rates occur on a daily time step. A daily time step was selected mainly because of the availability of a large amount of daily meteorological data (Burns et al., 2007) and the USEPA's historical use of EXAMS on a daily time step.

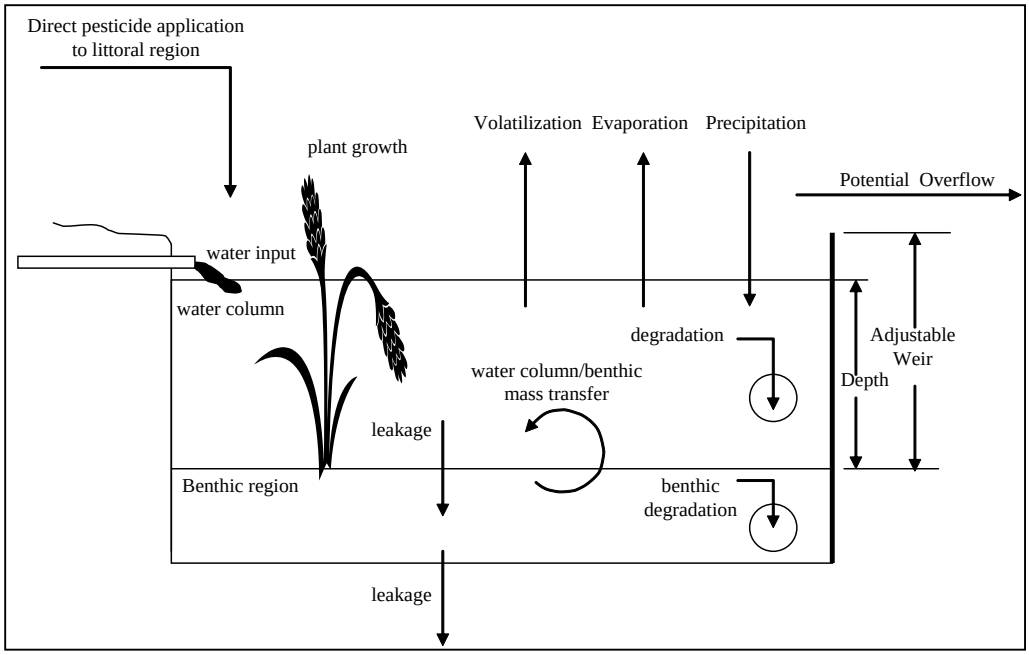

Figure 2-1. Pictorial of PFAM showing hydrological and chemical processes.

2.1.1 Flood and Overflow Control

In this conceptualization (Figure 2-1), water is held in a basin behind a weir. Similar paddy and weir models have been previously created (Yosinaga, et al. 2004, Jeon et al. 2005, Khepar et al. 2000). The maximum volume of water is controlled by the weir height, which can move up or down by user control. Users can schedule changes in water level by means of an external source of solute-free water. If weir height decreases below the current water level, then the volume of water along with the associated solute above the new weir height is instantaneously released. The depth of the water column is calculated from daily precipitation, refill, drainage, leakage, and evaporation. For any day, the water level is calculated as

$$d_1 = d_0 + P - L_1 - L_2 - E - D + R \qquad for\ 0 < d_1 < d_{weir} \tag{2-1}$$

where d_1 = the current aqueous depth for the day (m)
d_0 = the water depth of the previous day (m)
d_{weir} = weir level (m)
P = daily direct precipitation on water body (m)
L_1 = 1eakage through weir (m)
L_2 = leakage through sediment (m)
E = daily evaporation of runoff (m)
D = drainage due to weir height changes (m)
R = engineered flow into water body (m)

Daily precipitation and evaporation are taken from an associated meteorological file (Burns et al. 2007). The volume rises and falls on a daily basis based on this equation. If at the start of a time step, the newly calculated water depth (d_1) is greater than d_{weir}, then the volume

for the day is set to d_{weir}, and the excess water is used in the calculations for washout (see below). The minimum possible water volume is zero, but for practical purposes, it is set to a small value (*e.g.*, 10^{-6} m) to prevent numerical difficulties that are associated with calculations involving infinity and zero.

The computer implementation of the model allows for automation of the refill requirements. Refill occurs automatically if the water level reaches a user-specified minimum depth. The subsequent refill adds enough to reach the user-specified fill level. Additionally, the model can account for those scenarios in which the user needs to have a constant flow through the water body. In this case, the depth of the water body is maintained at the weir height with excess water overflowing the weir. The excess water enters into the washout calculations as described later.

2.1.2 Plant Growth

Plant growth is based on a simple linear increase in areal coverage of the plant, as described in the following equations:

$$\begin{aligned} f_p &= f_{p,\max}\left(\frac{t}{T_m - T_e}\right) && T_e < t < T_m \\ f_p &= f_{p,\max} && T_m < t < T_r \\ f_p &= 0 && T_r < t < T_e \end{aligned} \qquad (2\text{-}2)$$

where f_p = the fractional area of coverage at time t.
$f_{p,max}$ = the maximum fractional area of plant coverage
T_e = time of emergence
T_m = time of maximum coverage
T_r = time of removal

This routine allows the plant canopy to linearly increase from the date of emergence to the maturity date at which time the plant canopy coverage remains constant until the harvest date. In this version of PFAM, plant canopy only functions to shield the water body from light and thereby reduces photolysis (see below). The plant canopy was designed to not retain pesticide because data on plant interception efficiency, the breakdown of pesticide on foliage, and the pesticide washoff mechanics is not readily available in a pesticide assessment. This intentional omission is in keeping with the model-design plan to limit complexity to only processes that are well defined and have readily available input parameters. This design should normally result in a protective assessment since pesticide will more directly enter the water column.

2.1.3 Chemical Processes

The mathematical conceptualization of the water body is formed on daily piecewise solutions. A constant water body volume is assumed for the duration of a day (the time step of the model), but the volume can vary from one day to another day. In this way, an analytical solution for the daily concentrations can be retained. The ability to use an analytical solution greatly improves the reliability and serviceability of the model.

All individual dissipation processes (e.g., metabolism, hydrolysis, and volatilization) are represented as first-order in concentration. On any given day, the aquatic agriculture model is

described by two differential equations—namely, a mass balance on the water column region and a mass balance on the benthic region:

$$m_{sed1}\frac{ds_{sed1}}{dt}+m_{DOC1}\frac{ds_{DOC1}}{dt}+v_1\frac{dc_1}{dt}= \begin{aligned} & -Qc_1-QC_{sed}s_{sed1}-QC_{DOC}s_{DOC1}-\omega(c_1-c_2) \\ & -v_1\mu_{photo}c_1-v_1\mu_{bio-a1}c_1-v_1\mu_{hydr}c_1-v_1\mu_{vol}c_1 \\ & -m_{sed}\mu_{bio_sed1}s_{sed}-m_{DOC}\mu_{bio-DOC1}s_{DOC}-Q_Lc_1 \end{aligned} \tag{2-3}$$

$$m_{sed2}\frac{ds_{sed2}}{dt}+v_2\frac{dc_2}{dt}=-v_2\mu_{bio-a2}c_2-v_2\mu_{hydr}c_2-m_{sed}\mu_{bio-sed2}s_{sed2}+(\omega+Q_L)(c_1-c_2) \tag{2-4}$$

where
c_1 = aqueous concentration in water column, [kg/ m^3]
c_2 = aqueous concentration in benthic region, [kg/ m^3]
C_{sed} = concentration of suspended sediment in water column = m_{sed_1}/v_1 [kg/m^3]
C_{DOC} = concentration of DOC in water column = m_{DOC}/v_1, [kg/m^3]
m_{sed1} = mass of suspended sediment in water column, [kg]
m_{DOC1} = mass of DOC in water column, [kg]
m_{sed2} = mass of suspended sediment in water column, [kg]
s_{sed1} = sorbed concentration on suspended sediment in water column, [kg/ kg]
s_{DOC1} = sorbed concentration on suspended DOC in water column, [kg/ kg]
s_{sed2} = sorbed pesticide concentration on benthic sediment, [kg/ kg]
v_1 = volume of water in region 1 on the specific day, [m^3]
v_2 = volume of water in region 2, [m^3]
Q = volumetric flow rate of water out of water column, [m^3/s]
Q_L = volumetric leakage flow rate, [m^3/s]
ω = 1st order water-column-to-benthic mass transfer coefficient, [m^3/s]
μ_{hydr} = 1st order hydrolysis rate coefficient, [s^{-1}]
μ_{photo} =1st order photolysis rate coefficient, [s^{-1}]
μ_{vol} = effective 1st order volatilization rate coefficient, [s^{-1}]
μ_{bio-a1}=1st order aqueous-phase metabolic degradation rate coefficient in water column, [s^{-1}]
$\mu_{bio-sed1}$ = 1st order sediment-sorbed metabolic degradation rate coefficient in water column, [s^{-1}]
$\mu_{bio-DOC1}$ = 1st order DOC-sorbed metabolic degradation rate coefficient in water column, [s^{-1}]
μ_{bio-a2} =1st order aqueous-phase metabolic degradation rate coefficient in benthic region, [s^{-1}]
$\mu_{bio-sed2}$ = 1st order sediment-sorbed metabolic degradation rate coefficient in benthic region, [s^{-1}]

In this model (as well as in the current regulatory use of the EXAMS model) the following assumptions are made: (1) suspended matter in the water column occupies negligible volume, (2) hydrolysis, photolysis, and volatilization act only on dissolved species, (3) within a single region (water column or benthic), the rate coefficient for biological metabolism is the same for both dissolved and sorbed forms of pesticide (e.g., $\mu_{bio1} = \mu_{bio-a1} = \mu_{bio-sed1} = \mu_{bio-DOC1}$, and $\mu_{bio2} = \mu_{bio-a2} = \mu_{bio-sed2}$), (4) the hydrolysis rate coefficient in the benthic region is the same as that in the water column, (5) linear isotherm equilibrium exists within each region among all sorbed species. With these assumptions, we can rewrite equations (2-3) and (2-4) in a simpler form as follows:

$$\frac{dc_1}{dt} = -\Gamma_1 c_1 - \Omega\Theta(c_1 - c_2) \tag{2-5}$$

$$\frac{dc_2}{dt} = -\Gamma_2 c_2 + (\Omega + \Lambda)(c_1 - c_2) \tag{2-6}$$

where

$$\Gamma_1 = \frac{Q}{v_1} + f_{w1}\left(\mu_{photo} + \mu_{hydr} + \mu_{vol} + \frac{Q_L}{v_1}\right) + \mu_{bio1} \tag{2-7}$$

$$\Gamma_2 = f_{w2}\mu_{hydr} + \mu_{bio2} \tag{2-8}$$

$$\Omega = \frac{\omega}{(m_{sed2}K_{sed2} + v_2)} \tag{2-9}$$

$$\Lambda = \frac{Q_L}{(m_{sed2}K_{sed2} + v_2)} \tag{2-10}$$

$$\Theta = \frac{(m_{sed2}K_{sed2} + v_2)}{(m_{sed1}K_{sed1} + m_{DOC1}K_{DOC1} + v_1)} \tag{2-11}$$

where f_{w1} and f_{w2} are the fractions of solute in the aqueous phase within the water column and benthic regions, respectively, as defined by

$$f_{w1} = \frac{v_1}{(m_{sed1}K_{sed1} + m_{DOC1}K_{DOC1} + v_1)} \tag{2-12}$$

$$f_{w2} = \frac{v_2}{(m_{sed2}K_{sed2} + v_2)} \tag{2-13}$$

and where K_{sed1}, K_{DOC1} are the linear isotherm partitioning coefficients for suspended sediments, biota, and DOC in the water column, respectively, and K_{sed2} is the linear isotherm partitioning coefficient for sediment in the benthic region (units of m^3/kg).

The term, f_{w1}, for this varying volume model varies on a daily basis depending on the volume of the water body (v_1) as described below in *Daily Piecewise Calculations*. As a simplification in this model, the mass of sediment, biota, and DOC remain constant and in suspension. This assumption has very little impact on the model output in most cases since partitioning to these species is negligible for all but the most extremely high partitioning coefficients (described later and in USEPA, 2004).

Given a set of initial conditions, equations (2-5) and (2-6) completely describe the water body. It is clear, that there are only four parameters that influence the concentration—Γ_1, Γ_2, Ω, and Θ. Γ_1 is the effective overall dissipation rate in the water column region, [s^{-1}]. Γ_2 is the effective overall degradation rate in the benthic region, [s^{-1}]. Ω is a mass transfer coefficient describing transfer between the benthic region and water column, [s^{-1}]. Θ is the ratio of solute holding capacity in the benthic region to that in the water column. The following sections describe the details of these components.

2.1.3.1 Solute-Holding-Capacity Ratio (Θ)

The solute-holding-capacity ratio (Θ) is the ratio of solute holding capacity in the benthic region to the solute capacity in the water column, as defined by equation (2-11). The individual partitioning coefficients (K_{sed} and K_{DOC}) in equation (2-11) are generally not directly known for specific applications. To account for these unknowns, the various partitioning coefficients are

related to the organic carbon partitioning coefficient (which is typically known in a pesticide assessment) by the same relationships used in EXAMS.

For the sediment, the partitioning coefficient is directly proportional to K_{oc}, with the constant of proportionality equal to the fraction of organic carbon in the sediment. The carbon amount in the sediment is a user-adjustable input. The sediment partitioning coefficients can thus be determined from

$$K_{sed1} = K_{sed2} = f_{oc} K_{oc} \left(0.001 \frac{m^3/kg}{ml/g} \right) \tag{2-14}$$

where K_{oc} = organic carbon partitioning coefficient, [ml/g]
f_{oc} = fraction of organic carbon in sediment [—]

Note that the units of the coefficients in equations (2-1) to (2-11) are all given in the *s.i* form. The *s.i.* convention will be maintained throughout this paper. However, for some fundamental parameters such as K_{oc}, which is usually presented in units of ml/g, the common units will be used along with the necessary conversion factor.

The partitioning coefficient for DOC is determined from the default empirical relationships described in the EXAMS documentation (Burns, 2000). PFAM incorporates the assumption of Burns (2000) that benthic DOC has higher partitioning characteristics than water column DOC. The relations given by Burns (2000) and adopted for the current and proposed standard water bodies are as follows:

$$K_{DOC1} = 0.2114 K_{oc} \left(0.001 \frac{m^3/kg}{ml/g} \right) \tag{2-15}$$

Figure 2-2 shows an example of the relative capacities of the individual media (aqueous, DOC, and suspended sediment) in the water column as a function of K_{oc}. With the parameters from the USEPA standard water bodies for suspended solids and DOC (USEPA, 2004) and with a 10-cm depth, the water compartment holds 90 percent of the solute up to a K_{oc} value of about 70,000 ml/g. Up to K_{oc} value of about 700,000 ml/g, the aqueous capacity component is greater than the capacity of all sorbed species in the water column combined

Note that EXAMS and the USEPA standard pond, which were the bases upon which PFAM was developed, also include a biological partitioning component in the water column. However, a sensitivity analysis showed that little solute partitioned to the USEPA standard amount of biological material (0.4 mg/L) except at the highest of Koc values (fraction less than 0.0005 at K_{oc} of 10^3 ml/g and <0.09 at K_{oc} of 10^6 ml/g). Furthermore, it is unlikely that measurements of biological material would be available or would significantly contribute to a better estimate of pesticide concentrations. Therefore, a biological partitioning component was not included in PFAM. This elimination is in keeping with the PFAM development ideal to stay away from unreasonable complexity. Also note, the effect of suspended solids is equally insignificant; however, the suspended solids perform an additional function in photolysis quenching, so the suspended solids parameter is retained.

Figure 2-3 shows an example of the relative solute holding capacities for the benthic region of a typically parameterized water body. During PFAM development, sensitivity analyses showed that some parameters (i.e., benthic DOC and benthic biota) used in the USEPA EXAMS pond model (USEPA, 2004) had insignificant impact on results and were thus not included in PFAM. The only components that had significant impact were the sediment and the pore water and these are shown in Figure 2-3.

A sensitivity analysis was performed on the benthic components used in the USEPA standard pond, and the relative fractions for the DOC and biota are on the order of 10^{-4} and 10^{-6}, respectively, for K_{oc} values of 10^6 ml/g. For the benthic region, DOC and biota partitioning are negligible regardless of the K_{oc} value for this parameter set. Therefore benthic biota and benthic DOC were not included in PFAM.

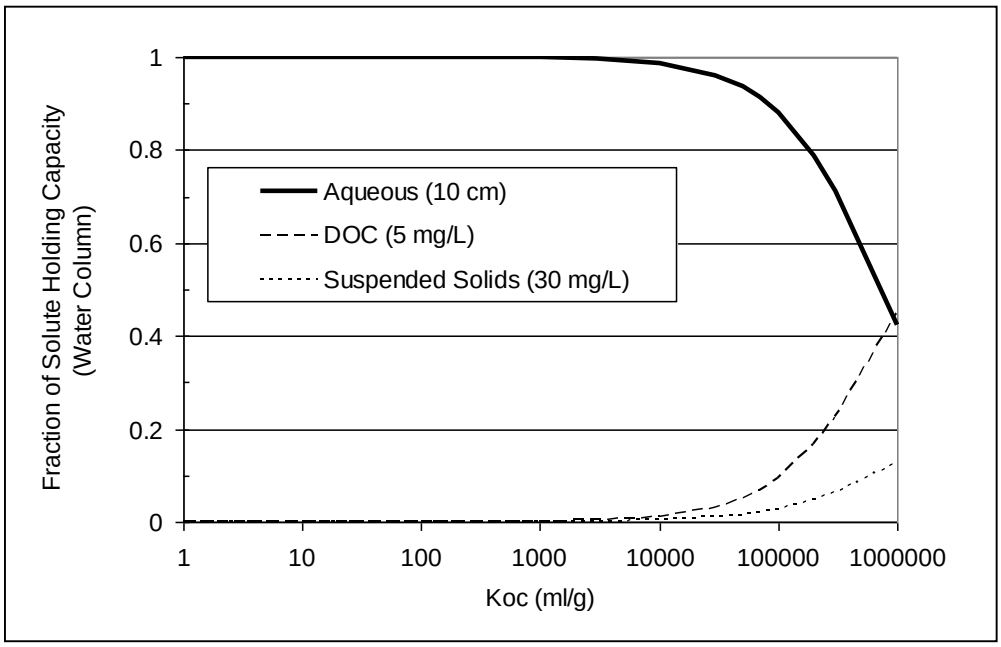

Figure 2-2. Relative solute holding capacity of individual components in the water column.

