Pesticides in Flooded Applications Model (PFAM): Conceptualization and Development (Version 0.65)

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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; user documentation that more thoroughly explains user inputs and model operation is available along with the model. The code for the mathematics of the model is written in Fortran 95/2003, while the user interface code is in Visual Basic. As is important for a regulatory model, PFAM is nonproprietary, with the model code and documentation being freely available.

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, 2007). 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 modeled 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. 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, 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).

2. Overview of the Processes in PFAM

PFAM is conceptualized in Figure 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. The selection of a daily time step was 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.

2.1 Flood and Overflow Control

In this conceptualization (Figure 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. Forn any day, the water level is calculated as

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

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 = 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.

2.2 Plant Growth

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

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

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.

2.3 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:

$$\begin{aligned} m_{sed1}\frac{ds_{sed1}}{dt} + m_{DOC1}\frac{ds_{DOC1}}{dt} + v_1\frac{dc_1}{dt} = \; & -Qc_1 - QC_{sed}s_{sed1} - QC_{DOC}s_{DOC1} - \omega(c_1 - c_2) \\ & - v_1\mu_{photo}c_1 - v_1\mu_{bio-a1}c_1 - v_1\mu_{hydr}c_1 - v_1\mu_{vol}c_1 \\ & - m_{sed}\mu_{bio\_sed1}s_{sed} - m_{DOC}\mu_{bio-DOC1}s_{DOC} - Q_Lc_1 \end{aligned} \quad (3)$$

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

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^{-1}]

μ_{hydr} = 1st order hydrolysis rate coefficient, [s^{-1}]

μ_{photo} =1st order photolyisis rate coefficient, [s^{-1}]

μ_{vol} = effective 1st order volatilization rate coefficient, [s^{-1}]

$\mu_{bio\text{-}a1}$=1st order aqueous-phase metabolic degradation rate coefficient in water column, [s^{-1}]

$\mu_{bio\text{-}sed1}$ = 1st order sediment-sorbed metabolic degradation rate coefficient in water column, [s^{-1}]

$\mu_{bio\text{-}DOC1}$ = 1st order DOC-sorbed metabolic degradation rate coefficient in water column, [s^{-1}]

$\mu_{bio\text{-}a2}$ =1st order aqueous-phase metabolic degradation rate coefficient in benthic region, [s^{-1}]

$\mu_{bio\text{-}sed2}$ = 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., $\mu_{bio1} = \mu_{bio\text{-}a1} = \mu_{bio\text{-}sed1} = \mu_{bio\text{-}DOC1}$, and $\mu_{bio2} = \mu_{bio\text{-}a2} = \mu_{bio\text{-}sed2}$), (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 (1) and (2) in a simpler form as follows:

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

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

where

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

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

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

$$\Lambda = \frac{Q_L}{\left(m_{sed2}K_{sed2} + v_2\right)} \tag{9a}$$

$$\Theta = \frac{\left(m_{sed2}K_{sed2} + v_2\right)}{\left(m_{sed1}K_{sed1} + m_{DOC1}K_{DOC1} + v_1\right)} \tag{10}$$

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

$$f_{w1} = \frac{v_1}{\left(m_{sed1}K_{sed1} + m_{DOC1}K_{DOC1} + v_1\right)} \tag{11}$$

$$f_{w2} = \frac{v_2}{\left(m_{sed2}K_{sed2} + v_2\right)} \tag{12}$$

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 (3) and (4) 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.

2.3.1 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 (10). The individual

partitioning coefficients (K_{sed} and K_{DOC}) in equation (10) 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

$$K_{sed1} = K_{sed2} = f_{oc} K_{oc} \left(0.001 \frac{m^3/kg}{ml/g} \right) \tag{13}$$

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 (1) to (10) 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:

$$K_{DOC1} = 0.2114 K_{oc} \left(0.001 \frac{m^3/kg}{ml/g} \right) \tag{14}$$

Figure 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 a with 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 basis upon which PFAM was developed, also include a biological partitioning component in the water column. However, a sensitivity analysis of the biological component showed that with the USEPA standard pond value of 0.4 mg/L biological material very little partitioned to the biological material occurs 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 typically be available for scenario development and even if they were they would not 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 suspended solids is as equally insignificant; however, the suspended solids perform an additional function in photolysis quenching, so the suspended solids parameter is retained.

