UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

WASHINGTON, D.C. 20460

OFFICE OF
PREVENTION, PESTICIDES
AND TOXIC SUBSTANCES

MAR 17 2004

MEMORANDUM

SUBJECT: March 30-April 2, 2004 FIFRA SAP Meeting (Refined (Level II) Terrestrial and Aquatic Models Probabilistic Ecological Assessments for Pesticides) Revised Chapters 3 and 4

TO: Addressees

FROM: Myrta Christian, Designated Federal Official
Paul I. Lewis, Designated Federal Official
FIFRA Scientific Advisory Panel
Office of Science Coordination and Policy

Due to difficulties in converting Chapters 3 and 4 from Wordperfect to PDF files, several equations and/or symbols became corrupted. Enclosed are the corrected chapters. Please disregard the previous chapter versions and focus your review on the enclosed documents. Thank you for your understanding and we look forward to working with you later this month. If you have any questions about these documents, please contact us at your earliest convenience.

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
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OFFICE OF
PREVENTION, PESTICIDES AND
TOXIC SUBSTANCES

March 16, 2004

SUBJECT: Transmittal of Revised *Chapter IV* for March 30 - April 2, 2004 Scientific Advisory Panel Meeting

FROM: Steven P. Bradbury, Director
Environmental Fate and Effects Division
Office of Pesticide Programs

TO: Paul Lewis,
Designated Federal Official,
FIFRA Scientific Advisory Panel

Apparently some problems also arose with Chapter IV of the document, "A Discussion with the FIFRA Scientific Advisory Panel Regarding the Refined (Level II) Terrestrial and Aquatic Models." Apparently some of the symbols in the text, such as ≤, did not print as a result of the conversion of the document file to a PDF format. Thus, we are transmitting hard copies to you.

Please feel free to call on us if you need anything further.

Attachment

cc: D. Randall
I. Sunzenauer

IV. The Aquatic Level II Refined Risk Assessment Model (Version 2.0) (3/16/04)

A. Introduction

In determining whether a pesticide use poses unreasonable adverse effects to the environment, EPA characterizes risks of the pesticide use to aquatic ecosystems (FIFRA Section 152). The Agency's implementation plan for refining its ecological risk assessment process (USEPA, 2000b) outlines a four-level assessment approach for the evaluation of risks posed by pesticide residues in surface water from use of agricultural (e.g., field and row crops, orchards, vineyards, ornamentals) and non-agricultural (e.g., forests, grassland) pesticides. As mentioned in Chapter I.C.1, Level I provides a screening level assessment, for aquatic groups that are vulnerable to pesticide exposure in edge-of-field situations, that is based on one point of exposure and one point of effects. At the next level (Level II), the risk assessment provides an estimate of the likelihood and magnitude of effect on aquatic species that are vulnerable to pesticide exposure in edge-of-field situations.

This chapter presents an overview of the aquatic Level II Refined Risk Assessment (RRA) model and proposed temporal and spatial modifications to the exposure characterization component of the model. Since the 2001 SAP review of case studies using the pilot (Version 1.0) Level II RRA model, EPA has made refinements to the Level II model and has instituted plans to make additional refinements in the future. As part of this effort, EPA has developed a user-friendly, self-contained software package that includes data storage, exposure, effects, risk calculation, and report modules. Use of this software package streamlines the exposure, effects, and risk calculations and eliminates the need to manually run and manipulate output from multiple programs.

The first two sections of the overview present the objectives of the Level II RRA model, a brief summary of the key Level II RRA model components, and a comparison of the Levels I and II aquatic RRA models, both Versions 1.0 and 2.0. In Sections C-E, discussions and supporting documentation for modifications to the aquatic Level II RRA Version 2.0 model are provided. Section C provides a description of the surface water fate model, the varying volume surface water model (VVWM). Section D presents tests of individual processes of the VVWM analytical solutions as well as combined processes of spray drift, erosion, and runoff. This section also provides an evaluation of exposure when the VVWM is used with field area and water body size parameters set to standard values (10 ha field, and water body with 1 ha surface area and 20,000 m^3 volume). Section E describes crop scenario-specific field drainage to water body size ratios that were developed for use with a varying volume scenario in different regions of the U.S. In the final section, Section F, potential options for future modifications to determination of curve number in the runoff model, a major factor that influences runoff volume, are discussed.

In the future, EPA expects to make a few remaining modifications to the aquatic Level II RRA methods, models, and tools based on the 2001 SAP comments as well as the experience of the RRA development team in implementing the existing methods and tools. Because the

information and/or tools needed to make these modifications are under development, they have not been incorporated at this time but will be considered in the near future. (See Section G of this Chapter for a description of the efforts and implementation plans for these modifications).