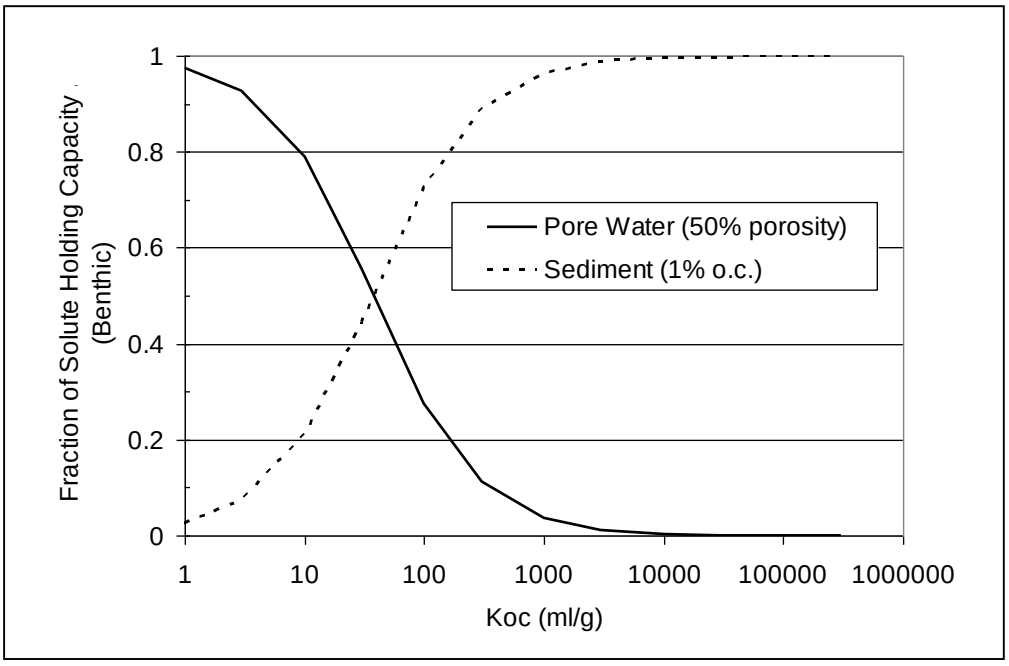

Figure 2-3. Relative solute holding capacity of individual components in the benthic zone. DOC and biological partitioning fractions are 10^{-4} or less and are not detectable on this graph.

2.1.3.2 Effective Water Column Dissipation (Γ_1)

The overall dissipation rate in the water column (Γ_1), as defined in equation (2-7), is the sum of contributions from hydrologic washout and degradation by mechanisms of biological metabolism, photolysis, and hydrolysis. The specific methods and assumptions that are used to determine these individual first-order dissipation processes are described below.

2.1.3.2.1 Hydrologic Washout $\left(\frac{Q}{v_1}\right)$

The first term in equation (2-7), Q/v_1, represents the effective first-order dissipation rate resulting from flow moving pesticide out of the water body. Flow out of the water body may occur due to high rainfalls (as dictated by the meteorological input data), by intentional irrigation flow through, or as leakage through the weir. (Benthic leakage is treated separately in PFAM, see below). The washout term acts on all forms of pesticide (both aqueous dissolved and sorbed to suspended matter), as is apparent from equation (2-3). This means that pesticide mass in both dissolved and suspended sorbed forms can flow out of the water body.

2.1.3.2.2 Water Column Leakage (Q_L/v_1)

The leakage term (Q_L/v_1) represents the dissipation of the pesticide in the water column due to leakage of the water column through the benthic region. The assumption here is that only aqueous-phase pesticide leaks into the sediment and that the leakage rate is constant and only downward such that there is never leakage in the reverse direction (i.e., into the water column). Therefore leakage in this conceptualization can only decrease water column concentrations. Daily leakage volume is constant and occurs until water column is emptied. Further note that this process is constructed as a first-order process, which facilitates and streamlines the mathematical formulation and solution methods. Because the depth is assumed constant during the course of any day, the leakage as a first-order mechanism will be most representative of the actual process when daily volume changes are small. The assumption will produce more conservative (protective) results as leakage rate increases and daily depth changes are greater. In a pesticide risk assessment, the leakage parameter would likely be set to zero, as this would be a reasonable screening-level approach and would provide conservative estimates for a term that is difficult to parameterize.

In the registration process of pesticides, an estimate of the aqueous degradation rate under aerobic conditions is supplied by the registrant. Such estimates are derived from laboratory tests which are typically conducted in aqueous/sediment systems at 20 to 25°C. These tests generally cannot differentiate between degradation occurring on the dissolved forms and sorbed forms of the pesticide; an overall degradation rate is generally all that is determinable from these studies. Therefore, PFAM treats the sorbed-phase and aqueous-phase degradation rates as the same in the water column, which makes both equal to the overall rate as described previously under equation (2-4).

Because temperature impacts degradation rates, an adjustment was included in this model, which corresponds to the USEPA standard temperature adjustment when data are not available on temperature effects on metabolism (Burns, 2000). The relationship is as follows:

$$\mu_{bio1} = \mu_{measured}\left[Q_{10}^{\left(\frac{T-T_{ref}}{10}\right)}\right] \quad (2\text{-}16)$$

where $\mu_{measured}$ = laboratory measured aerobic metabolism rate , [s^{-1}]
Q_{10} = factor by which degradation increases for a 10°C temperature rise.
T = temperature of modeled water body [°C]
T_{ref} = temperature at which laboratory study was conducted [°C].

In a standard EPA assessment, the Q10 is equal to 2, so this temperature modification doubles the degradation rate for every 10°C rise in temperature. In this model, the water temperature of the simulations varies on a daily basis. The water temperature is estimated from the backward 30-day average of the daily air temperatures as specified in the meteorological data input.

2.1.3.2.3 Hydrolysis (μ_{hydr_1})

The hydrolysis degradation acts only on the dissolved phase in the water column. The hydrolysis rate is directly obtained from experimental measurements, as supplied by pesticide registrant data submissions. Variations in pH are not explicitly simulated in the model, so the hydrolysis rate that is used should correspond to the total hydrolysis rate under the conditions that are to be simulated. It is assumed that hydrolysis acts only on dissolved species. Therefore, the effective hydrolysis rate is reduced by the factor f_{w1}, as presented in equation (2-7). The factor f_{w1} represents the fraction of total pesticide that is present in dissolved aqueous form, as previously described.

2.1.3.2.4 Photolysis (μ_{photo})

Photolysis rates are derived from standard laboratory tests following EPA-approved protocols. These tests are designed to estimate the photodegradation rate for near-surface conditions at specific latitude and under clear-sky conditions. The input value for μ_{photo} should be the average value over a 24 hour period. PFAM adopts the methods used in EXAMS (Burns, 2000) to account for latitude adjustments, light attenuation, and cloud cover. These adjustments are implemented as follows:

$$\mu_{photo} = f_p f_{lat}\, f_{atten}\, \mu_{measured} \quad (2\text{-}17)$$

where f_p = the fractional area of plant coverage (see equation 2-2)
f_{lat} = latitude adjustment factor, [—]
f_{atten} = attenuation factor to absorption, [—]
$\mu_{measured}$ = measured near-surface photolysis rate coefficient at reference latitude and clear atmospheric conditions [s^{-1}]

The simulated latitude may vary depending on the desired location in the U.S. where a pesticide assessment is to be made. The effect that latitude has on incident light is accounted for by the latitude adjustment factor (f_{lat}). This model adopts the latitude adjustment described in the EXAMS documentation (Burns, 2000). The latitude adjustment is as follows:

$$f_{lat} = \frac{191700 + 87050\cos(0.0349 \text{ x } L_{sim})}{191700 + 87050\cos(0.0349 \text{ x } L_{ref})} \quad (2\text{-}18)$$

where L_{ref} = reference latitude at which the measured photolysis rate was determined, [degrees]
L_{sim} = latitude of the simulated scenario, [degrees]

The light attenuation factor (f_{atten}) described by Burns (2000) has also been adopted into PFAM. Again, full details are given in the EXAMS documentation, and only the resulting equation is given here:

$$f_{atten} = \frac{1 - \exp\left(-D_{fac} d_1 a\right)}{D_{fac} d_1 a} \tag{2-19}$$

where D_{fac} = EXAMS-defined distribution factor default value = 1.19, [-]
d_1 = depth of water column, [m]
a = total absorption coefficient, [m^{-1}]

The absorption coefficient (a) is calculated from the EXAMS default conditions—that is, calculated from the spectral absorption coefficient assuming that the wave length of maximum absorption occurs at 300 nm. Using the default EXAMS assumptions, the total absorption coefficient is as follows:

$$a = 0.141 + 101[C_{CHL}] + 6.25[C_{DOC}] + 0.34[C_{Sed}] \tag{2-20}$$

where C_{DOC}, C_{Sed} have been previously defined under equation (2-3), and C_{CHL} is the chlorophyll concentration [mg/L].

As a simplification for this varying-depth model, the concentrations of the physical components in equation (2-20) remain constant as depth changes. Because this model does not attempt to simulate the complex sedimentation processes that would inevitably occur with varying depths, and in keeping with the simple nature of this model, the corresponding suspended concentration changes were kept constant, with the values for the suspended concentrations being user inputs. The overall photolysis rate does change, however, due to the effect of depth on equation (2-19). Figure 2-4 shows a typical expected reduction in the half-life as a function of depth. When depth is effectively zero (no water volume in the water compartment) the program switches the photolysis rate to zero. Photolysis on dry soil should be considered along with the overall dry soil degradation rate.

Temperature affects the photolysis in this model only if the temperature reaches 0°C at which point photolysis ceases to occur, with the assumption that there will be ice cover below 0°C.

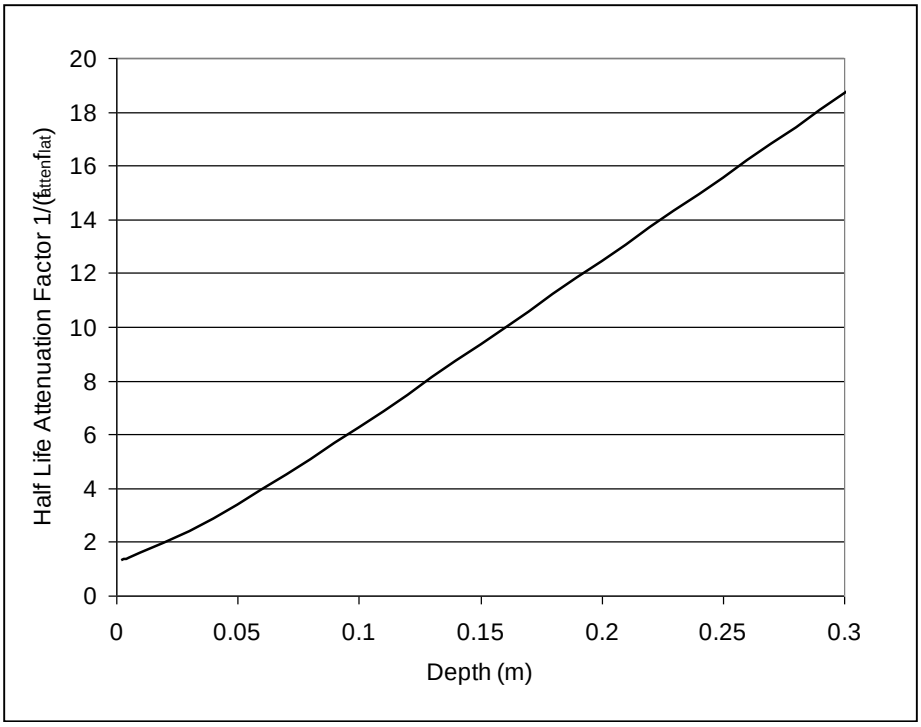

Figure 2-4. Multiplicative factor for effective half-life in the water column as a function of water body depth. Measured half-life at 0 degrees latitude; simulated half-life at 34 degrees. Suspended solids at 30 mg/L, DOC at 5 mg/L; Chlorophyll at 0.005 mg/L. No plant cover.

2.1.3.2.5 Volatilization ($\mu_{volatilization}$)

The standard water bodies use a two-film model for volatilization calculations, as described in the EXAMS documentation (Burns, 2000). The concentration of pesticide in the atmosphere is assumed to be negligible, and thus volatilization becomes a first-order dissipation process. This model uses all of the volatilization default assumptions described in the EXAMS documentation. The overall volatilization rate coefficient may be expressed as

$$\mu_{vol} = \frac{Ak_{vol}}{v_1} \tag{2-21}$$

where A = surface area of the water column, [m^2]
k_{vol} = volatilization exchange coefficient, [m/s]

The volatilization exchange coefficient is defined in the conventional manner as comprising a liquid-phase and an air-phase component as follows:

$$\frac{1}{k_{vol}} = \frac{1}{k_w} + \frac{1}{\left(\frac{H}{RT_k}\right)k_a} \tag{2-22}$$

where k_w = liquid-phase resistance [m/s]
k_a = gas-phase resistance, [m/s]
H = Henry's law constant [m^3atm/mol]

R = the universal gas constant (8.206 x 10^{-5} m^3atm/mol/K)
T_K= temperature (K)

This model uses the EXAMS method of referencing the liquid exchange resistance of pesticides to the liquid resistance of oxygen, and uses molecular weight as a sole surrogate for molecular diffusivity variations among compounds. Further details can be found in the EXAMS documentation (Burns 2000). The resulting relationship is as follows:

$$k_w = k_{O2}\sqrt{\frac{32}{MW}} \tag{2-23}$$

where k_{O2} = oxygen exchange constant at 20°C, [m/s]
MW = molecular weight of pesticide.

The oxygen exchange constant is determined from the empirical relationship of Banks (1975). Adjustments are also made for temperatures other than 20°C. Note that although EXAMS uses a reference temperature of 20°C for the Banks (1975) relationships, it is not clear from Banks (1975) what the actual reference temperature should be. Schwarzenbach et al. (1993), for example, used a 10°C reference for this same relationship. Until this is clarified, the 20°C reference temperature will be used in the model. For wind velocities (v_{wind}) less than 5.5 m/s, the relationship used is as follows:

$$k_{O2} = 4.19 \text{ x } 10^{-6}\sqrt{u_{10}}\left(1.024^{(T-20)}\right) \tag{2-24}$$

where u_{10} = wind velocity at 10 m above water surface [m/s].

For wind velocities greater than or equal to 5.5 m/s, the relationship is

$$k_{O2} = 3.2 \text{ x } 10^{-7}\left(u_{10}\right)^2\left(1.024^{(T-20)}\right) \tag{2-25}$$

Wind speeds are read from meteorological files in which wind speed is given from measurements 10 m above the surface (Burns et al., 2007). The following general relation is used:

$$\frac{u_1}{u_2} = \frac{\log\left(z_1/z_0\right)}{\log\left(z_2/z_0\right)} \tag{2-26}$$

where z_0 is the boundary roughness height, which is assumed to be 1 mm. For the case where wind speeds are read from a meteorological file in which wind speed measurements were made at 10 m, the equivalent wind speed at 0.1 m ($u_{0.1}$) is as follows:

$$u_{0.1} = \frac{\log\left(0.1/0.001\right)}{\log\left(10/0.001\right)}u_{10} = 0.5u_{10} \tag{2-27}$$

The gas phase resistance is referenced to water vapor resistance, and an empirical relationship relates the water vapor exchange rate to wind speed. A linear regression of the

laboratory-derived data of Liss (1973) is used to develop a correlation to describe the effect of wind speed on water evaporation rate:

$$k_{a,H_2O} = 0.00005 + 0.0032u_{0.1}$$

where $k_{a,H2O}$ = the water vapor exchange velocity (m/s)
$u_{0.1}$ = wind speed velocity measured at 0.1 m above the surface (m/s)

The exchange rate of a pesticide is related to the exchange rate of water by

$$k_a = k_{a,H2O}\left[\frac{D_a}{D_{a,H_2O}}\right]^{\alpha} \tag{2-28}$$

where D_a and $D_{a,\,H2O}$ are gas-phase diffusion coefficients for pesticide and water respectively; α is a value that depends upon the conceptual model believed to describe the volatilization process and ranges from 0.5 for the surface renewal model to 1.0 for the stagnant film model (Cusler,1984; Schwarzenbach et al., 1993). The standard water bodies use a value of 1.0 for α thus implying a stagnant film model; however, some laboratory data suggest that α may be better represented by a value of 0.67 (Mackay and Yuen, 1983). The diffusion coefficient of the pesticide is related to the diffusion coefficient of water by the common approximate relationship (e.g., Schwarzenbach et al., 1993):

$$\frac{D_a}{D_{a,H_2O}} \cong \left[\frac{18}{MW}\right]^{0.5} \tag{2-29}$$

Substituting (30) into (29) and assuming that α is equal to one results in the following relationship:

$$k_a = k_{a,H2O}\left[\frac{18}{MW}\right]^{0.5} \tag{2-30}$$

The resulting relationship is

$$k_a = \left[0.00005 + 0.0032u_{0.1}\right]\sqrt{\frac{18}{MW}} \tag{2-31}$$

The Henry's Law constant is generally not available for pesticide registration, and in such cases, it is approximated from vapor pressure and solubility as follows:

$$H = \frac{(vp/760)}{(Sol/MW)} \tag{2-32}$$

where vp = vapor pressure [torr]
sol = solubility [mg/l]

The Henry's Law constant varies with temperature according to a Van't Hoff relation as follows (Staudinger and Roberts, 2001):

$$H(T) = H_{ref}\exp\left[\frac{\Delta h}{R}\left(\frac{1}{T_K} - \frac{1}{T_{ref}}\right)\right] \tag{2-33}$$

where H(T) is the Henry's Law constant as a function of temperature
Δh = enthalpy of phase change from solution to gas [J/mol]

R = universal gas constant = 8.314 J/K/mol
H_{ref} = known Henry's Law constant at T_{ref} [m^3atm/mol]
T_K = ambient (water) temperature [K]
T_{ref} = temperature at which H_{ref} was measured [K].

The heat of enthalpy is generally not supplied for the pesticide registration process; however, because of its important effect on volatilization and because estimation methods are available (e.g. USEPA 2009b), it is included in PFAM. Enthalpies for pesticides are around 20,000 to 100,000 J/mol (Staudinger and Roberts, 2001; Feigenbrugel et al. 2004). The temperature effects on volatilization dissipation are given in Figure 2-5 for several cases that span the likely range of enthalpies for pesticides. The solvation enthalpy can have important effects on volatilization as the figure shows. The effect of the reference Henry's coefficient and temperature are given in Figure 2-6. Both 2-5 and 2-6 show that temperature is an important consideration.

Aside from the temperature effects associated with the equations above, this model also ceases volatilization if the temperature goes below 0°C, with the assumption that there will be ice cover below 0°C which hinders volatilization. Also when depth is effectively zero (no water volume in the water compartment) the program switches the volatilization rate to zero. If volatilization from dry soil is an important process for a specific chemical, then model users can incorporate the volatilization component of dissipation into the overall dry-soil degradation rate.

In this model, wind speed varies on a daily basis. The effect that wind speed has on effective half-life is given in Figure 2-7 for a 10-cm deep pond. The figure shows that wind speed variations will have an increasingly dramatic effect as Henry's law coefficient is reduced. The use of daily wind speeds will thus likely have significant short-term implications (e.g., for acute concentrations) for low Henry's law compounds.