Figure 3 shows an example of the relative solute holding capacities for the benthic region of a typically parameterized water body. Note that prior to finalization of the PFAM structure and parameter requirements, sensitivity analysis were performed on possible parameters to be taken from the standard USEP EXAMS pond model (USEPA, 2004). Shown also in this figure are that relative capacities benthic biological material and benthic DOC as they are incorporated in the US EPA

Sensitivity analysis was performed on the benthic components used in the US EPA 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.

2.3.2 Effective Water Column Dissipation (Γ_1)

The overall dissipation rate in the water column (Γ_1), as defined in equation (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.

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

The first term in equation (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) or by intentional irrigation flow through (as specified by the model user). The washout term acts on all forms of pesticide (both aqueous dissolved and sorbed to suspended matter), as is apparent from equation (3). This means that pesticide mass in both dissolved and suspended sorbed forms can flow out of the water body.

2.3.2.2 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, this parameter would likely be set to zero, as this would be a reasonable screening level approach and would provide conservative estimates for a difficult to parameterize term. Although in this parameter is in contradiction to the underlying principles of model simplification, it was added due to numerous requests from potential users for use in exploratory work and for comparisons with other models that incorporate leakage.

2.3.2.3 Metabolism (μ_{bio1})

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

following standard EPA-approved protocols, which are typically conducted in aqueous/sediment systems at 20 to 25°C. These tests generally can not 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 (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:

$$\mu_{bio1} = \mu_{measured}\left[Q_{10}^{\left(\frac{T-T_{ref}}{10}\right)}\right] \qquad (17)$$

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.

2.3.2.4 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 (7). The factor f_{w1} represents the fraction of total pesticide that is present in dissolved aqueous form, as previously described.

2.3.2.5 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 a 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:

$$\mu_{photo} = f_p f_{lat} f_{atten} \mu_{measured} \quad (18)$$

where f_p = the fractional area of plant coverage (see eqn. 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:

$$f_{lat} = \frac{191700 + 87050\cos(0.0349 \text{ x } L_{sim})}{191700 + 87050\cos(0.0349 \text{ x } L_{ref})} \quad (19)$$

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:

$$f_{atten} = \frac{1 - \exp(-D_{fac} d_1 a)}{D_{fac} d_1 a} \quad (20)$$

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:

$$a = 0.141 + 101[C_{CHL}] + 6.25[C_{DOC}] + 0.34[C_{Sed}] \quad (21)$$

where $C_{DOC,}$ C_{Sed} have been previously defined under equation (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 (21) 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 concentrations 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 (20). Figure 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 affect the photolysis in this model only if the temperature reaches 0°C at which point photolysis ceases to occur, with the assumption being that there will be ice cover below 0°C.

2.3.2.6 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

$$\mu_{vol} = \frac{Ak_{vol}}{v_1} \quad (22)$$

where A = surface area of 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:

$$\frac{1}{k_{vol}} = \frac{1}{k_w} + \frac{1}{\left(\frac{H}{RT_k}\right)k_a} \tag{23}$$

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:

$$k_w = k_{O2}\sqrt{\frac{32}{MW}} \tag{24}$$

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:

$$k_{O2} = 4.19 \text{ x } 10^{-6}\sqrt{u_{10}}\left(1.024^{(T-20)}\right) \tag{25}$$

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

$$k_{O2} = 3.2 \text{ x } 10^{-7}\left(u_{10}\right)^2\left(1.024^{(T-20)}\right) \tag{26}$$

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

$$\frac{u_1}{u_2} = \frac{\log(z_1 / z_0)}{\log(z_2 / z_0)} \tag{27}$$

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:

$$u_{0.1} = \frac{\log(0.1/0.001)}{\log(10/0.001)} u_{10} = 0.5u_{10} \tag{28}$$

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

$$k_a = k_{a,H2O}\left[\frac{D_a}{D_{a,H_2O}}\right]^{\alpha} \tag{29}$$

where D_a and $D_{a,H2O}$ are gas-phase diffusion coefficients for pesticide and water respectively, and 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):

$$\frac{D_a}{D_{a,H_2O}} \cong \left[\frac{18}{MW}\right]^{0.5} \tag{30}$$

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

$$k_a = k_{a,H2O}\left[\frac{18}{MW}\right]^{0.5} \tag{31}$$

The resulting relationship is

$$k_a = \left[0.00005 + 0.0032u_{0.1}\right]\sqrt{\frac{18}{MW}} \tag{32}$$

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:

$$H = \frac{(vp/760)}{(Sol/MW)} \tag{33}$$

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):

$$H(T) = H_{ref}\exp\left[\frac{\Delta h}{R}\left(\frac{1}{T_K} - \frac{1}{T_{ref}}\right)\right] \tag{34}$$

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 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 6. Both 5 and 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 being 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 5 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.