At this time, the Agency seeks the SAP's recommendations regarding the proposed changes in the approach, methods, and/or tools described in this chapter. In Chapter 2, the Agency poses specific questions for the SAP to address.

B. Overview of the Aquatic Level II Assessment Objectives and Model

1. Objectives

The objectives of the Level II risk assessment are as follows:

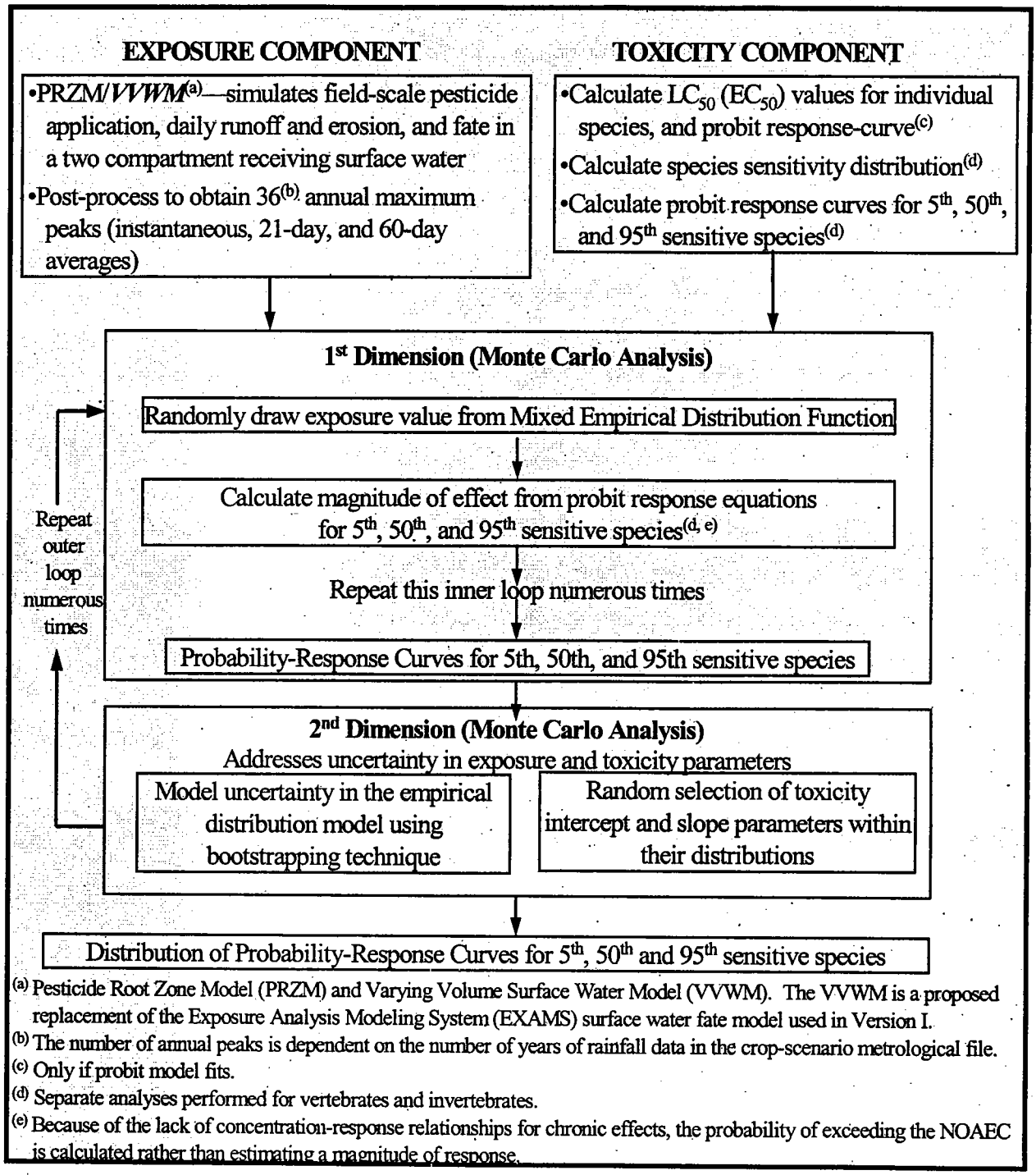
- Provide probabilistic estimates of risk (i.e., the likelihood and magnitude of effect) using data available for a Level I (screening) assessment;
- Characterize temporal variations in risk to organisms that are vulnerable to pesticide exposure in edge-of-treated-field situations ;
- Improve characterization of risk through the use of the full annual peak exposure distributions (instantaneous, and 21-day and 60-day running averages) and full concentration-response curves;
- Identify those regional/cropping patterns or effects that may require additional refinement in Level III; and/or
- Permit preliminary evaluation of mitigation options.