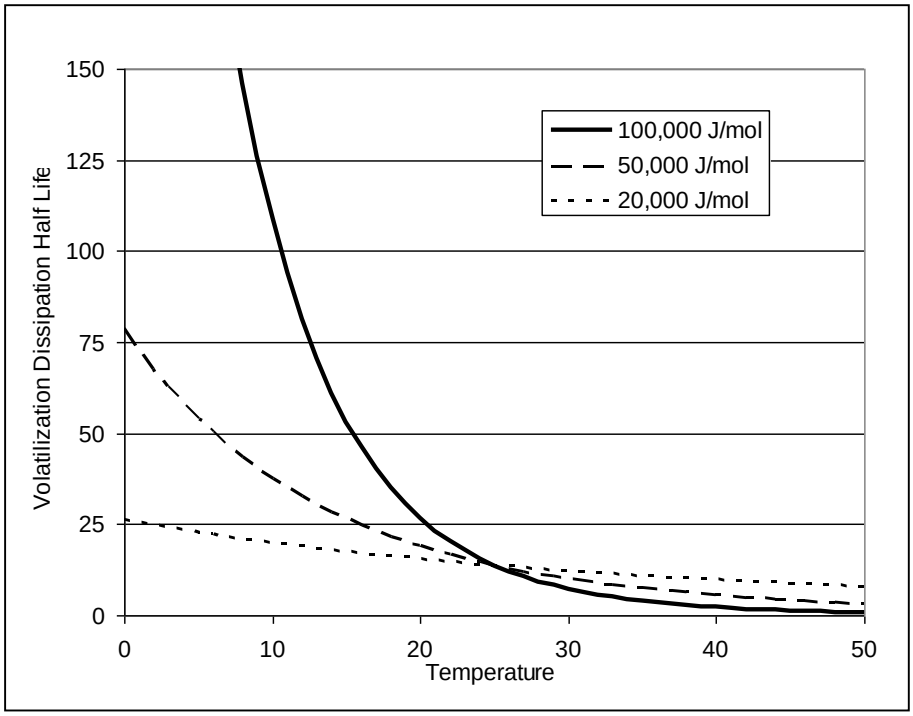

Figure 2-5. Sensitivity of temperature and enthalpy of solvation (in legend) on dissipation by volatilization. This example represents a Henry's coefficient of 10-6 atm·m3/mol and a reference temperature of 25°C.

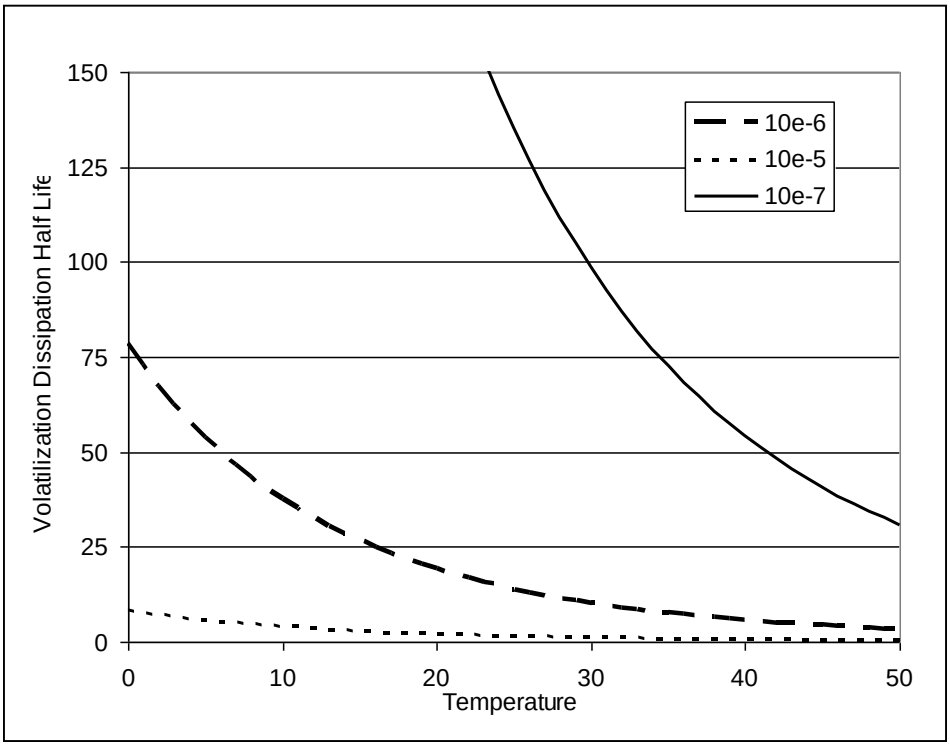

Figure 2-6. Sensitivity of temperature and Henry's coefficient (atm·m^3/mol, in legend) on dissipation by volatilization. This example represents an enthalpy of 50,000 J/mol and a reference temperature of 25°C.

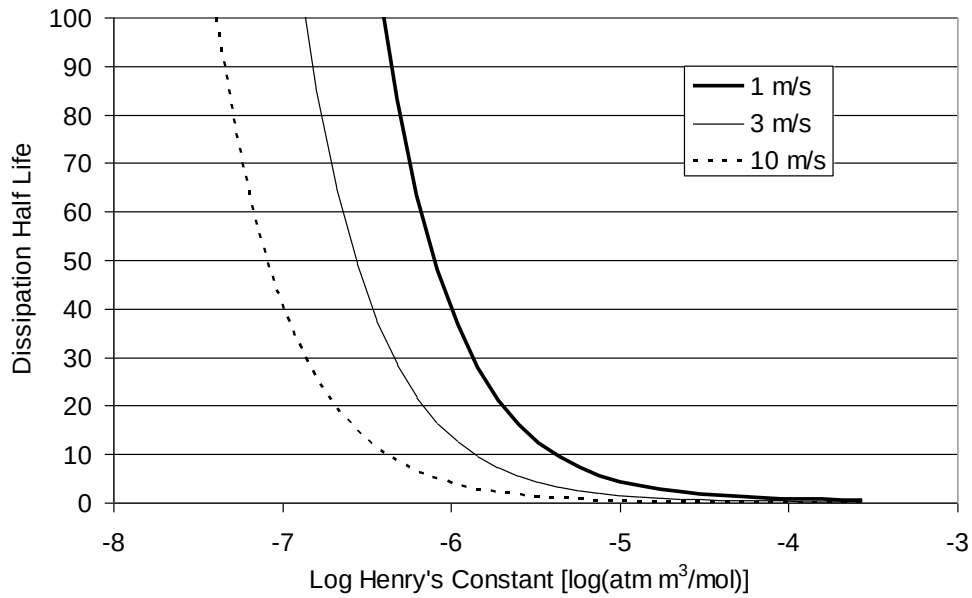

Figure 2-7. Sensitivity of volatilization half-life to wind speed (values in legend) and Henry's Law Constant. Simulations were created with a 10-cm pond at 25°C and a compound with a molecular weight of 200.

2.1.3.3 Effective Benthic Region Dissipation (Γ_2)

The overall benthic degradation in the standard water bodies, as defined in equation (2-8), is affected only by biodegradation and hydrolysis. As with the water column, EPA assumes that biodegradation in the benthic region affects all forms of pesticide (both dissolved and sorbed forms) and that hydrolysis affects only aqueous dissolved forms.

2.1.3.3.1 Benthic hydrolysis (μ_{hydr_2})

Benthic hydrolysis is assumed to occur at the same rate as hydrolysis in the water column, and the previous discussion of hydrolysis in the water column applies for the benthic region. Thus,

$$\mu_{hydr2} = \mu_{hydr1} \tag{2-34}$$

2.1.3.3.2 Benthic Metabolism (μ_{bio_2})

Benthic metabolism may occur under aerobic or anaerobic conditions. Either rate can be derived from laboratory tests following standard EPA-approved protocols. These studies are typically conducted in aqueous/sediment systems at 20 to 25°C. As with water column metabolism, EPA assumes that sorbed-phase degradation occurs at the same rate as aqueous-phase degradation because of the inability of the test to distinguish the two. Temperature effects on metabolism are accounted for in an identical manner as for the water column (see previous discussion on water column metabolism). The effective rate is thus

$$\mu_{bio_2} = \mu_{measured}\left[Q_{10}^{\left(\frac{T-T_{ref}}{10}\right)}\right] \tag{2-35}$$

where $\mu_{measured}$ = laboratory measured anaerobic metabolism rate at T_{ref}

T = temperature of modeled water body [°C]

T_{ref} = temperature at which anaerobic laboratory study was conducted [°C].

2.1.3.3.3 Dry soil degradation

When water level is effectively zero, the model provides for a separate input to account for unflooded soil degradation. Typically this will be taken from an aerobic soil degradation study following standard EPA-approved protocols. Under unflooded conditions equation 2-35 still applies, but the measured value ($\mu_{measured}$) will be taken from the aerobic soil studies.

2.1.3.3.4 Benthic Leakage Coefficient (Λ)

The leakage coefficient in the benthic region represents the flow through the benthic region. Unlike in the water column, the benthic region concentration can increase or decrease due to leakage, depending on the relative concentrations in the water column and benthic regions. It has a similar effect on the benthic region as the mass transfer coefficient does, as evidenced by its position in equation 2-6. This parameter can be readily calculated from equation 2-9 or equivalently, as would be done in a computer program, by using previously calculated terms as in the following:

$$\Lambda = \left(\frac{Q_L}{v_1}\right)\frac{f_{w1}}{\Theta} \tag{2-36}$$

2.1.3.4 Mass Transfer (Ω)

The mass transfer term is best thought of as an overall coefficient that includes all means of pesticide exchange between the water column and benthic regions. This includes exchange through the aqueous phase as well as by mixing of sediments between the two compartments. The physical process of this combined mixing is assumed to be completely described by a first-order mass transfer coefficient (ω). The parameter ω is referenced to the aqueous phase, but implicitly includes exchange due to mixing of sediments as well as aqueous exchange. In compartment modeling, it is unnecessary to explicitly model the individual exchange mechanisms since all phases of a 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.

As developed elsewhere (USEPA, 2004), the volumetric mass transfer equation (2-9) can be broken into somewhat more fundamental terms as follows:

$$\omega = \frac{\mathrm{k_{xfer}}}{d_2}\left(\mathrm{m_{sed2}K_{sed2}} + \mathrm{v_2}\right) \tag{2-37}$$

And therefore

$$\Omega = \frac{k_{xfer}}{d_2} \tag{2-38}$$

where d_2 is the benthic depth, and where the term k_{xfer} is a geometry-independent mass transfer coefficient [m/s]. This latter term is best viewed as an empirical estimator of overall water column to benthic mass transfer. The term k_{xfer} is on the order of 10^{-8} m/s according to several sources (Vanderborght and Wollast, 1977, Schwarzenbach et al., 1993, Burns, 2000).

2.1.4 Pesticide Applications

PFAM allows the user to apply pesticides in ways that should cover most application possibilities. Users may apply pesticide to the dry soil or to the flood water. Additionally users may specify that the pesticide is manufactured to be slowly released into the application area. Dry applications will occur if the user specifies that the pesticide is applied to an unflooded field. In this case, the pesticide is automatically applied to the soil, which becomes the benthic region upon flooding. Upon flooding, the pesticide may enter the water column through physical mass transfer processes. If the user applies pesticide during a flood, then all pesticide is initially placed into the water column. This latter application occurs regardless of the presence of a canopy. Canopy interception does not occur in PFAM because the required foliar degradation and washoff parameters are typically unavailable for pesticide assessments. Thus, until better foliar studies and better data become available, PFAM makes the environmentally protective assumption that all pesticide enters the water column when an above canopy application occurs.

When the slow release option is selected the pesticide is assumed to be released in a first-order manner in which the amount of pesticide unreleased is

$$M_u = M_0 e^{-ksrt} \tag{2-39}$$

where M_u is the mass of unreleased pesticide (kg), M_0 is the original amount of pesticide (kg), k_{sr} is the release rate (day^{-1}) and t is time (days). PFAM calculates the mass released each day by

$$M_t = M_0 \left(e^{-ksrt} - e^{-ksr(t+\Delta t)} \right) \tag{2-40}$$

where M_t is the mass release for time t and Δt is the time interval (1 day). For practical purposes, the mass released does not extend to infinity. Rather PFAM allows the slow release to occur until 95% of the pesticide is released and the remaining (5%) is applied on the following day.

When multiple years are simulated, PFAM will automatically apply the pesticide in the same manner for all years. This practice is in keeping with the standard way that the US EPA performs exposure assessments for pesticides.

2.1.5 Degradates

Degradates are handled exactly like the parent in regard to their transformations. The production of degradates is from the first-order degradation of the parent compound and can be due to water, dry soil, or benthic metabolic degradation, photolysis or hydrolysis. Users can specify the stoichiometry of the degradate production. Up to two degradates in series are possible with PFAM as in

$$P \rightarrow X\ D1 \rightarrow Y\ D2$$

Where P is the parent compound, D1 is the first degradate, X is the number of moles of D1 created when one mole of P degrades, D2 is the second degradate that forms by the degradation of D1 and Y is the number of moles of D2 formed for one mole of D1 degraded. The molar ratios should be available from the stoichiometric equations supplied by the pesticide study submissions.

2.2 Computations

Because of the advantages of using an analytical solution for the chemical concentrations, the model is solved in a daily piecewise fashion. This is achieved by approximating the water volume changes by discrete daily changes in which the volume of the water column changes at the beginning of the day and remains constant for the duration of that day, as shown previously by equation 2-1. With the approximation of constant within-day volume, the concentration calculations are amenable to an analytical solution for the daily time steps. Mass is conserved in the water column by recalculating a new beginning day concentration with consideration of the volume change.

2.2.1 Initial Conditions

Initial concentrations for the standard water bodies are determined by the pesticide mass inputs. Depending on the pesticide-management practice, a pesticide may be applied during a flooded condition or directly to the ground prior to flooding. For pesticide applications during a flooded period, the model places all applied pesticide into the water column. For pesticide applications during dry periods, the model places all pesticide mass into the soil compartment.

For this model, there is an instantaneous water depth change at the beginning of the day due to hydrologic conditions (see *Flood and Overflow Control* above), and the pesticide concentration in the water column is adjusted accordingly. The initial concentrations, upon addition of new pesticide inputs, are then expressed as:

$$C_{10} = \frac{f_{w1}}{v_1}\left[\left(M_{input,1}\right) + \frac{v_{1,prior}}{f_{w1,prior}} C_{10,prior}\right] \tag{2-41}$$

$$C_{20} = \frac{f_{w2}}{v_2}\left(M_{input,2}\right) + C_{20,prior} \tag{2-42}$$

where $M_{input,1}$ = mass of pesticide applied to water column (kg)
$M_{input,2}$ = mass of pesticide applied to benthic/soil compartment (kg)
C_{10} = initial aqueous concentration of water column for current time (kg/m^3)
C_{20} = initial aqueous concentration in benthic region for current time (kg/m^3)
$C_{10,prior}$ = aqueous concentration in water column before new mass additions (kg/m^3)
$C_{20,prior}$ = aqueous concentration in benthic region before new mass additions (kg/m^3)
$v_{1,\ prior}$ = the water column volume from the previous day (m^3)
$f_{w1,prior}$ = f_{w1} from the previous day

2.2.2 Analytical Solution for Concentrations

Equations (2-5) and (2-6) along with the initial conditions represent the two equations describing the standard water bodies. These equations are in the form of

$$\frac{dc_1}{dt} = Ac_1 + Bc_2 \tag{2-43}$$

$$\frac{dc_2}{dt} = Ec_1 + Fc_2 \tag{2-44}$$

where:

$$A = -\Gamma_1 - \Omega\Theta \tag{2-45}$$
$$B = \Omega\Theta \tag{2-46}$$
$$E = \Omega + \Lambda \tag{2-47}$$
$$F = -\Gamma_2 - \Omega - \Lambda \tag{2-48}$$

These equations have the following solution:

$$c_1 = X_1 e^{\lambda_1 t} + Y_1 e^{\lambda_2 t} \tag{2-49}$$
$$c_2 = X_1 \frac{(\lambda_1 - A)}{B} e^{\lambda_1 t} + Y_1 \frac{(\lambda_2 - A)}{B} e^{\lambda_2 t} \tag{2-50}$$

where:

$$\lambda_1 = \frac{A + F + \sqrt{(A+F)^2 - 4(FA - BE)}}{2} \tag{2-51}$$
$$\lambda_2 = \frac{A + F - \sqrt{(A+F)^2 - 4(FA - BE)}}{2} \tag{2-52}$$
$$X_1 = \left[\left(\frac{\lambda_2 - A}{B}\right) C_{10} - C_{20}\right] \frac{B}{\lambda_2 - \lambda_1} \tag{2-53}$$
$$Y_1 = \left[C_{20} - \left(\frac{\lambda_1 - A}{B}\right) C_{10}\right] \frac{B}{\lambda_2 - \lambda_1} \tag{2-54}$$

Average concentrations can be determined over any interval in which all parameters remain constant. In the case of the proposed model, parameters change on a daily basis, so the average water column concentration over any of these time intervals, is expressed as

$$C_{1,avg} = \frac{X_1}{\lambda_1 (t_2 - t_1)} e^{\lambda_1 t2} + \frac{Y_1}{\lambda_2 (t_2 - t_1)} e^{\lambda_2 t2} - \frac{X_1}{\lambda_1 (t_2 - t_1)} e^{\lambda_1 t1} - \frac{Y_1}{\lambda_2 (t_2 - t_1)} e^{\lambda_2 t1} \tag{2-55}$$

where $C_{1,avg}$ = average water column concentration from t_1 to t_2 [kg/m^3]
t_1 = beginning of the time interval [s^{-1}], (zero for the case of daily estimates)
t_2 = end of the time interval [s^{-1}], (86400 seconds for PFAM case of daily estimates)

2.3 Post Processing

Effluent from PFAM can be optionally routed to various user-defined water bodies, including two standard EPA water bodies: the EPA Index reservoir and the EPA farm pond. Both flowing and static water bodies may be simulated. The receiving water body hydrology and chemical processes are calculated by a program nearly identical to the PFAM program already described. The receiving water body, however, receives influent water from PFAM effluent as well as runoff from the surrounding area.

Receiving water body possibilities are shown in Figure 2-8. In this figure, the receiving bodies (or mixing cells) are depicted by the blue cubes. These mixing cells, with user-defined dimensions, represent the outlet or terminal point of a watershed and could represent a section of a flowing water body or a large reservoir, depending upon the parameterization. The

postprocessor automatically calculates the runoff from the water shed and tracks the effluent from the flooded plots within the watershed. Influent water into any receiving water body is determined by the following equation:

$$Q = Q_{PFAM} + Q_{WS} + B + P \tag{2-56}$$

Where
Q = flow entering the receiving water body
Q_{PFAM} = PFAM water releases
Q_{WS} = Runoff from surrounding watershed
B = Baseflow through water body
P = Direct Precipitation-Evaporation

The PFAM releases are calculated as previously described. PFAM will give the daily amount of water that leaves the system, and this release feeds into the receiving water on a daily basis. The runoff from the surrounding area is calculated by the NRCS curve number method (NRCS, 2003). This calculation requires a user estimate of the watershed area and an appropriate curve number. A base flow may also be appropriate and the post processor allows for this entry. This base flow value should represent the flow through the receiving water body during periods not dramatically affected by local rain event or flooded agriculture releases.