2.3.3 Effective Benthic Region Dissipation (Γ_2)

The overall benthic degradation in the standard water bodies, as defined in equation (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.

2.3.3.1 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,

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

2.3.3.2 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

$$\mu_{bio\_2} = \mu_{measured}\left[Q_{10}^{\left(\frac{T-T_{ref}}{10}\right)}\right] \tag{35}$$

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].

2.3.3.3 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 35 sill applies, but the measured value ($\mu_{measured}$) will be taken from the aerobic soil studies.

2.3.4 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 6. This parameter can be readily calculated from equation 9 or equivalently, as would be done in a computer program, by using previously calculated terms as in the following:

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

2.3.5 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 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 (9) can be broken into somewhat more fundamental terms as follows:

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

And therefore

$$\Omega = \frac{k_{xfer}}{d_2} \tag{37}$$

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).

2.4 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 as its designers considered foliar degradation and foliar washoff to be unparameterizable. 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

(38)

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 will

(39)

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 percent of the pesticide is released and the remaining (5%) of pesticide is then applied on the following day.

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

2.5 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

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 stoichioemtric equations supplied by the pesticide study submissions.

3. 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 discreet 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 1. With the approximation of constant within-day volume, the concentrations 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.

3.1.1 Initial Conditions

Initial concentrations for the standard water bodies are determined by the pesticide mass inputs. Depending on the pesticide-management practice, 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:

$$C_{10} = \frac{f_{w1}}{v_1}\left[\left(M_{input,1}\right) + \frac{v_{1,prior}}{f_{w1,prior}} C_{10,prior}\right] \tag{38}$$

$$C_{20} = \frac{f_{w2}}{v_2}\left(M_{input,2}\right) + C_{20,prior} \tag{39}$$

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

3.1.2 Analytical Solution for Concentrations

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

$$\frac{dc_1}{dt} = Ac_1 + Bc_2 \tag{40}$$

$$\frac{dc_2}{dt} = Ec_1 + Fc_2 \tag{41}$$

where:

$$A = -\Gamma_1 - \Omega\Theta \tag{42}$$

$$B = \Omega\Theta \tag{43}$$

$$E = \Omega + \Lambda \tag{44}$$

$$F = -\Gamma_2 - \Omega - \Lambda \tag{45}$$

These equations have the following solution:

$$c_1 = X_1 e^{\lambda_1 t} + Y_1 e^{\lambda_2 t} \tag{46}$$

$$c_2 = X_1 \frac{(\lambda_1 - A)}{B} e^{\lambda_1 t} + Y_1 \frac{(\lambda_2 - A)}{B} e^{\lambda_2 t} \tag{47}$$

where:

$$\lambda_1 = \frac{A + F + \sqrt{(A+F)^2 - 4(FA - BE)}}{2} \tag{48}$$

$$\lambda_2 = \frac{A + F - \sqrt{(A+F)^2 - 4(FA - BE)}}{2} \tag{49}$$

$$X_1 = \left[\left(\frac{\lambda_2 - A}{B}\right)C_{10} - C_{20}\right]\frac{B}{\lambda_2 - \lambda_1} \tag{50}$$

$$Y_1 = \left[C_{20} - \left(\frac{\lambda_1 - A}{B}\right)C_{10}\right]\frac{B}{\lambda_2 - \lambda_1} \tag{51}$$

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

$$C_{1,avg} = \frac{X_1}{\lambda_1(t_2 - t_1)} e^{\lambda_1 t2} + \frac{Y_1}{\lambda_2(t_2 - t_1)} e^{\lambda_2 t2} - \frac{X_1}{\lambda_1(t_2 - t_1)} e^{\lambda_1 t1} - \frac{Y_1}{\lambda_2(t_2 - t_1)} e^{\lambda_2 t1} \quad (52)$$

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)

4. Computer Implementation and Availability of Model

The mathematics for this model is coded with standard Fortran 95/2003. The Fortran mathematics program is compiled separately from the user interface. This separation is to maintain flexibility and portability for users desiring to create their own user interface. The current user interface supplied with the software package is written in Visual Basic. A user manual is supplied with the installation package which provides recommendations for inputs..