2. Summary of Aquatic Level II RRA Model

Figure 4-1 presents a flow chart of the aquatic Level II model, a two-dimensional Monte Carlo risk model consisting of three main components: exposure, toxicity (or effects), and risk. This two-dimensional risk model was presented to the SAP in 2001 with the exception of one variation: a surface water fate model (VVWM) is being proposed as a replacement for the previous surface water fate model (Exposure Analysis Modeling System (EXAMS)) which operates as a fixed-volume model.

The exposure component of the model simulates field-scale pesticide application, daily field run-off and erosion, and fate to a surrogate surface water. Currently, the Level II Version 1.0 aquatic model uses PRZM to simulate temporal run-off and erosion of a pesticide from an agricultural field, and EXAMS to simulate the fate of the pesticide in this run-off in a fixed volume of surface water. In the Level II Version 2.0 aquatic model, EPA is proposing to replace EXAMS with a new surface water fate model, VVWM, which simulates the fate and temporal hydrology in a receiving water using stochastic temporal variations in weather. For both versions, the simulated daily surface water concentrations are post-processed to provide typical 36-year maximum annual peaks: instantaneous peaks for acute exposure and peak 21-day and

Figure 4-1. Flowchart of the Level II Two-Dimensional Monte Carlo Risk Assessment Model



[a] Pesticide Root Zone Model (PRZM) and Varying Volume Surface Water Model (VVWM). The VVWM is a proposed replacement of the Exposure Analysis Modeling System (EXAMS) surface water fate model used in Version I.

[b] The number of annual peaks is dependent on the number of years of rainfall data in the crop-scenario metrological file.

[c] Only if probit model fits.

[d] Separate analyses performed for vertebrates and invertebrates.

[e] Because of the lack of concentration-response relationships for chronic effects, the probability of exceeding the NOAEC is calculated rather than estimating a magnitude of response.

60-day running averages for chronic exposure of aquatic invertebrates and fish, respectively. After calculating these peak values, the maximum annual peak data are fit to a mixed empirical distribution function.

The agricultural field and meteorological conditions used in PRZM are defined by a crop scenario that consists of a combination of climatology, soil, and cropping practice conditions. The risk assessments conducted at Levels I and II are national or regional assessments in the sense that a given crop scenario is used as a surrogate for that crop across the U.S. or a region, respectively. Currently, EPA has developed four categories of crop scenarios: (1) national—a crop scenario that is a surrogate for that crop nationwide; (2) regional—a crop scenario that is a surrogate for that crop within a region; (3) organophosphate (OP) cumulative —a group of crop scenarios for addressing cumulative risk from use of OP pesticides across the nation or within a region; and (4) location specific—crop scenarios that specifically address a crop use in a specific locale. A single soil series that is selected for a crop scenario assumes soils properties are homogenous across the field. The soil series is selected to represent those soils, within the actual crop growing region represented, that are more vulnerable to soil erosion.

The exposure scenarios used at Level II are intended to provide estimates of vulnerable, edge-of-field situations across a wide range of geographical conditions under which the product is used. These surface waters are considered vulnerable because of their size (e.g., low-order streams, and small wetlands, pools, and ponds), and spatial relationship to the treated field. In addition, as mentioned in the previous paragraph, the soil series selected for use in crop scenarios are those that are considered, based on professional judgement, to be more vulnerable to soil erosion in the use area. In the field, these surface waters would be expected to be among the highest exposure concentrations observed. However, the focus on these surface waters does not automatically make the assessment overly conservative as there are large portions of the U.S. where low-order streams, small wetlands, pools, and ponds are adjacent to or surrounded by agricultural fields. Formulating the assessment endpoints in this way focuses on those situations nationally or regionally for a given crop/use that will tend to have the greatest risks. The challenge is to develop a surrogate aquatic exposure scenario (or conceptual model) that produces estimated environmental concentrations (EECs) that are not worst case (i.e., holds only for a few limited circumstances), and does not underestimate pesticide concentrations frequently and are scientifically defensible for vulnerable, edge-of-field surface waters across a wide range of geographical conditions in the continental U.S., Alaska, Hawaii, and U.S. territories.