Chemical processes are calculated the same way as described in PFAM above with the same chemical inputs. Concentrations in the receiving water body are reported in a manner similar to the way that the US EPA reports concentrations for standard pesticide assessments (i.e., as 1-in-10-year events for the peak, 4-day, 21-day 60-day and yearly averages).

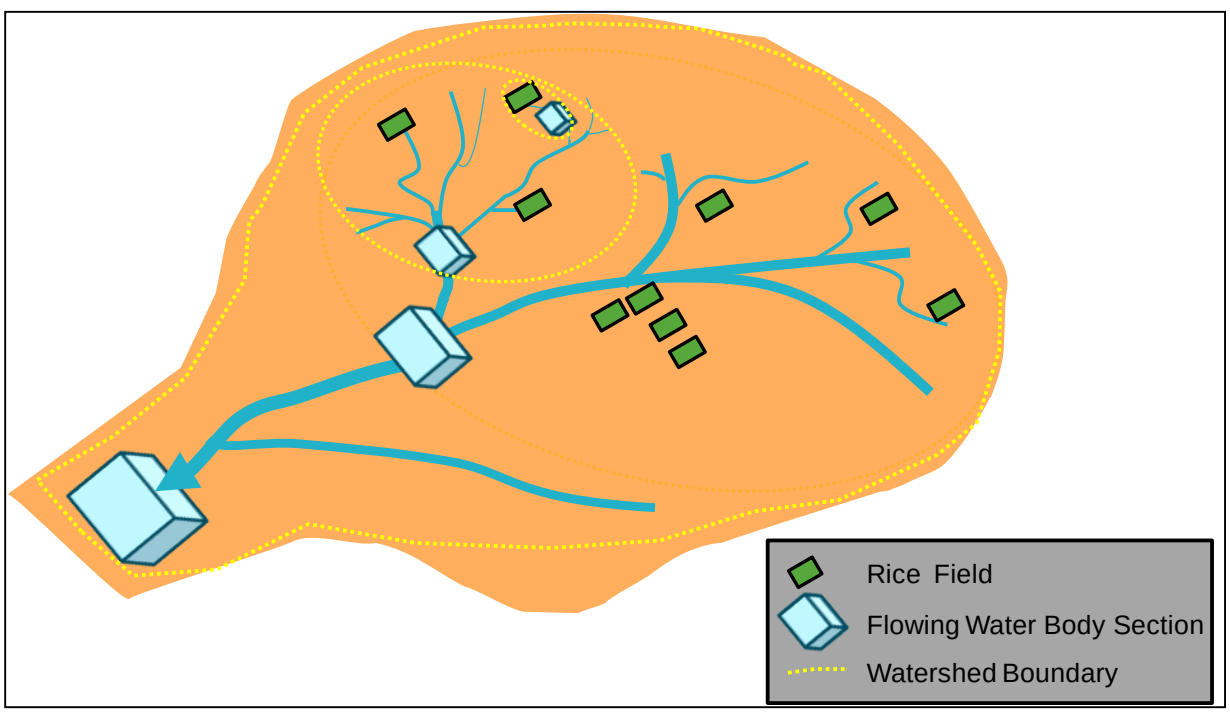

Figure 2-8. The conceptualization of the water body and watershed. Various setups such as these are available by use of the post processor.

3. Evaluation of PFAM Using Criteria for Regulatory Assessments

In general, pesticide-exposure models should be able to reasonably represent pesticide behavior, capturing the most environmentally salient physical and chemical properties of pesticide use. At the same time, such models should not be overly complex because only a few chemical properties are available from the pesticide registration process. Furthermore, pesticide exposure assessments are typically generic with regard to their representation of the environment. In other words, the model scenarios are often surrogates for large areas or an entire nation and are rarely site-specific. On a large spatial scale with commensurate large-scale variability, it may not be productive to create complex models and populate them with site-specific parameters since such efforts would not raise the accuracy of the model above the background noise. However, because regulatory pesticide exposure models are primarily used for environmental protection, they should provide reasonable high-end estimates of environmental concentrations when appropriately parameterized and compared to a sampling of field data. The purpose of this investigation is to evaluate PFAM in the context of a regulatory application by comparing the model-predicted results with actual field data and evaluate whether PFAM can produce high-end, but reasonable estimates.

PFAM was developed consistent with the guidance documents of the USEPA Council for Regulatory Environmental Models (CREM) (USEPA, 2009a) and the USEPA quality assurance (QA) program (USEPA 2002). The CREM guidance (USEPA, 2009a) covers development, evaluation, and use of models intended for environmental regulatory decisions. The QA guidance describes specific information concerning what is required to plan for model development to ensure that a model is scientifically sound, robust, and defensible for regulatory purposes. These two guidance documents are complementary and provide a solid basis for model development and application in a regulatory setting.

According to USEPA (2009a), model evaluation is the process for determining whether a model's results are of sufficient quality to serve as the basis for a decision, where the meaning of *quality* depends on the model's application or intended purpose and is defined by *quality objectives*. Evaluation addresses whether model development incorporates sound science, whether the model requirements are suitable for the available data, and whether the model compares sufficiently well with real data. Model verification (code checking) has been performed throughout PFAM development and has been documented by US EPA Science Advisory Panels (USEPA, 2004) and by other agencies (Luo, 2011). The model's quality objectives concerning data corroboration, often referred to as *validation* (Rykiel, 1996), are covered in this chapter.

The quality objectives of regulatory models such as PFAM, which are surrogate representations of pesticide use over large spatial scales, focus on their performance as screening-level tools. Because of the high uncertainty associated with large-scale assessments, a regulatory model's output should provide reasonable but appropriately conservative estimates of exposure in order to be protective. That is, the quality objectives are (1) that the possibility of incorrectly giving passage to a chemical that is dangerous is at an acceptable level and (2) that

there is not an unreasonable burden on the regulated community due to excessive over predictions of exposure.

How well a screening model minimizes the potential for false negatives (the first objective) can be evaluated by comparing model estimates to measured concentrations in the field. Determining whether model estimates do not place undue burden by excessive false positives (the second objective) is less straightforward. One evaluation measure for the second objective is to compare PFAM's predicted concentrations to that of the currently used and presumably more conservative screening model. In this sense, the second objective is met if the model predicts concentrations that are less than the currently used screening model, thereby allowing passage of chemicals that otherwise would require more testing

3.1 Methods

3.1.1 Field Studies

Field data used in this evaluation came from pesticide registration studies submitted to the United States Environmental Protection Agency (USEPA). Manufacturers interested in using their pesticides for aquatic agriculture or other aquatic applications may submit aquatic field studies that characterize the fate of a pesticide after its application to a water body such as a rice paddy or pond. Typically, these studies follow the course of a pesticide's existence at the study site, from the time of its application until either the pesticide completely disappears from the site or the water body completely drains.

These studies vary widely in quality and usability for PFAM evaluations. Out of the hundreds of aquatic field studies, five were selected based on the completeness of site characterization, the temporal and spatial resolution of the pesticide measurements, and the persistence of the pesticide. Complete site characterization requirements include daily weather, soil and sediment characterization, and water levels. The need for temporal and spatial completeness of the data required that both sediment and overlying pesticide concentrations were measured frequently enough over a long enough period such that important hydrological and chemical events would be captured (i.e., flooding, draining, as well as pesticide degradation). With regard to pesticide degradation, somewhat persistent pesticides typically gave better temporal resolution than fast-degrading pesticides. Studies with pesticides that disappeared within a few days lacked enough temporal data points to be useful. In addition, the final chosen studies exhibited a range of aquatic management practices, in order to allow examination of a variety of pesticide-application schemes, including preflood applications, post-flood applications, flow-through systems, and static ponds. Table 3-1 provides a summary of the relevant characteristics of the five selected studies.

These five studies (Table 3-1) represent a range of potential applications. Four of the studies are for rice applications, which will likely be the most frequent application for PFAM, and one study is for aquatic weed control in a small pond. Study A represents a rice culture application in which the pesticide is applied to the soil before the field is flooded, as is often the case for weed control. Studies B and D represent cases in which a pesticide is applied to a flooded field, which is common for fungicides or insecticides. Study C represents another common rice application involving a continuous flow system in which flowing water is maintained at a constant level by a weir. In addition to these rice applications, Study E provides an example of a natural pond-type application of pesticide. The next sections further describe the details of the studies.

Table 3-1. Field Properties relevant to simulation.

Property	Study A [(a)]	Study B [(b)]	Study C [(c)]	Study D[(d)]	Study E[(e)]
Location	Stutgart, AR	Carlisle, AR	Bay City, TX	Pattison, TX	Elk Grove, CA
Water Management Practice	Preflood Application	Post-Flood Application	Continuous Flow	Post-Flood Application	Static Pond
Chemical	Pendimethalin	Bispyribac Sodium	Propiconazole	Carbaryl	Triclopyr
Area (m^2)	2800	94	7100	929	1200
Organic Carbon (%)	1.1	0.57	1.55	0.66	0.88
Application date	June 2	June 12	Sep 5 & 20	June 18 & 23	July 26
Pesticide Mass Applied (kg/ha)	1.1	0.060	0.189	1.68	20
Flood level (cm)	7.6	15	7.6	4 to 12	80
Tolerance (cm)	5.1	7.6	--	9.5	80
Flood Date	June 22	May 31	--	May 28	--
Drain Date	Sep 20	Aug 23	--	July 30	--
Turn Over (d^{-1})	--	--	1.06	--	--
Crop Plant Date	May 29	April 12	Aug 15	April 15	--
Crop Full Height Date	August 8	July 12	Oct 1	50 % on June 20	--
Crop Harvest Date	not harvested	October 3	Oct 30	not harvested	--
Max Crop Coverage (fraction)	0.90	0.90	0.90	0.90	0
pH	8		7.2	7.9	8
SS (mg/L)	--	40	--	--	8
Bulk Density (g/ml)	--	0.94	1.35	--	1.1

(a) US EPA (1998a), (b) US EPA (1999), (c) US EPA (1992), (d) US EPA (1994), (e) Petty et al. (2001)

3.1.1.1 Study A: Stuttgart AR Pendimethalin Study Summary

This study (USEPA, 1998a) is an example of a pre-flood application. The study took place near Stuttgart, Arkansas on two dry-seeded rice plots. The soil was a silt loam with organic carbon content of 1.1 percent. Each plot was about 1400 m^2. The study reflected typical rice agronomic management practices for the region, including flooding of the field, adding makeup water, and eventual draining of the floodwater. Table 3-1 presents the characteristics that are relevant to modeling.

Because the two plots in this study were nearly identical, samples from the two plots are treated as replicates rather than as different studies. The two plots were separated by about 30 feet. The plots differed in the time that the rice crop was planted (May 11 and May 29), but were otherwise equivalent with regard to management practices. Note that planting date (and effectively canopy development) only affects the photolysis rate in PFAM. Because degradation

by aerobic metabolism (as discussed later under Chemical Parameters) will overwhelm photolysis in this case, the model will be insensitive to planting, thus allowing the plots to be treated as replicates.

Plots were flooded on June 22 and maintained in flood stage until September 20. The flood level varied from 5 cm to 10 cm (average 7.6 cm). Water was supplied as needed, typically in amounts of about 5 cm at a time, with the total estimated water input ranging from 60 cm to 84 cm for the duration of the study (ending Sep 9). Pendimethalin was applied as a broadcast spray by a backpack sprayer at 1.1 kg/ha to dry plots on June 2. Rice plants were at early germination stage to 4-leaf stage for the two plots, so plant interception of pendimethalin was minimal.

Precipitation, temperature, and wind speed were measured at an offsite weather station about eight miles from the site. Evaporation was not included in the data, so evaporation was estimated by Hamon's formula (Hamon, 1961) which bases evaporation on temperature and latitude. The study report recorded the weather during this period to be typical.

Samples were taken from both the water column and the soil (before and after flooding). Soil/sediment samples were taken from 0 to 15 cm deep and divided into subsamples of 0 to 7.6 cm and 7.6 to 15 cm, with pesticide mass measured for each subsample. The vast majority of benthic pesticide mass (96 to 100%) remained in the top 7.6-cm meter core. Water samples were taken as grab samples after flooding. Sampling continued until near complete dissipation of the chemical.

3.1.1.2 Study B: Carlisle AR, Bispyribac Sodium Summary

This study (US EPA, 1999) is an example of a post-flood application of pesticide; that is, the farmer first flooded the field and then applied pesticide directly to the water. The study took place on a 94-m^2 plot in a rice paddy near Carlisle, Arkansas. The soil was a poorly drained silt loam with an organic carbon content of 0.57 percent. Table 3-1 summarizes relevant modeling parameters. For this Arkansas study, typical agricultural practices were used, including flooding and draining of the field.

The field was flooded May 31 to a depth of about 15 cm. Bispyribac sodium was applied to the flooded field on June 12 at 0.06 kg/ha to the plot by a backpack sprayer. At application, the rice was about 0.42 m high with a 50% canopy cover. For the duration of the study, irrigation water was added as needed in about 7.6-cm amounts (tolerance was thus assumed to be 7.6 cm).

Water samples were taken up to 56 days after application. Sediment samples were taken up to 112 days after application from 0-15 cm and from 15 cm to 30 cm. No pesticide was detected below 15 cm. Because soil samples were drained of excess water, there is potentially some added uncertainty regarding mass of pesticide lost. However, the samples remained quite wet after draining (25% by weight) so that losses would be fairly negligible. Sampling continued until depletion of the chemical.

Weather, rain, and air temperature were recorded on site. Pan evaporation was taken from the US EPA data set (Burns et al., 2007) for the nearby Little Rock weather station. The study kept records of the recharge water used to maintain field flood level, but the study did not directly track water level in the field. The total recharge water was 310 cm through day 112.

3.1.1.3 Study C: Bay City, TX Site Propiconazole

This test (US EPA, 1992) is an example of a continuous flow-through system. In this type of system, the water level remains fixed by water continually flowing through the system and over a weir, a practice that is typical for this Texas area. The study took place on a 0.71-ha plot near Bay City, Texas. The average turnover due to flow through the water body was 1.06 volumes per day. The depth of the water was 15 cm. The sediment was clay with an organic carbon content of 1.55%.

The plot received aerial applications of propiconazole at 0.189 kg/ha on September 5 and again on September 20 to the flooded field under calm winds (0-3 mph). The original rice crop had been harvested on August 1, and the pesticide applications were applied during the ratoon crop. The applications occurred about mid-way through the ratoon-growing season, allowing for the possibility of canopy interception of propiconazole; however, the study did not report the amount of canopy coverage. Because PFAM does not account for canopy interception, this study will provide for some information concerning the interception significance in regard to PFAM output. Above-canopy application efficiency was reported to be 59% and 75% for the two applications, respectively. The cause of these inefficiencies is unknown. The field was drained over the period from Sep 30 to Oct 2.

Weather measurements were taken on site and included temperature, precipitation, and wind speed. Evaporation was not recorded on site, so it was taken from US EPA data (Burns et al., 2007) for the nearest available site which was Victoria, TX. A digital flow meter kept track of outflow from the water body.

Both sediment and water samples were collected in the paddy. Soil/sediment samples of at least 25 cm were taken from three locations on each sampling day. Sediment samples were taken and composited from depths of 0 to 10 cm and from 10 to 20 cm. No pesticide was detected below 10 cm. Water samples of 1.3 liters were taken at three locations on each sampling day and composited into a single sample. Water quality measurements such as pH and dissolved oxygen were also recorded.

3.1.1.4 Study D: Pattison Texas, Carbaryl

This study (US EPA, 1994) is another example of a post-flood application of a pesticide in which the pesticide is applied directly to the water of a flooded field. This study took place near Pattison, TX. The water level varied over the course of the study but was typically about 7 cm deep. The plot area was 929 m^2, with levees surrounding it to retain water. The soil in the plot was a silt loam with an organic carbon content of 0.66%.

Rice planting occurred on April 15, followed by flooding of the plot on May 28. Carbaryl was applied by spray boom above the rice canopy two times, once on June 18 and again on June 23. At the time of the applications, canopy coverage was about 50 percent, so canopy interception of carbaryl should have occurred. However, as stated in Young (2012), foliar washoff and foliar degradation data is almost never available for pesticide assessments. For this reason, PFAM developers elected to take a conservative approach and allowed only direct application of pesticide to the water body rather than to the plant canopy (Young, 2012). This study will allow a test of the protectiveness of that assumption.

The site was equipped with a siphon mechanism that maintained a minimum water level in the plot. The water level varied over the course of the study with a maximum of 12 cm. The minimum allowed depth was around 2.5 cm. It was clear from the water level data that the water level was allowed to rise during the study from 4 cm to 12 cm. The minimum acceptable level

also appeared to rise, although these management practices were not detailed in the study report. Because the exact water level was unknown and because of its potential impact on the results, the water level for the simulation was calibrated to roughly approximate these changes in depth by changing the simulated depth and tolerance three times during the simulation. The plot was drained on July 30, and the rice was left standing in the plot for the duration of the study.

Both soil and water samples were taken during the course of the study and analyzed for carbaryl. Soil was sampled to 15 cm and segmented into two 7.5-cm segments. Top segments were combined to create a single sample. Carbaryl did not move below the top 7.5-cm segment. The study reported weather data, including daily rainfall, pan evaporation, and air temperature. The study did not report wind speeds, so wind speed was obtained from the closest NOAA weather station (Houston-Bush Airport).

For carbaryl, system pH is very important for degradation by hydrolysis. Carbaryl degradation is highly dependent on pH, with the degradation rate increasing as pH increases. For the measured water pH of 7.9 for this system, the half-life of carbaryl was estimated to be about 3 days based on data in US EPA (2007b).

3.1.1.5 Study E: Sacramento, CA Triclopyr

This study (Petty et al., 2001, USEPA 1997a) was conducted near Elk Grove, CA at the California Department of Fish and Game Aquatic Toxicology Lab in two fabricated ponds. The test ponds were 0.12 hectare with a depth of 0.8 m. The sediments were generally sandy clay loams with an average organic carbon content of 0.88%. This study is different from the other studies in that it is a non-crop water body without water release or resupply. This study uses the chemical triclopyr, which is highly susceptible to photodegradation; hence this study will allow for the evaluation of the photolysis routine in PFAM. The photolysis routine depends upon the actual latitude of the study (38.25 N latitude) as well as factors responsible for light attenuations, such as suspended solids. Table 3-1 reports the properties obtained from the study and used as model inputs.