The required chemical inputs are the basic properties regarding degradation, partitioning, and volatilization. The inputs for pesticide application information are the dates and masses of pesticide applied. Weather information is input as the name of a text file that contains the weather information. A vast number of 30-year meteorological files are available for many parts of the country from the US EPA (Burns et al., 2007). Weir and flood control information allows the specification of flooding, draining, and water level changes. Physical properties of the water body allow specification of mass transfer rates and the physical properties of the water column and the benthic compartment. The output tab allows basic file manipulations to specify the location of output.

The program produces an intermediate output file that includes enough information for a post processor to produce any results desired by the user. It is anticipated that user needs regarding output will evolve and thus post processing is achieved through an additional separately compiled program that is easily changed out as specific needs arise. Currently the post processor delivers daily water and soil concentrations, daily released pesticide mass, and

daily released water. Specifics are available in the user manual that comes with the program. This program operates in a Windows operating system and is freely available from the author.

5. Disclaimer

The information in this document has been subjected to review by the Environmental Fate and Effects Division in the Office of Pesticide Programs and approved for publication. Approval does not signify that the contents reflect the views of the Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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Table 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.

Figure Captions

Figure 1. Pictorial of the aquatic agriculture model showing hydrological and chemical processes included.

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

Figure 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.

Figure 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.

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

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

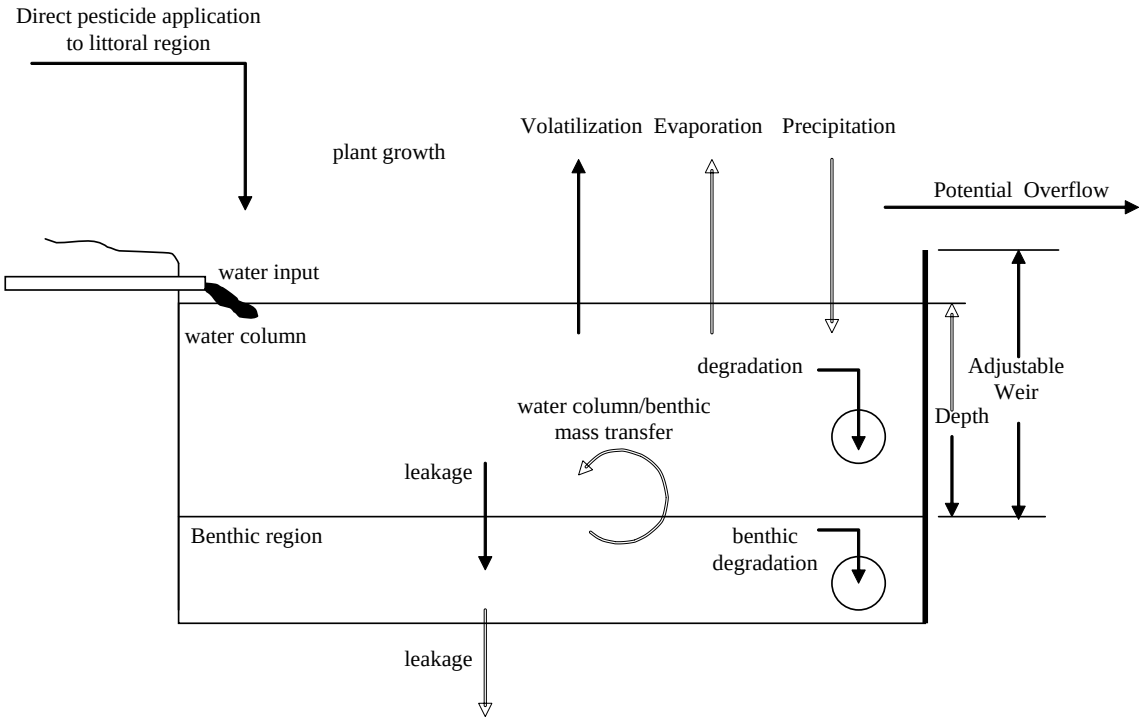


Figure 1. Pictorial of the aquatic agriculture model showing hydrological and chemical processes included.

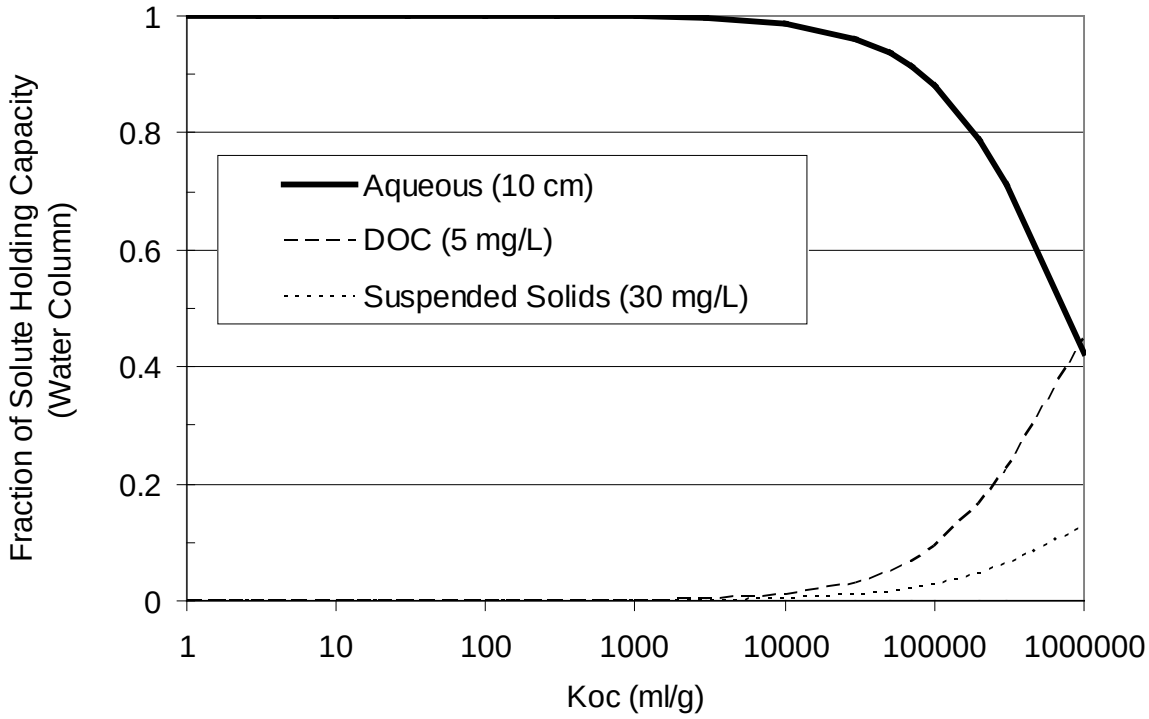

Fraction of Solute Holding Capacity (Water Column)
1
0.8
0.6
0.4
0.2
0
Aqueous (10 cm)
DOC (5 mg/L)
Suspended Solids (30 mg/L)
1
10
100
1000
10000
100000
1000000
Koc (ml/g)