Using a 20-liter powered sprayer with a hand wand, triclopyr was applied to the ponds to achieve a concentration of 2.5 mg/L in the water. The pesticide was sprayed slightly above or just within the water surface. Application to both test ponds occurred the morning of July 26.

A weather station at the site collected weather data, including air temperature, relative humidity and wind speed. Daily evaporation was estimated from temperature using Hamon's formula (Hamon, 1961). No precipitation occurred during the study period, and during the course of the study the ponds did not receive additional water to offset evaporation.

Water samples were taken in duplicate at two depths at each water sampling station, and a 400-mL grab sample was collected at each sampling event at 1/3 and 2/3 total depth of the water column. Sediment samples of approximately 300 g were collected from the top 5 cm of benthic sediment, using clamshell post-hole diggers.

3.1.2 Chemical Properties

Chemical properties required to populate the model (i.e., sorption, degradation) are readily available from studies submitted by pesticide manufacturers to support pesticide registrations. These laboratory studies are conducted on soils and in environments that are not necessarily representative of the field conditions, and thus the laboratory-derived chemical properties values may vary from the actual site values. Direct chemical property measurements from a particular field study site are usually nonexistent, as measurement of those properties is

not a requirement for field-study submissions. Even though direct measurements are not available, simulations can still be made using the best available resources. This approach would be similar to the way a regulator would make a pesticide assessment as well, since only laboratory-derived, non-site specific chemical properties are available for registration. This limitation is not particularly disadvantageous, since regulators are not typically concerned with the concentrations at any particular single site, but instead are concerned with the broader question of concentrations for all potential use sites.

Whenever possible, chemical inputs were taken from easily accessible publically available sources such as internet-accessible databases of pesticide registration documents or other public databases. Occasionally when chemical parameters were not available through publically available documents, alternate means of estimations such as EPI Suite (USEPA 2009b) were used. No effort was made to make the input parameters conservative (protective or worst-case) as would be typically done in a purely regulatory use of an environmental model, since application of conservativeness into the assessment is a policy decision for which none has been made at this time. Instead, since the purpose here is to evaluate the model's performance rather than produce regulatory values, best estimates (which for the most part, were assumed to be the mean value of any values found) were used. Table 3-2 presents these generic non-site-specific properties used for the PFAM simulations.

Table 3-2. Relevant chemical properties of compounds in the field studies.

Property	Pendimethalin[a]	Bispyribac Sodium[c]	Propiconazole[d]	Carbaryl[e]	Trichlopyr Acid [f]
Study	Study A	Study B	Study C	Study D	Study E
PC Code	108501	078906	122101	056801	116001
Molecular Wt	281	452	342.2	201	256
Soil Aerobic Half-life (day) /(°C)	126/25	19/25	53/25	4/20	13/25
Water Aerobic Half-life (day)/(°C)	10 / 25	64 / 25	426/25	stable	142/25
Water Anaerobic Half-life (day)/(°C)	50/20	99 / 25	363/25	72/20	1300/25
Photolysis Half-life (day)/(°N latitude)	21/42	stable	stable	21 / 40	0.6/ 42
Hydrolysis Half-life (day)	stable	stable	stable	1.67 @ pH 7.9	stable
Vapor Pressure (torr)	3e-5	1e-7	1e-6	1.36e-6	1.26e-6
Solubility (mg/L)	0.375	73000	110	32	435
Heat of Henry (J/mol)	62,000[b]	--	45,000[b]	58,000[b]	--
K_d (ml/g)	--	0.6 – 2.0	--	--	0.6
K_{oc} (ml/g)	15000	114	648	198	--

(a)US EPA (1997b), (b)US EPA (2009b), (c)US EPA (2001), (d)US EPA (2006) , (e)US EPA (2007b), (f)US EPA (1998b)

3.1.3 Simulations and Comparisons

Most PFAM inputs can be readily determined from the field study reports or from the methods for obtaining chemical properties as described above and given in Table 3-1 and 3-2. Some parameters were not available from the studies, and in those cases, the PFAM default

values were used. These defaults are the same as those used in EPA's standard water bodies (USEPA, 2004) and are listed in Table 3-3.

Table 3-3. Default Parameter Values for PFAM (parameters defined in Young 2012)

Parameter	Value
Mass Transfer Coefficient (m/s)	10^{-8}
Benthic Depth (m)	0.05
Benthic Porosity (m^3/m^3)	0.5
Bulk Density (g/cm^3)	1.35
f_{oc} Benthic (—)	0.01
f_{oc} Water Column (—)	0.01
Suspended Solids (mg/L)	30
Chlorophyll (mg/L)	0.005
Water Column DOC (mg/L)	5
Benthic DOC (mg/L)	5
Q10	2
DFAC	1.19

Water concentrations and water levels were simulated with PFAM and compared to the available data. Comparison of water-column concentration was straightforward by observing the PFAM output of daily average concentrations along with the available study data. As for water management, PFAM simulates water additions, releases, and overflows, and level; however, the studies did not always report this information, so only limited direct comparisons could be made regarding hydrology (typically only water additions were reported). Comparisons were made when these data were available.

Soil concentration comparisons are presented here in terms of mass per area since the field sampling strategy did not indicate how the pesticide was distributed within the sample core. Thus, it is not possible to determine a volumetric concentration that is comparable to PFAM estimates that are based on a 5-cm sediment zone (see Table 3-3). This strategy of comparing the mass-per area values of the PFAM simulation with the sample core data allows an evaluation of how well PFAM simulates the total mass of pesticide in the sediment rather than the concentration.

3.1.4 Hypothetical Regulatory Simulations

Historically, the US EPA bases regular (non-flooded agriculture) aquatic assessments of pesticides on a 30-year simulation in which a pesticide is used at its maximum application every year. This type of assessment allows for the analysis of the temporal variability, which is primarily due to changes in the weather from year to year. In order to evaluate the potential use of PFAM in such a likely regulatory application, PFAM simulations were also conducted with a 30-year simulation. These simulations were conducted using the scenarios and chemical properties previously described but with the USEPA regional rainfall data (Burns et al., 2007) and with the additional condition that the same application pattern was made every year of the 30-year simulation. Table 3-4 presents the identification information for the weather data (Burns et al., 2007) used in the long-term simulations.

Table 3-4. Weather data used for long-term simulations.

Study	Actual Location	CEAM Weather File	WBAN
A	Stuttgart AR	Little Rock (1961-1990)	13963
B	Carlisle, AR	Little Rock (1961-1990)	13963
C	Bay City, TX	Victoria (1961-1990)	12912
D	Pattison, TX	Houston (1961-1990)	12960
E	Sacramento, CA	Sacramento (1961-1990)	23232

Chemical and scenario information were kept the same as in the field-study-comparison sections described above. Because there is yet no guidance or policy regarding PFAM inputs, no effort was made to make the chemical input parameters conservative, as is done in other US EPA aquatic assessments (e.g., using 90th percentile degradation half-lives as inputs rather than typical values). Thus, there is no built-in conservatism for the evaluations that follow.

In addition to the long-term analysis of PFAM variability, comparisons with the current first tier screening calculation was also conducted. This first-tier screening concentration is equivalent to the concentration that would occur if the pesticide application were equilibrated with 10 cm of water and 1 cm of soil that has a bulk density of 1.3 g/mL and 1% organic carbon. The resulting Tier 1 concentration estimate is only dependent on the partition coefficient and is calculated as follows:

$$C_w = \frac{M_a}{0.00105 + 0.00013K_d} \tag{3-1}$$

Where C_w = the Tier 1 water concentration

M_a = mass of pesticide applied per area (kg/ha)

K_d = distribution coefficient (ml/g) = $0.01K_{oc}$

K_{oc} = organic carbon partition coefficient (ml/g)

3.2 Results and Discussion

3.2.1 Study A: Arkansas, Pendimethalin Simulation Results

Figure 3-1 shows the PFAM-simulated water levels for the Study A site along with the reported amounts of water additions. This study reported water additions but not water levels. Therefore, hydrology comparisons focus on the additions rather than on water level. As Figure 3-1 shows, the predicted water additions match well in frequency and magnitude to the actual water additions, except for the period between 40 and 50 days. Between 40 and 50 days, there were two more actual additions than what PFAM predicted. Primarily because of the refills during this 10-day period, which amounted to about 1 m, the total PFAM estimates (0.52 m) are lower than the actual total water additions 0.71 m (±0.12). The discrepancy is possibly due to the offsite measurements of the weather data, which may not exactly correspond to the local weather at the site.

Figure 3-2 shows the predicted water column concentration for Study A along with the measured data. Note that this was a preflood application of pesticide, and therefore water column concentrations do not appear until after the field is flooded (20 days after pesticide application). The actual water column concentrations do not achieve the initial PFAM-simulated value. The most likely reason for this is that the simulation is also over predicting the available

pesticide in the soil at the time of the flood, which may be due to an underestimation of the soil degradation rate, an overestimate of the actual amount of pesticide applied, or possibly extraction and recovery issues. Note that chemical fate parameters did not come from direct field measurements at this site, as described in the Chemical Properties section. As a result, there is uncertainty regarding the accuracy of the soil degradation estimates. Nevertheless, the predictions are on the same order of magnitude as the data, and as is desirable for a regulatory model, the simulations err on the high side of the data. One additional noticeable quality of the PFAM prediction is that it fluctuates considerably and coincides with the fluctuation in the water level. In this case, water level decreases cause increases in concentration, as water is volatilizing at a faster rate than the pesticide.

Figure 3-3 shows the simulated benthic concentrations. The initial measured mass is similar to the simulated mass, as would be expected from an acceptable field study. (This result indicates good recovery of pesticide from the field). PFAM predicts the remainder of the data reasonably well, although PFAM concentrations are consistently higher than the data, which is an acceptable quality for a regulatory model. Actual dissipation occurs somewhat faster than PFAM predictions, and this outcome may be due to the underestimation of degradation rates. Again, as with all the studies here, the environmental fate properties did not come from direct measurements at this site and thus the actual degradation rate at this site is unknown.

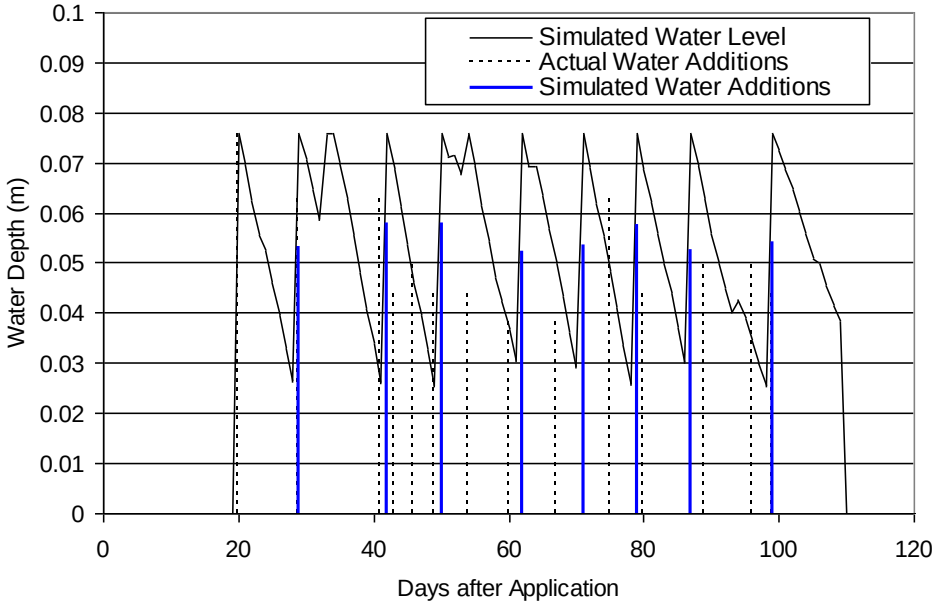

Figure 3-1. Simulated water level of Study A along with the reported and simulated water additions.

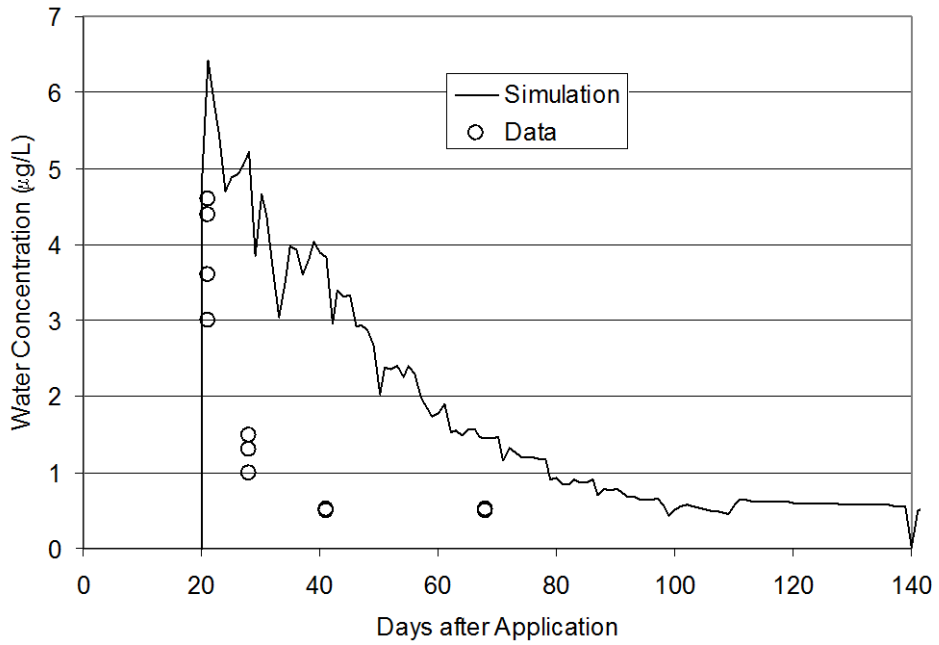

Figure 3-2. The simulated floodwater pesticide concentration and the measured data for Study A. (Water column concentrations do not exist until after flooding on Day 20.)

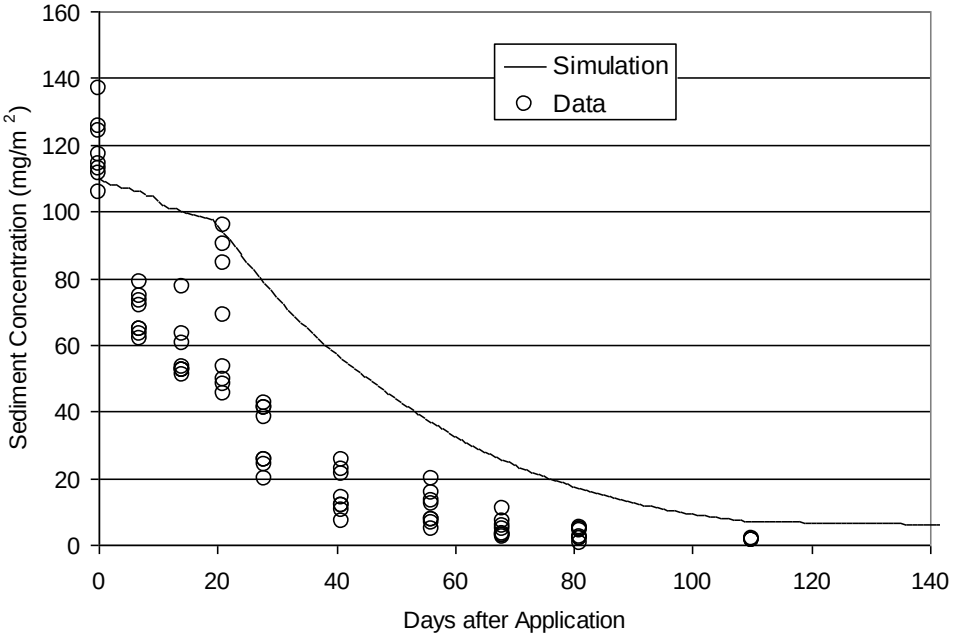

Figure 3-3. The simulated sediment pesticide concentration and the measured data for Study A.

3.2.2 Study B: Arkansas, Bispyribac Sodium Simulation Results

Figure 3-4 shows the simulated water levels and the reported and simulated water additions. Like Study A, this study gave water additions but not water levels over time. Comparisons thus focus on these additions rather than the direct water levels. The actual water additions are very similar in magnitude and timing to the simulated additions, inferring that PFAM captures the hydrologic functions reasonably well. Predicted total additions were 0.58 m, which was about 20 percent higher than the actual reported additions of 0.48 m. This is a reasonably good simulation especially since pan evaporation was not measured on site but instead taken from a station 40 km away.

Figure 3-5 shows the water column concentration over time. Note that this was a preflood application, so water column concentrations do not appear until the flood occurs on day 11. The simulated initial concentration (day 11) is similar to the measured concentration, indicating good application efficiency. This good initial simulation occurs despite the presence of a canopy with 50% coverage, which supports neglecting pesticide canopy holdup, as does PFAM.

With regard to the pesticide's temporal decline in the water column, the simulated concentration drops slower than the measured data, indicating that the actual pesticide moves into the soil faster or degrades faster than the simulation. Note also that the simulation clearly pulsates due to water level changes; however, the data have lower temporal resolution and thus do not confirm this effect.

Figure 3-6 shows the simulated and measured benthic concentration over time. Both the simulated concentration and the data exhibit an increase, a peak, and a decline over time. The increasing benthic mass is initially well simulated, but the actual data peak and begin to decline much sooner than the simulation. The actual degradation rate in the sediment appears to be faster than the simulated rate, which is not unexpected given that the degradation rates were not measured at this particular site. However, PFAM does err on the high side, which is an acceptable feature in a regulatory model. The apparent poor representation of the benthic mass should be placed into context: the amount of pesticide mass in the benthic region at any time according to the data is about 0.1% of the total mass in the system. Because of the relatively small amount of mass transferred to the benthic region, it is reasonable that there should be a large uncertainty in the measurements.

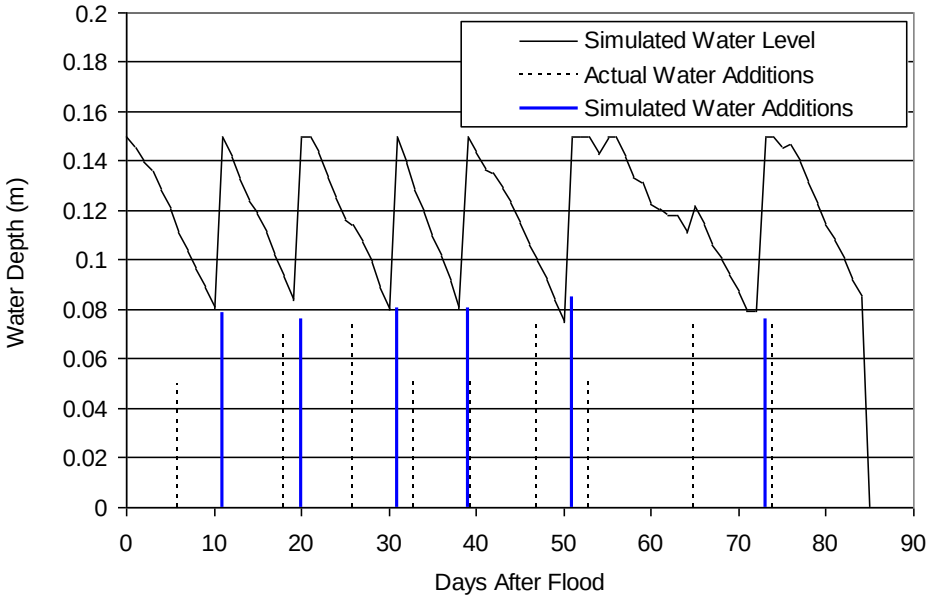

Figure 3-4. Simulated water level of Study B along with the reported and simulated water additions.