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

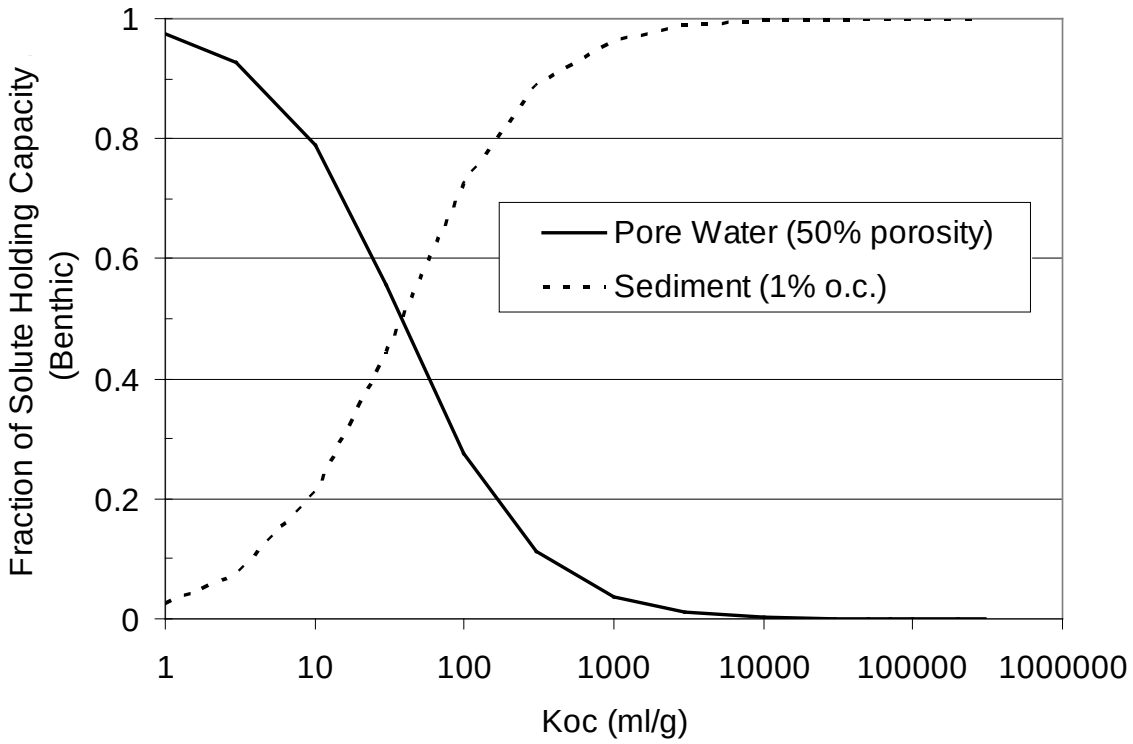
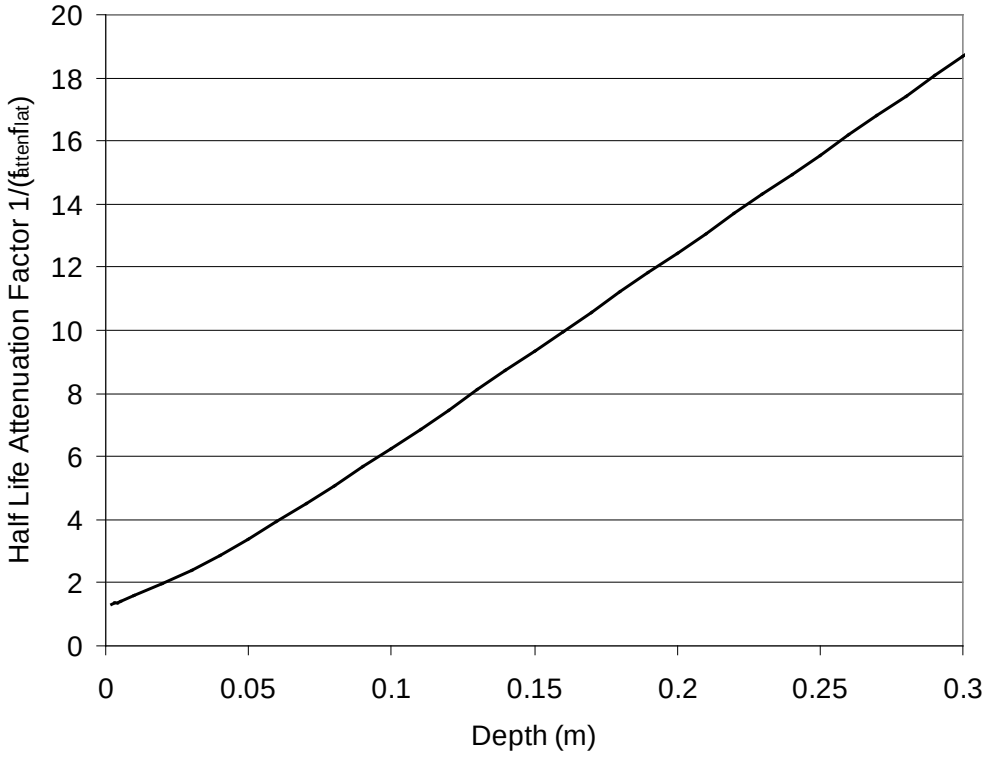


Figure 3. Relative solute holding capacity of individual components in the benthic zone. DOC and biological partitioning fractions are 10^{-4} or less and are not detectable on this graph.



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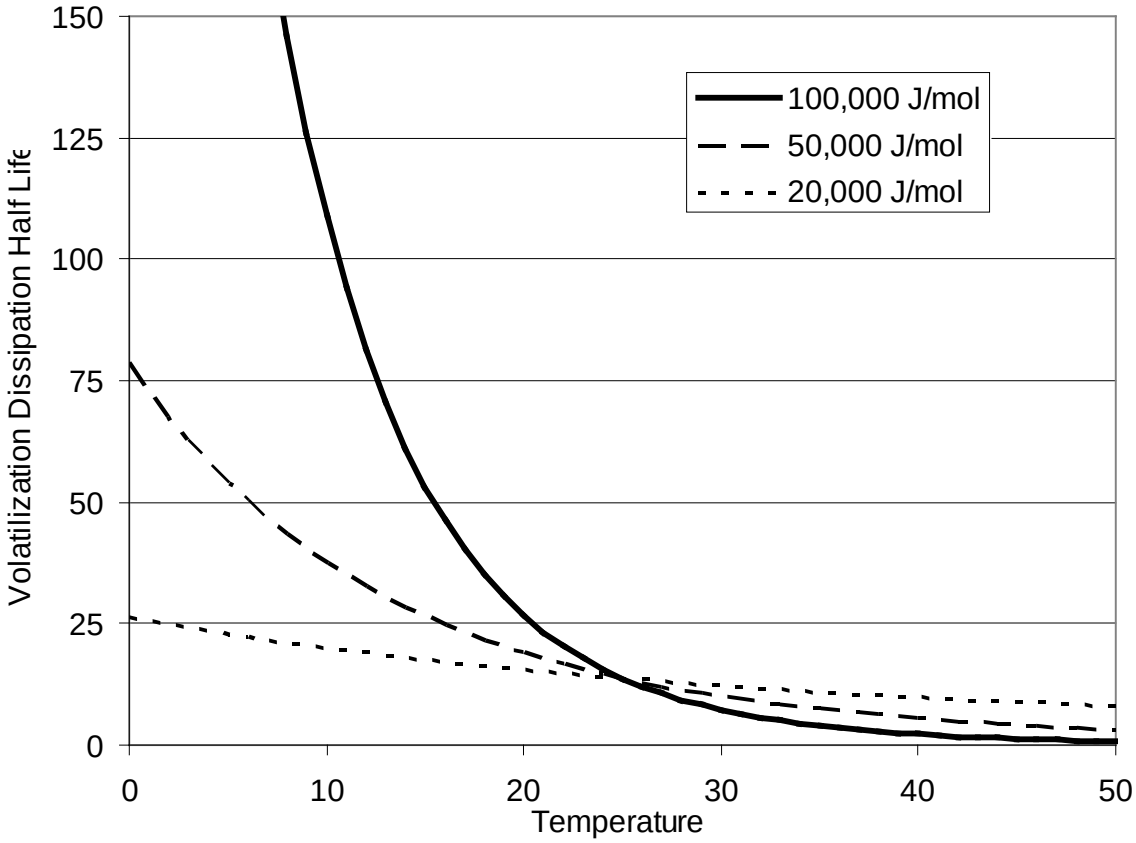

150
125
100
75
50
25
0
Volatilization Dissipation Half Life
0
10
20
30
40
50
Temperature
100,000 J/mol
50,000 J/mol
20,000 J/mol

Figure 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.