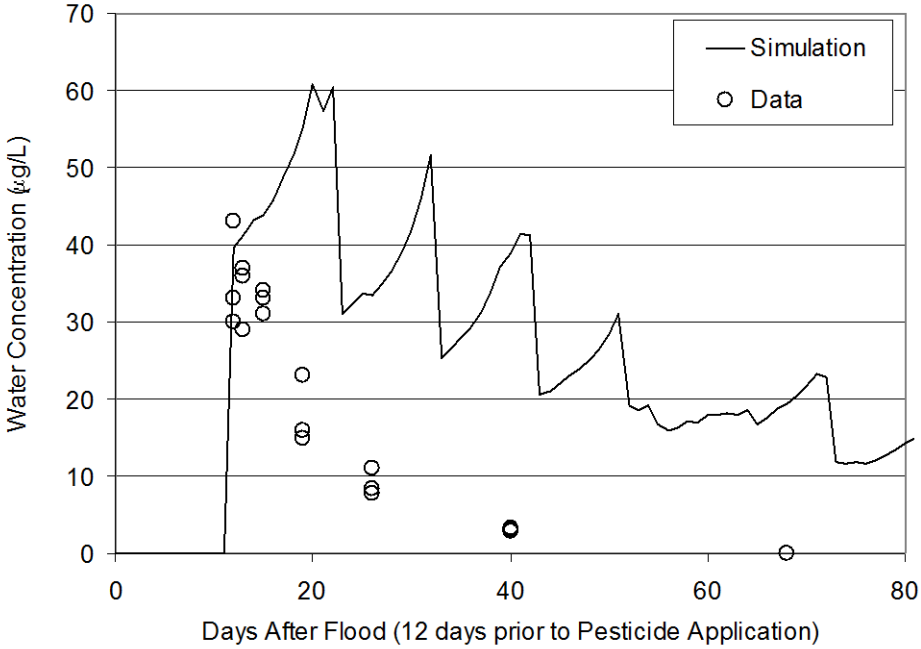

Figure 3-5. Simulated flood water concentration and measured data for Study B.

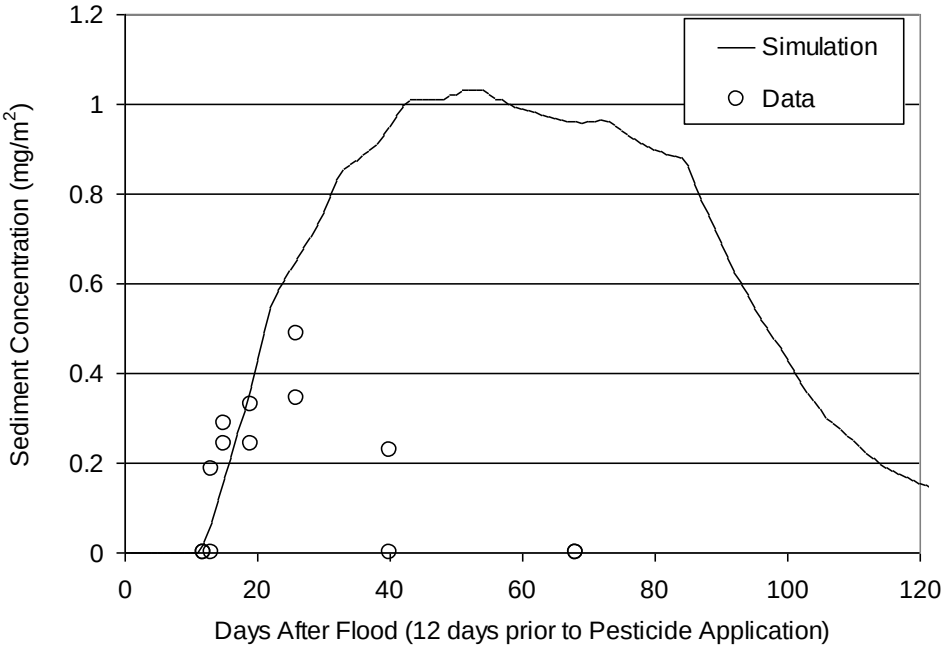

Figure 3-6. Simulated sediment concentration and measured data for Study B

3.2.3 Study C: Texas, Propiconazole Results

Study C site was a flow-through system in which a weir held water levels constant, so hydrologic simulations are not provided here. The constant flow occurred at a rate of 1.06 volumes per day, resulting in a water column half-life of about 0.65 days. Because of the very long half-lives due to degradation of the applied pesticide (hundreds of days, Table 3-2), washout is expected to be the dominant source of dissipation in the system. Figure 3-7 shows the fast washout-driven dissipation.

Figure 3-7 also shows the water column concentrations for Study C. The simulated initial concentration is about five times higher for the first application and about twice as high for the second application. These discrepancies are due in part to the low reported pesticide application efficiencies for the study (59% and 75%, respectively). The differences could also be due in part to canopy interception, but this possibility cannot be verified. (The study reported that a rice crop was in place, but it did not report the canopy coverage). The PFAM simulation captures the long-term concentration better than the short-term concentrations although the measured concentrations appear to drop off slower than PFAM predicts. This additional discrepancy supports to some extent the possibility of pesticide hold up and subsequent slow washoff from the foliage into the water column. Canopy holdup and washoff are areas needing additional research for models such as PFAM, but including those processes without commensurate data would be guesswork and inappropriate in an environmental protection context. Nevertheless, PFAM does give protective concentrations for the bulk of the simulation.

Figure 3-8 shows the simulated and measured benthic concentrations for Study C. The data clearly show the distinct influence of the two pesticide applications to the overlying water. PFAM also simulates the two applications quite well. As expected and as Figure 3-8 shows, benthic pesticide mass tends to accumulate because of the slow benthic degradation. PFAM

also captures the timing of the benthic peaks, which provides support for the default benthic mass transfer coefficient.

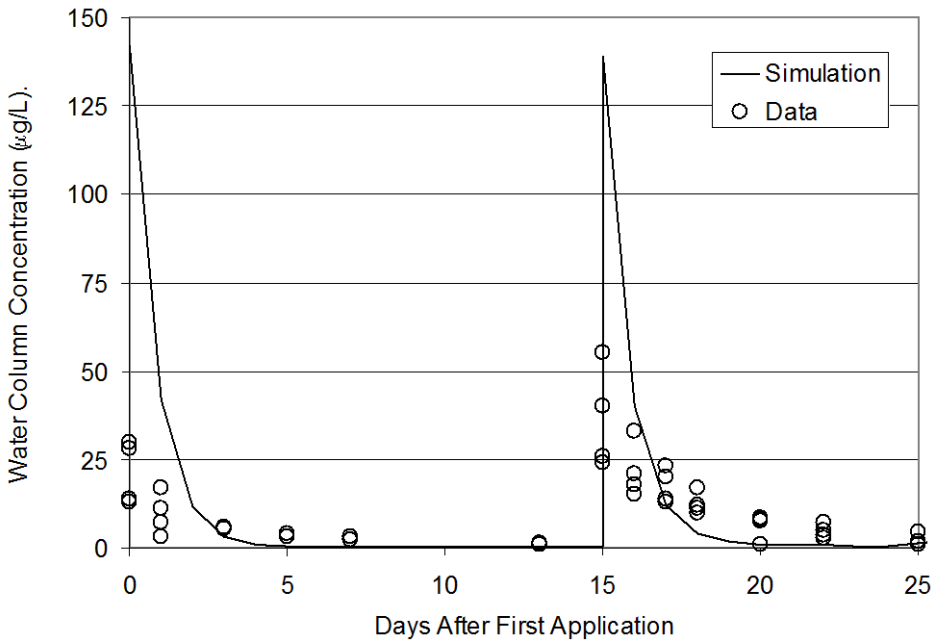

Figure 3-7. Simulated water column concentration and measured data for Study C.

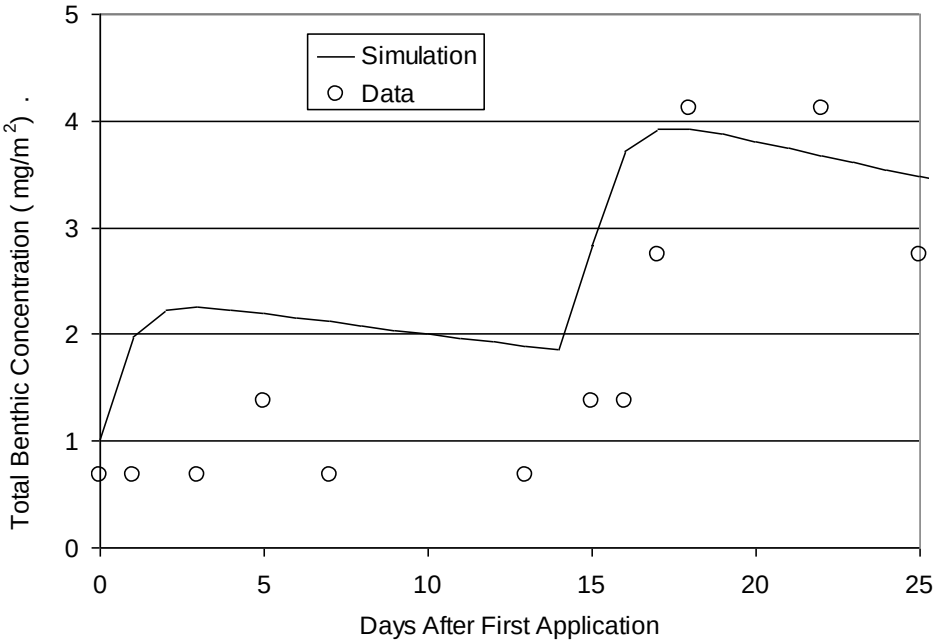

Figure 3-8. Simulated benthic concentration and measured data for Study C.

3.2.4 Study D: Texas, Carbaryl Results

Figure 3-9 shows the simulated and reported water levels for Study D. As indicated earlier, the simulated water level was calibrated by adjusting the weir level three times during the simulation. The calibration captures the rise and fall of the water level for the most part.

Figure 3-10 shows the water column concentrations and the measured data for Study D. The two pesticide applications clearly appear in the simulation and the data. The initial concentration of the first simulated application is similar to the data (about 70% of the simulation), while the simulated concentration for the second application is about twice that of the measurements. There was 50% canopy coverage during the application, and crop interception could be a reason for the discrepancy. In any case, the PFAM simulation is higher than the data, which is desirable for a regulatory model, and reinforces the appropriateness of the neglect of the canopy. Again, canopy holdup is an area in need of further research.

Figure 3-11 shows the benthic concentrations for study D. In this case, PFAM simulates benthic concentrations very well. PFAM captures both the peak and the degradation of the concentrations in the benthic region. PFAM also captures the lag time for the benthic pesticide level to reach its peak, providing support for the appropriateness of the assumed value of the benthic mass transfer coefficient.

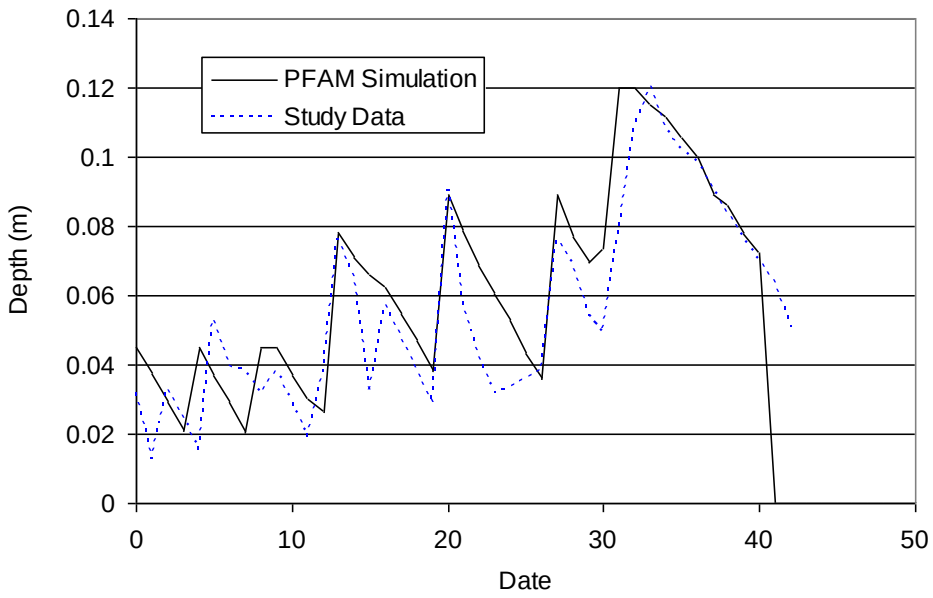

Figure 3-9. Simulated water level of Study D along with the reported water level.

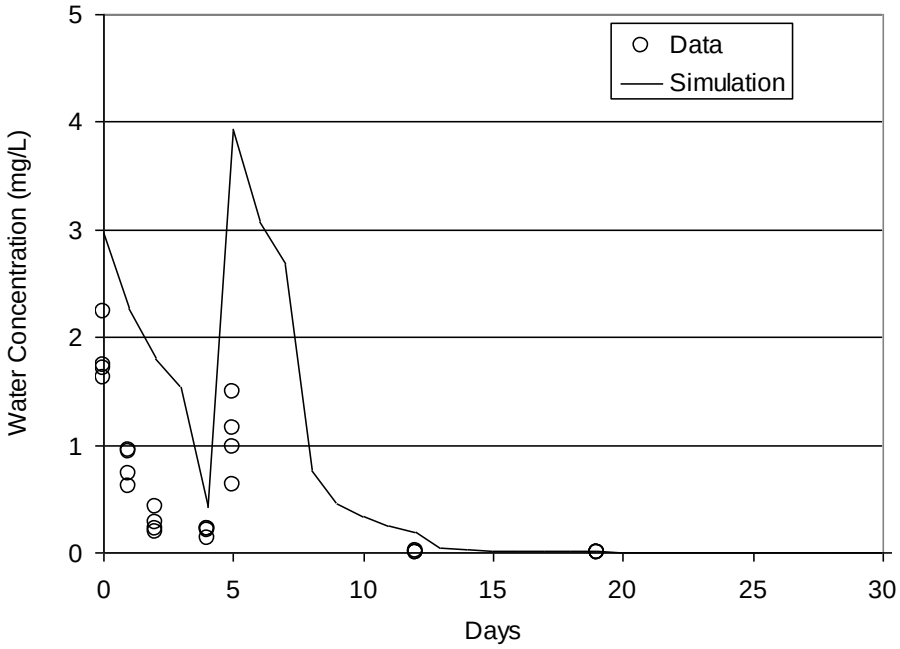

Figure 3-10. Simulated water column concentration and measured data for Study D.

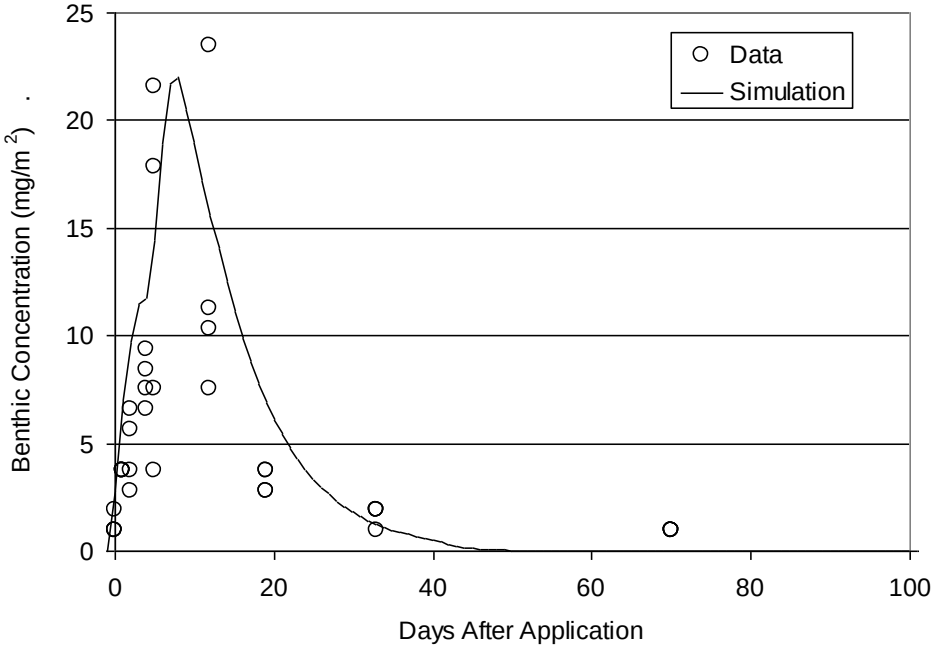

Figure 3-11 Simulated benthic concentration and measured data for Study D.

3.2.5 Study E: California, Triclopyr Results

Study E was a pond study in which the pond level was not regulated but rather allowed to evaporate without refill. Because the study did not record pond depths during the study, the hydrodynamics of this study cannot be crosschecked with PFAM output. However, for purposes of explaining the hydrodynamic effects on pesticide behavior, the water depth simulation is shown in Figure 3-12. Depth decreases over time during this study, which would tend to buffer declines in pesticide concentration, but also increase the effective photolysis rate.

Figure 3-13 shows the measured water concentrations along with the PFAM simulation for Study E, and PFAM captures the data very well. Since trichlopyr degrades predominantly by photolysis, this study allows a check for the PFAM photolysis routine. The PFAM-simulated concentration follows a general pattern of decline but degrades somewhat slower than the data show. This could be due to misestimating the evaporation or could be due to an inexact estimate of the photolysis rate among other things.

Figure 3-14 shows the measured sediment concentrations along with the PFAM simulations. PFAM substantially overestimates the sediments concentrations. This overestimation may be due to the non-site specific fate parameters used for trichlopyr (e.g., the K_d, benthic degradation, photodegradation rate). Alternatively, the benthic mass could be influenced by an overestimation of the benthic mass transfer coefficient or a combination of all of the above. Nevertheless, PFAM errs on the high side, which is acceptable for a regulatory model.