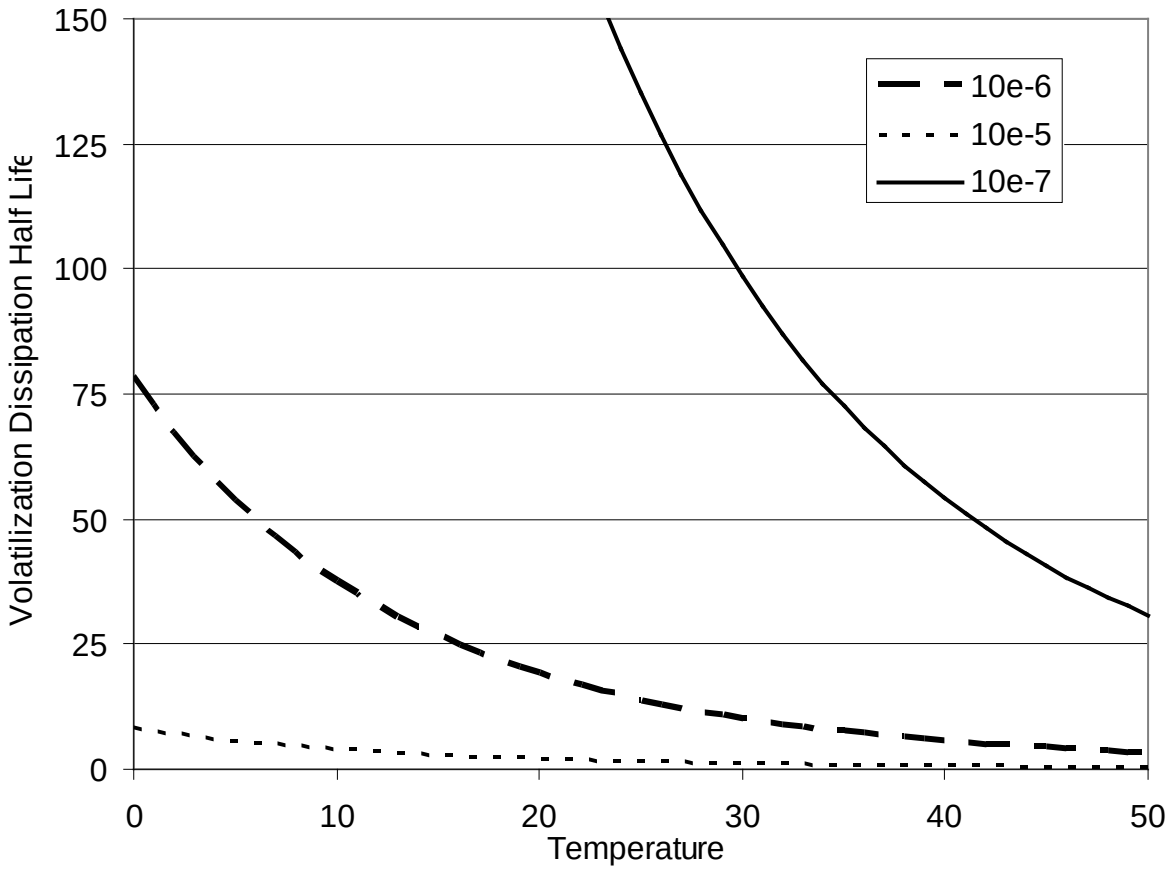
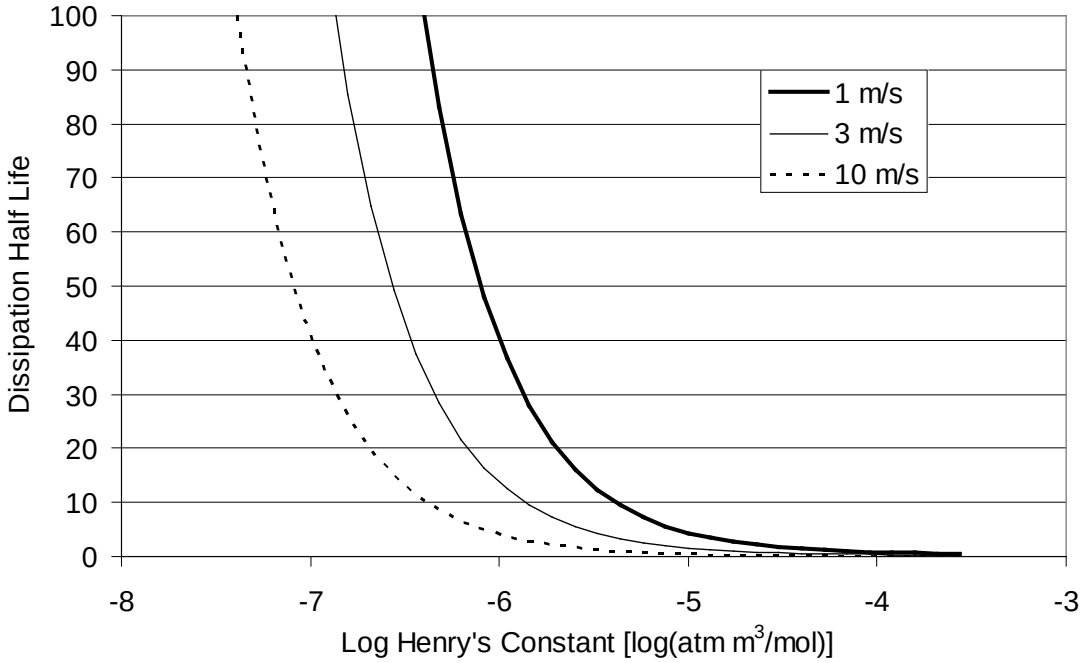

150
125
100
75
50
25
0
Volatilization Dissipation Half Life
0
10
20
30
40
50
Temperature
10e-6
10e-5
10e-7

Figure 6. Sensitivity of temperature and reference Henry 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.



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