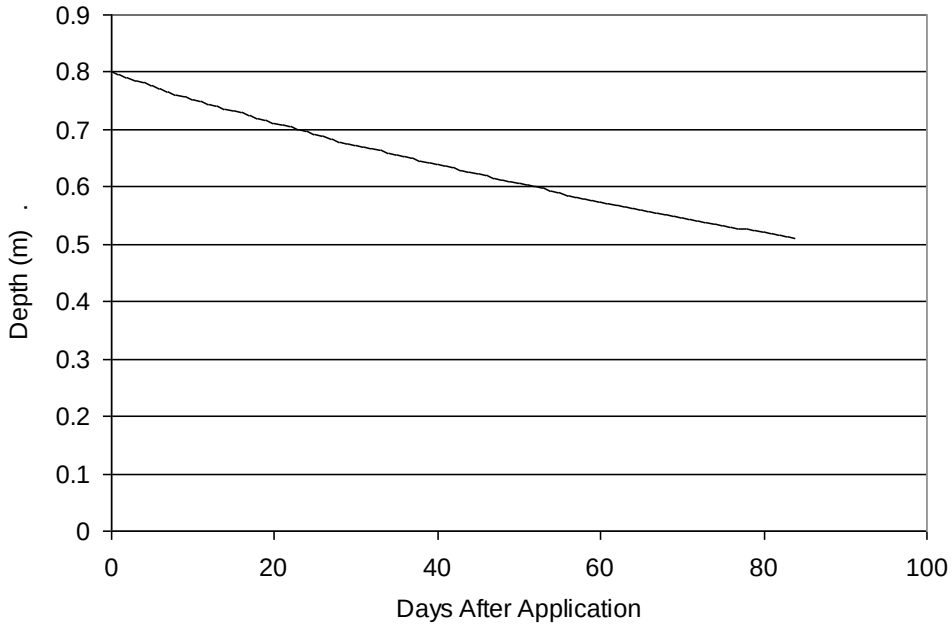

Figure 3-12. Simulated water depths in the pond for Study E.

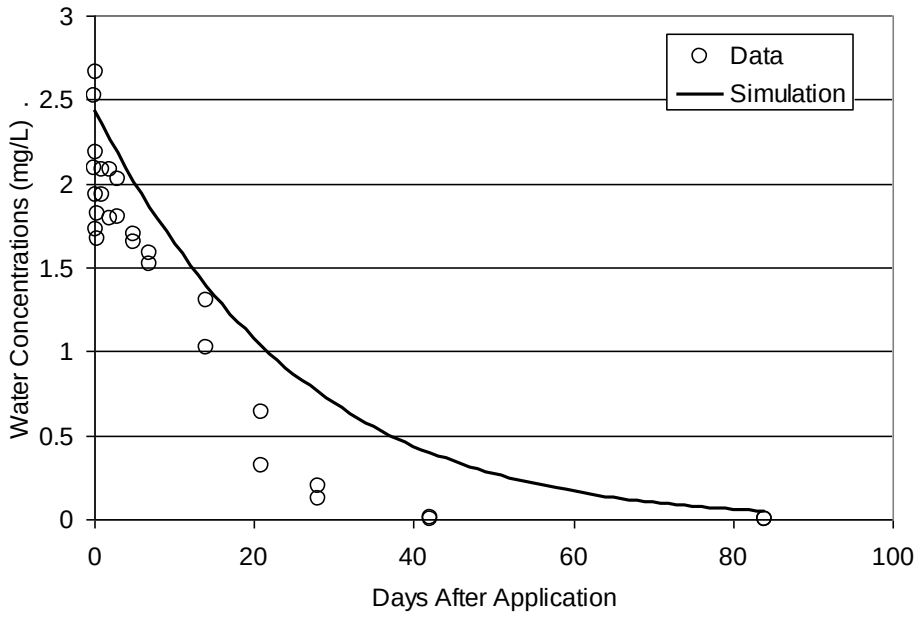

Figure 3-13. Water column concentrations for Study E.

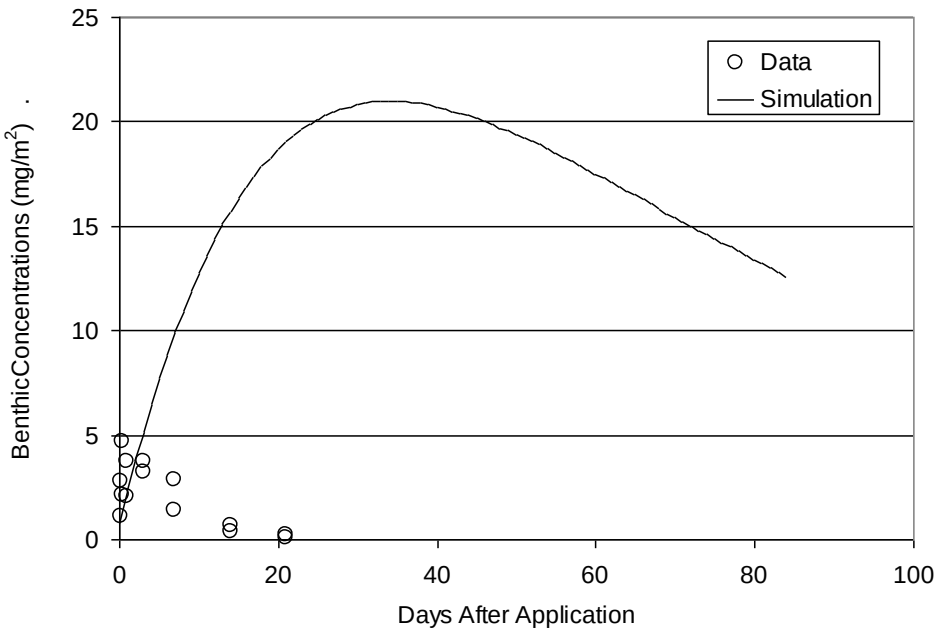

Figure 3-14. Benthic concentrations for Study E.

3.3 Long-Term Regulatory-Type Evaluation

The following section describes the results of the long-term simulations meant to represent what regulatory assessors may do with PFAM. A regulatory pesticide assessment will often address temporal variability that may result from weather by simulating long-term use of a pesticide with 30 years or so of weather data. Such long-term simulations are often referred to as Tier 2 assessments. It is also of interest to evaluate the response of PFAM with that of the currently used simple equilibrium Tier 1 model to identify conditions when PFAM use may be advantageous. This latter point is the second quality objective of the PFAM validation, that is, PFAM should provide more refined estimates of concentration over that of the Tier 1 model. Only the four rice studies (A,B,C, and D) are analyzed here; the pond study (study E) has no Tier 1 equivalent for comparison and was not included in this long-term analysis.

Figure 3-15 shows the long-term simulation of PFAM along with the current Tier 1 model estimates for the scenario described by Study A. For these long-term simulations, PFAM was run with the pesticide and water management practices specified in the studies for each year in the simulations (replicated over 30 years). PFAM estimates in Figure 3-15 include both a water column concentration as well as the concentration of any released water. Released concentrations include both intentional releases (i.e., weir is lowered) and overflow releases (i.e., excessive rainfall). The Tier 1 concentration in Figure 3-15 is a single value, which represents a concentration resulting from equilibration with no degradation. PFAM values are substantially less than the Tier 1 value for both water column and released water. Peak water concentrations are about 7 ppb, while the maximum released concentration is about 6 ppb as compared with a Tier 1 estimate of 54 ppb. PFAM chronic concentrations (temporally averaged) are 6 ppb over 7 days and 5 ppb over 30 days, which are also substantially lower than the Tier 1 estimates.

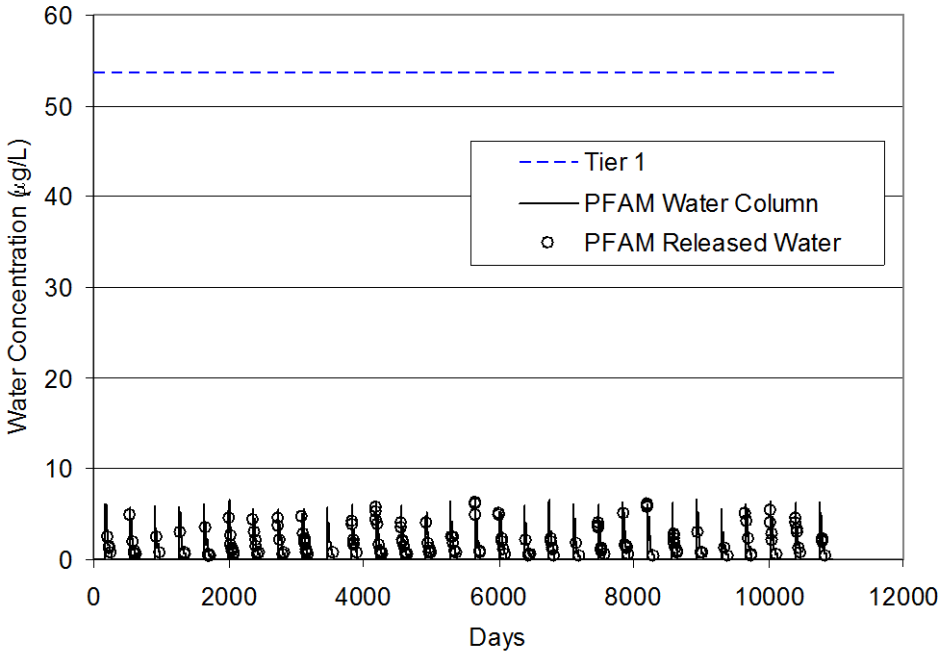

Figure 3-15. Regulatory evaluation using a scenario similar to Study A.

Figure 3-16 shows the long-term simulation of PFAM along with the current Tier 1 model estimate for the scenario described by Study B. The maximum PFAM water column value (80 ppb) exceeds the Tier 1 value (50 ppb), but the maximum released concentration (39 ppb) is well below the Tier 1 value, and released values are the most likely concentrations that would be used in a risk assessment. The PFAM values exceed the Tier 1 values because the water level in the simulation dropped below the 10 cm default depth that the Tier 1 model uses. Therefore, pesticide concentrations in the water column were higher at some times during the simulation due to the occasional lower amounts of water simulated in PFAM than in the Tier 1 estimate. The PFAM maximum 7-day average (63 ppb) was greater than the Tier 1 value, whereas the PFAM 30-day average (44 ppb) was slightly less than the Tier 1 value. Released concentrations were all lower than the Tier 1 values.

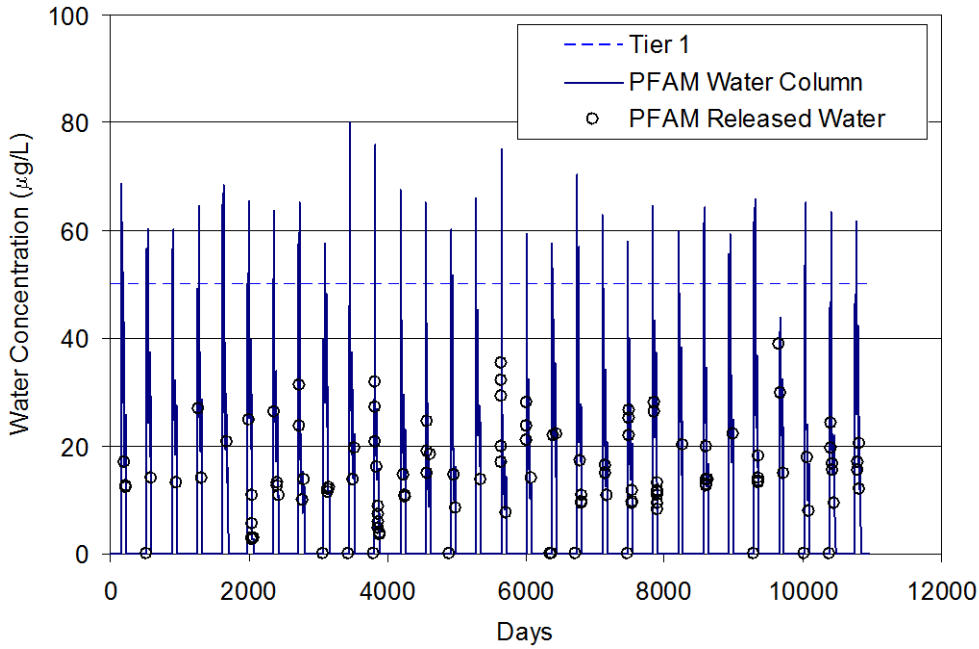

Figure 3-16. Regulatory evaluation using a scenario similar to Study B.

Figure 3-17 shows the long-term simulation of PFAM along with the current Tier 1 model estimate for the scenario described by Study C. In this flow-through scenario, water continually flows out of the system, so water column and released concentrations are equal. PFAM values (both released and water column) are less than the Tier 1 value for all times. Peak water concentrations are about 144 ppb, whereas the Tier 1 estimate is 200 ppb. The 7-day chronic concentration maximum is 30 ppb and the 30-day maximum average is 14 ppb.

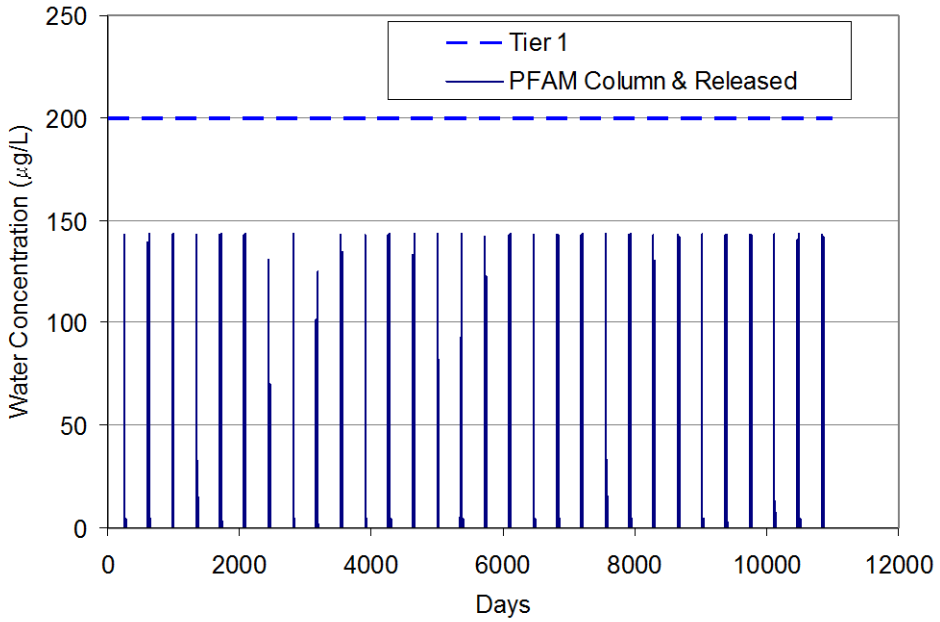

Figure 3-17. Regulatory evaluation using a scenario similar to Study C.

Figure 3-18 shows the long-term simulation of PFAM along with the current Tier 1 model estimate for the scenario described by Study D. The maximum PFAM water column value (9 ppm) exceeds the Tier 1 value (2.6 ppm), but the maximum released concentration (1.8 ppm) is well below the Tier 1 value. The PFAM values exceed the Tier 1 values because the water level in the simulation was allowed to drop to around 4 cm, which is well below the 10 cm that the Tier 1 model uses. Thus the pesticide could become more concentrated in PFAM than in the Tier 1 simulation. The 7-day chronic concentration maximum is 3.2 ppb, which is above the Tier 1 value, and the 30-day maximum average is 0.89 ppb, which is below the Tier 1 value.

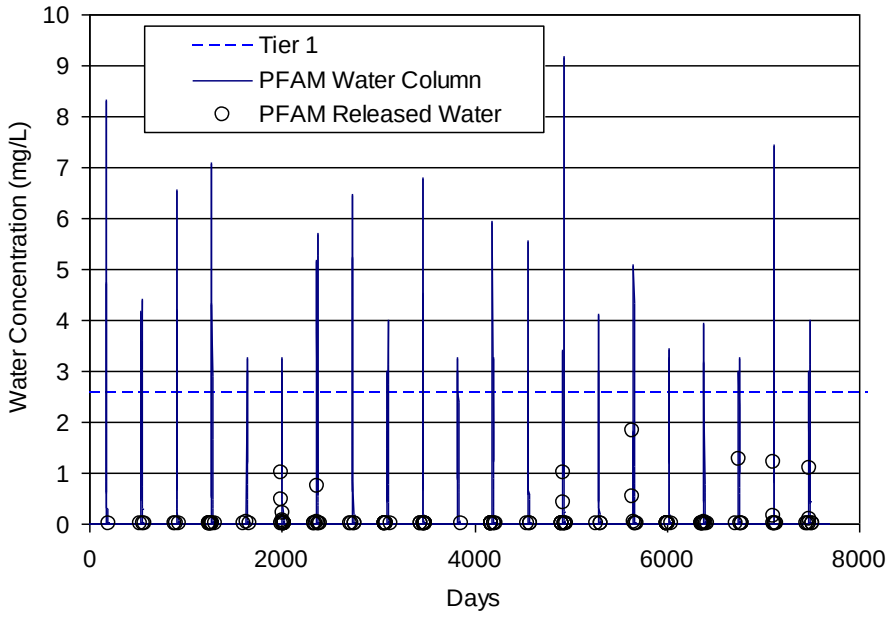

Figure 3-18. Regulatory evaluation using a scenario similar to Study D

These figures show that PFAM can provide significant refinements of water concentrations resulting from flooded agriculture as compared to the Tier 1 model. PFAM has many features not accounted for in the Tier 1 model, such as actual water levels, degradation, and water management practices. Additionally, PFAM provides estimates for concentrations of water releases rather than simply a water column concentration, as does the Tier 1 model. Finally, PFAM considers temporal variability and is able to provide temporal averages that the Tier 1 model cannot.

3.4 **Summary**

This work reviewed five aquatic dissipation studies and compared them to PFAM simulations. PFAM met the two specified quality objectives: 1) PFAM tended to err on the high side when compared to the actual study data, and 2) PFAM offered more refined estimates than the Tier 1 model. PFAM estimates, although conservative, were generally within an order of magnitude of the data but always below the Tier 1 estimates. Thus, PFAM should provide advantage in the regulation of chemicals for flooded agriculture.

Most of the studies were in reasonable agreement, but there were a few cases, most notably (Studies B and E), where PFAM estimated the water column concentrations reasonably well but substantially overestimated the benthic concentrations. The cause of those discrepancies is difficult to evaluate because of the complex nature of the field studies coupled with the unavailability of site-specific environmental fate data. Future work may be warranted in the area of benthic mass transfer coefficient and benthic compartment sizes as these are two default parameters that could account for some of these discrepancies. Nevertheless, the default values do provide appropriately conservative estimates with respect to a regulatory model.

When compared with the Tier 1 model, PFAM provided improved estimates that are closer to field data. Most notably PFAM could account for temporal variability and degradation that the Tier 1 model does not consider. PFAM water column estimates were generally lower than the Tier 1 estimates. However, there were cases where the actual water levels in the field were lower than the preset value in the Tier 1 model, and in those cases, the PFAM estimates were higher for short periods, as would be expected. In all cases, however, PFAM estimates of the concentration of releases water were lower than the Tier 1 model, and these released concentrations are the most relevant concentrations for pesticide risk assessments on non-target areas.

As previously stated, a regulatory model will be successful if it is protective by not underestimating the concentrations of measured data and shows reasonable trends in concentrations in response to the environment. Additionally a higher-tiered regulatory model should provide advantages over models of lower tiers. PFAM meets these criteria and can provide appropriate water concentrations for regulatory work involving pesticide use for flooded agriculture applications.

4. User Guidance

4.1.1 Background and Purpose

The goal of PFAM development was to produce a flooded agriculture model for use in pesticide regulatory work. The user interface was specifically designed with this intent. Although PFAM can be readily used for analysis of specific sites in a research capacity, its greatest strength is for analysis of long-term pesticide use for hypothetical scenarios, as is typically done during the pesticide registration process.

As is typical in a regulatory pesticide assessment, model simulations are performed over a long period with pesticide applications occurring every year. The PFAM user interface is designed for this application. The duration of PFAM simulations will be as long as the available meteorological data (typical available files are 30 years). Pesticide application and flooding sequences are mapped onto the time series in 1-year cycles for as long as the simulation continues. Thus, as is typical of a U.S. exposure assessment, the pesticide is assumed to be used every year for 30 years (the length of the U.S. meteorological files). Currently output is delivered as released mass of pesticide as well as a daily time series of concentrations.

4.1.2 Quick Start

The installation package comes with a test input file *Test.pfa* and an example meteorological file *wTest.dvf*. After start up, use File/Retrieve on the upper left menu bar to load the example file (*Test.pfa*). The user will need to specify where the output is delivered and should go to the *Output* tab and specify the desired location and name. The user will also need to specify the location of the meteorological data and should go to the *Location* tab and specify the file (the *wTest.dvf* file in the program directory is available as an example meteorological file). Press the *Run* button and output should be delivered in two files: raw data into the file previously specified as the output and processed data in a similarly named file but appended with *.pp1*. (There will also be receiving water body output if that option was selected).

4.1.3 Menu Items

File manipulations are performed on the menu bar. The first menu item is *File*, with submenus *Retrieve Input* and *Save Input*. *Retrieve Input* will open up a file browser dialog and allow a user to upload a previously created input file into the PFAM interface. The input files are text files that can be created either with the PFAM interface or with a text editor. The *Save Input* command will open a file browser and allow the user to save the inputs from the PFAM interface into a text file.

4.1.4 Chemical Tab Sheet

The chemical properties tab sheet allows entering of the chemical properties of the pesticide. The definitions are typically those generally accepted by the scientific community and are summarized here:

Water Column Half-Life [d] is the half-life of a pesticide resulting from metabolic processes. This parameter acts on all phases of the pesticide in the water column. As is typical for the type of metabolism studies submitted for pesticide registration, no distinction is possible between sorbed-phase degradation and aqueous-phase degradation, and only total system degradation is

known. Thus no distinction is made for this application either. A half-life of zero is interpreted to mean that the compound does not degrade by this process.

Temperature Associated with the Water Column Value [°C] is the temperature at which the water column degradation study was conducted. Degradation rate is adjusted by temperature with this temperature input being the reference.

Benthic Compartment Half-Life [d] is the half-life of a pesticide in the flooded benthic compartment. Typically, this value could be an anaerobic metabolic half-life. This parameter acts on all phases of the pesticide in the benthic compartment. As is typical for the type of metabolism studies submitted for pesticide registration, no distinction is possible between sorbed-phase degradation and aqueous-phase degradation, and only total system degradation is known. Thus no distinction is made for this application either. A half-life of zero is interpreted to mean that the compound does not degrade by this process.

Temperature Associated with the Benthic Compartment Value [°C] is the temperature at which the anaerobic metabolism study was conducted.

Unflooded Soil Half-Life [d] is the half-life of a pesticide on the soil in unflooded conditions. This half-life acts on the "benthic" compartment when that compartment is not flooded. This value should include all expected mechanisms of degradation in the soil compartment, including metabolism, volatilization, and photolysis. This parameter acts on all phases of the pesticide in the benthic compartment. As is typical for the type of metabolism studies submitted for pesticide registration, no distinction is possible between sorbed-phase degradation and aqueous-phase degradation, and only total system degradation is known. Thus no distinction is made for this application either. A half-life of zero is interpreted to mean that the compound does not degrade by this process.

Note that the routines to account for photolysis and volatilization are turned off when the field is not flooded and users must manually enter the effective half-life to include photolysis or volatilization on dry soil. The photolysis and volatilization routines are turned back on when the field floods. The reason for this behavior is that the photolysis and volatilization routines were written specifically for aquatic systems, not dry fields. Furthermore, OPP has not yet accepted a field volatilization or photolysis routine for any of its models (*e.g.*, PRZM) for use in risk assessments; therefore those processes were left out until approval by USEPA OPP.

Temperature Associated with the Unflooded Soil Value [°C] is the temperature at which the soil degradation study was conducted.

Photolysis Half-Life [d] is the near-surface 24-hr average aquatic half-life of the pesticide due to photolysis. A half-life of zero is interpreted to mean that the compound does not degrade by this process.

Photolysis Reference Latitude [°] is the latitude that the photolysis value is intended to simulate.

Hydrolysis Half-Life [d] is the half-life of the pesticide due to hydrolysis at whatever pH is to be simulated. A half-life of zero is interpreted to mean that the compound does not degrade by this process.

K_{oc} [mL/g] is the organic-carbon-normalized sorption coefficient. In some situations, use of K_{oc} may not be appropriate, and a K_d value may be preferred. K_d can be applied by making note of the oc content (*Foc Benthic* under *Physical* Tab) and recognizing that $K_d = K_{oc}$ x oc, and adjusting the K_{oc} as appropriate.

Molecular Weight [g/mol] is the molecular weight of the pesticide. Molecular Weight is used only in the volatilization routine. This parameter only affects the volatilization rate.

Vapor Pressure [torr] is the vapor pressure of the compound at a representative temperature to be simulated. This parameter only affects the volatilization rate.

Solubility [mg/L] is the solubility of the pesticide at a representative temperature to be simulated. Solubility is used only in the volatilization routine; it does not cap concentrations in this program. This parameter only affects the volatilization rate.

Heat of Henry [-] is the enthalpy of phase change from aqueous solution to air solution (Joules/mole). This enthalpy can be approximated from the enthalpy of vaporization (Schwarzenbach et al., 1993), which can be obtained from EPISuite among other sources. Enthalpy for pesticides obtained in a literature review ranged from 20,000 to 100,000 J/mol (average 59,000 J/mol). Some example enthalpies for pesticides are

Metalochlor	84,000	Feigenbrugel et al. 2004
Diazonon	98,000	Feigenbrugel et al. 2004
Alachlor	76,000	Gautier et al., 2003
Dichlorvos	95,000	Gautier et al., 2003
Mirex	91,000	Yin and Hassett, 1986
Lindane	43,000	Staudinger et al. (2000)
EPTC	37,000	Staudinger et al. (2000)
Molinate	58,000	Staudinger et al. (2000)
Chlorpyrifos	17,000	Staudinger et al. (2000)

Enthalpies can also be estimated by the US EPA EPI Suite software. Open the software, then select the HENRYWIN subprogram on the left of the EPI Suite screen. On the top menu of the HENRYWIN window item, select the *ShowOptions*, then select *Show Temperature Variation with Results*. Enter the chemical name of interest and then push the *Calculate* button. EPI Suite will give the temperature variation results in the form of an equation: HLC (atm-m3/mole) = exp(A-(B/T)) {T in K}. The enthalpy of solvation in Joules/mol is equal to 8.314*B. Example enthalpies from EPI Suite are:

Pendamethalin	62,000 J/mol
Carbaryl	58,000 J/mol
Carbofuran	54,000 J/mol

Molinate	54,000 J/mol
Endosulfan	37,000 J/mol

Henry Reference Temperature [°C] is the temperature at which the vapor pressure, solubility, and Henry's Law constant apply.

4.1.5 Applications Tab Sheet

The *Applications* tab refers to pesticide applications and contains a table that allows entry of a number of pesticide applications during a growing season. Each application is identified by the date (month and day) at which it is applied and the amount of pesticide that is applied (kg/hA).

Number of Applications. Enter the number of applications and press the ***Update*** button. This will make available only the number of applications requested. (Information is retained in the invisible text boxes, but it is not used.).

Day is the entry for the calendar day (1 through 31) of pesticide application.

Mon is the calendar month (1 through 12, corresponding to January to December) of pesticide application.

Applied Mass [kg/ha] is the mass per area at which the pesticide is applied on the associated date.

Slow Release [d^{-1}] specifies whether the pesticide is designed as a slow-release agent. The release rate is first order with the mass of pesticide remaining after time t equal to $M_0\exp(-kt)$, where k is the user specified release rate (per day), M_0 is the *Applied Mass* (see above), and t is time in days. A slow release of zero by convention means that there is an instantaneous full release. As a note of reference, a Slow Release rate of 0.6 per day will result in 95% of the pesticide released in 5 days.

4.1.6 Location Tab Sheet

The *Location* sheet allows specification of particular weather files. The weather file should be organized without a header and into the following white-space-delimited columns: date, precipitation (cm), pan evaporation (cm), average temp (°C), wind speed (cm/s).

The date should be presented as a number consisting of the two digit numerical values for month day year and compiled together. For example December 15, 1992 should be written as 121592, and January 3, 1991 should be written as 010391 (or 10391). The program will read the entire date value in as a single integer and parse the value. Because the file is recognized as being white-space delimited, the date should not contain any internal spaces. For example, February 7, 1992 which is 020792 can be written as 20792 but not as 2 792.

Daily meteorological files for the United Sates that will work for PFAM are available from the US EPA at: http://www.epa.gov/ceampubl/tools/metdata/index.htm. The files at that address contain additional columns of information that have no effect on PFAM.

4.1.7 Flood Events Tab Sheet

The *Flood Events* sheet allows specification of up to 11 flood events, in which an event refers to a manually controlled change in water level. Flood events are mapped onto the time series every year with the mapping unit defined as Event 1 to Event 1 of the next year and does not depend on the calendar year. Thus flood event series can be defined across calendar years if so desired. The events should be listed in chronological order and no event should occur past 365 days. There does not have to be any actual significance to the Event 1 date. It could simply be January 1 and then all events would be referenced to the first of the year. Or, it could be the actual day of the first flood event, and then all subsequent events would be referenced to the first flood. However, at the start of the simulation weir height, fill height, minimum level, and turnover are initialized to 0 and remain that way until the first event. Thus, if it is desired to have other than zeroes for these values at the start of the simulation, then Event 1 should be defined as the earliest event relative to the start of the simulation (in cases for USEPA dvf files this would be January 1).

Event 1 Day is an arbitrary calendar day that when used along with the *Event 1 Month* represents a reference point for specifying flood events. This should be entered as an integer calendar day with an acceptable value range dependent upon the month selected.

Event 1 Month is an arbitrary calendar month that when used along with the *Event 1 Day* will be used as a reference point for specifying flood events. This should be an integer calendar month (1 through 12, corresponding to January to December).

Number of Days represents the number of days since the Event 1 date when a respective event occurs. This should be entered as an integer. (Event 1 is always zero.)

Weir Level [m] represents the level that the weir was set to on the respective event. This level is the level at which overflow occurs.

Fill Level [m] is the level that the water is filled to for a refilling event. If a Fill Level value is higher than the previous Fill Level value, then it is assumed that the user wants to increase the water level manually, and on that day, the water level will be increased to the Fill Level. (Reductions in the Fill Level value do not have any immediate effect in a likewise manner, but it will affect the subsequent refill events.)

Minimum Level [m] represents the water level that the water body can be reduced to (by evaporation) before the level is returned to the weir level by refill.

Turn Over [d^{-1}] represents the turnover rate for each event. It is determined by dividing the flow through the water body by the volume of the water body. Turnover is used for those systems that use a continuous flow through the system and are maintained at a set depth. (Turnover should be set to zero when weir level is zero.)

4.1.8 Crop Tab Sheet

The *Crop* sheet allows specification of crop growth characteristics.

Zero Height Reference Day represents the day of the month when a crop just emerges (*i.e.*, zero height). It is used along with a *Zero Height Reference Month*.

Zero Height Reference Month represents the month when a crop just emerges (*i.e.*, zero height). It is used along with a *Zero Height Reference Day*.

Days from Zero to Full Height represents the number of days between the zero reference day and the time that the plant reaches full height.

Days from Zero to Removal represents the number of days between the zero reference day and the time that the plant is removed.

Maximum Fraction Areal Coverage represents the maximum fractional area that the plant covers at full height.

4.1.9 Physical Tab Sheet

The *Physical* sheet allows manipulation of parameters that characterize the physics of the water body.

Mass Transfer Coefficient [m/s] represents the mass transfer coefficient between the water column and the benthic zone. It accounts for all means of mass transport and is referenced to the surrogate driving force of aqueous concentration differences. It is a difficult parameter to measure. Literature and EPA's own calibrations suggest a starting estimate of 10^{-8} m/s.

Leakage [m/d] is the rate of water flowing from the water column through the benthic layer and out of the bottom of the system. Leakage will only occur if there is water in the water column.

Reference Depth [m] represents the depth that aquatic measurements were made when determining factors such as suspended solids, biota, and DOC [m]. This usually will be set to the typical depth of the water body.

Benthic Depth [m] is the depth of the benthic compartment. This is another difficult to estimate parameter; however, literature and EPA's own calibrations suggest about 0.05 m.

Benthic Porosity is the porosity of the benthic compartment: [pore space volume per total volume]. The default value is set to that used by the EPA standard farm pond.

Dry Bulk Density [g/cm^3] is the rationally defined bulk density: [mass of sediment per total volume of sediment]. The default value is set to that used by the EPA standard farm pond.

Foc Water Column SS is the fraction of organic carbon associated with suspended sediment. The default values are set to those used by the EPA standard farm pond.

Foc Benthic is the fraction of organic carbon associated with benthic sediment. The default value is set to that used by the EPA standard farm pond.

SS [mg/L] is the suspended mass in the water column. The default value is set to that used by the EPA standard farm pond.

CHL [mg/L] represents the chlorophyll concentration in the water column. The default value is set to that used by the EPA standard farm pond. This parameter only affects the photolysis rate.

Water Column DOC [mg/L] represents the dissolved organic carbon concentration in the water column. The default value is set to that used by the EPA standard farm pond. This parameter only affects the photolysis rate.

QT [-] is the Q_{10} value for metabolism. A value of 2 is typical for such models.

DFAC [-] is a parameter defined as is in the model EXAMS. It represents the ratio of vertical path lengths to depth. Default value is set to1.19 as suggested by EXAMS documentation.

4.1.10 Tab Sheet for Output

The *Output* sheet allows specification of a file and a directory that will contain output. The *Select Output File* button opens a file browser and allows a user to select or create an output file name and location. A raw data file will be created with the user-specified name. An additional file will also be created that contains post-processed results derived from the raw data file. The post processed file will have the same name as the raw data file but will be appended with ".pp1". Users may produce their own post processor and replace the post processor if so desired. The post processor is pfampp1.exe. The command line call that PFAM uses internally to call the post processor is the name *pfampp1.exe* and a command line argument that contains the raw data file location in quotation marks, that is,

>pfampp1.exe "*full path and file name of raw data file*"

Additionally the program will also check for the existence of a second post processor that a user may create. If a file exists with the name pfampp2.exe, then the program will execute the following command:

>pfampp2.exe "*full path and file name of raw data file*"

Area of Application [m^2] Area where the applications are made (field or paddy area)

Route effluent check box will start a post processor that will route the effluent from PFAM into EPA standard water bodies (pond and reservoir). This parameter also routes a surrounding field runoff into the receiving body.

Area of Surrounding Watershed [m^2] Area of the watershed excluding the application areas. This value along with the curve number will determine the amount of runoff the receiving water body gets from non-application areas.

Curve Number of Surrounding Field is the Natural Resources Conservation Service (NRCS) curve number of the surrounding watershed. This will determine the amount of runoff the receiving body gets from non-application areas.

Width of Mixing Cell [m] is the width of the receiving water body.

Depth of Mixing Cell [m] is the depth of the receiving water body.

Length of Mixing Cell [m] is the length of the receiving water body. Note that for a flowing water body such as a stream or river, this length value should correspond roughly to twice the dispersivity (2D/v, where D is the dispersion coefficient and v is the velocity of the stream or river) characteristic of the flowing water body. A good starting value may be around 30 meters as estimated from the median of data in Fisher *et al.* (1979).

Base Flow [m3/sec] is the base flow through the receiving water body.

See *Current Output and Post Processing* at the end of this manual for details on the currently supplied post processing.

4.1.11 Degradate 1

The *Degradate 1* tab sheet is used if a degradate is to be produced from degradation of the main chemical. If degradate calculations are desired, then check the **Perform Degradate Calculation** checkbox. Chemical properties for Degradate 1 are defined in the same manner as those described on the Chemical tab sheet for the parent chemical, except with the additional entries as follows:

Moles of Degradate Produced per Mole of Parent. These entries indicate how many moles of degradate are produced by the degradation of the parent for each of the specific processes.

4.1.12 Degradate 2

The *Degradate 2* tab sheet is similar to the *Degradate 1* sheet except that the molar productions of Degradate 2 are referenced to Degradate 1.

4.1.13 Run Button

The run button gathers all input from the controls in the PFAM interface. The program performs some checking of the values and then runs PFAM. Output is produced as described above.

<u>Current Output and Post Processing</u>

Assuming that the output file is named *output.txt*, then the following files will be generated:

Output.txt: raw daily output data from PFAM

*Output*_Efffective_Halflife.txt: summary of the effective average dissipation processes for the PFAM simulation

*Output*_ProcessedOutput.txt: summary of PFAM releases and the reason for the releases. Also gives the daily concentrations in the water column and the benthic/soil compartment.

*Output*_ReceivingBodies.txt: water column results for receiving body. Result of post processing the PFAM output by routing the PFAM effluent into the standard pond and the standard reservoir and through a flowing water body (mixing cell).

*Output*_ReceivingBodies_daily.txt: daily water column concentrations in the receiving water bodies

*Output*_ReceivingBodies_Benthic.txt: benthic pore water results for receiving body. Result of post processing the PFAM output by routing the PFAM effluent into the standard pond and the standard reservoir and through a flowing water body (mixing cell).

*Output*_ReceivingBodies_daily_Benthic.txt: daily benthic pore water concentrations in the receiving water bodies

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