For the Level II (Version 1.0) risk assessment and later versions of Level I, the exposure scenario, which has historically been used as a surrogate, is a small, permanent (perennial), fixed-volume standing (lentic) surface water body adjacent to or surrounded by a pesticide-treated field. The source of water is solely precipitation and run-off, and all run-off, eroded soil, and spray drift from the treated-field is routed into this surface water body. The surface water body has no outlet, no groundwater seepage or surface water input from non-treated areas, and pesticide removal by leaching out of the water body is not a route of dissipation. Evaporation is assumed to balance run-off and precipitation inputs. In the Levels I and II (Version 1.0) exposure scenarios, the field area is 10 ha (100,000 m^2), and the water body has 1 ha of surface area, is 2 m

deep, and has a surface water volume of 20,000 m^3 (Table 4-1). Although the selected scenario is not a flowing (lotic) water exposure scenario, the equivalent dilution represented for a flowing water can be determined. Dissipation from volatilization will be more conservative in the standing water scenario than a comparable flowing water scenario because of higher turbulence in a flowing system.

Concern has been expressed that the field-size-to-volume ratio used in the current scenario may not represent (1) small, low-order perennial streams receiving multiple inputs from adjacent fields, (2) smaller volume surface waters receiving an equivalent level of runoff and/or drift as is estimated by the model, or (3) similar volume surface waters as the model but that receive runoff from fields larger than 10 ha. Proposed changes to the field-size-to-volume ratio should address most of these concerns.

The Level II acute effects or toxicity component uses current acute toxicity tests for freshwater and saltwater fish and invertebrates required for a Level I risk assessment and includes slopes of the concentration-response curves. Toxicity measurement endpoints are 96-h median lethal concentration (LC_{50}) values for fish species and 96-h LC_{50} or median effective concentration (EC_{50}) values for aquatic invertebrates; for some aquatic invertebrates, such as the daphnid, 48-h rather than 96-h values are used. It is assumed that the distributions of sensitivity observed in test species represent the range of responses that are likely to be encountered in the U.S. Using log LC_{50} (EC_{50}) values, a species sensitivity distribution is constructed for each group (e.g., freshwater fish, saltwater fish, freshwater invertebrates, saltwater invertebrates) that is being analyzed. The 5^{th}, 50^{th}, and 95^{th} percentiles of the distribution, representing the generic 5^{th}, 50^{th}, and 95^{th} most sensitive species LC_{50} (EC_{50}) values, are identified. Probit concentration-response curves are constructed for each of these percentile species by using the mean of the individual species probit slopes (assumes all species in the species sensitivity distribution have the same mean probit slope) and back-calculating the intercept at the given LC_{50} (EC_{50}) value.

The Level II chronic effects assessment includes current early-life stage and sensitive partial and full life-cycle tests. Measurement endpoints are no observable adverse effects concentrations (NOAECs) for survival, reproduction, and growth effects for invertebrates and embryo and larval/juvenile survival and larval/juvenile growth effects in fish. If a test contains more than one measurement endpoint (e.g., survival and growth), the lowest value for a given test is used. If there are sufficient chronic effects data, a species sensitivity distribution of NOAECs is constructed, and the 5^{th}, 50^{th}, and 95^{th} percentiles are determined. However, in most cases, chronic NOAEC data are limited, and the risk analyses are restricted to individual species.

The Level II risk evaluation process yields estimates of likelihood and magnitude of effects for acute exposures. For the estimate of acute risks, a distribution of estimated exposure and a distribution of lethal effects are combined through a two-dimensional Monte Carlo analysis to obtain a distribution of joint probability functions. For a given crop scenario, a joint probability function expresses risk in terms of the likelihood or probability of an exposure concentration occurring and the related magnitude of effect in percent mortality for a given generic species. The concentration-response curve for an individual species is considered to

Table 4-1. Level I and II Aquatic Risk Assessment Exposure Components

Structure	Level I		Level II	
	Tier I	**Tier II**	**Version 1.0**	**Proposed Version 2.0**
Field Runoff Model	Simple percentage [a]	PRZM	PRZM	
Field Drainage Area	10 hectares (100,000 m^2)		10 hectares (100,000 m^2)	
Surface Water Model	GENEEC - Fixed volume - Single runoff event [a] - Multiple spray drift events - No overflow/ outflow - No evaporation	EXAMS - Fixed volume - Multiple runoff events - Multiple spray drift events - No overflow/ outflow - No evaporation	EXAMS - Fixed volume - Multiple runoff events - Multiple spray drift events - No overflow/ outflow - No evaporation	VVWM - Varying-volume - Multiple runoff events - Multiple spray drift events - Overflow - Evaporation
Surface Water Dimensions and Volume	Depth: 2 m Surface area: 1 ha (10,000 m^2) Volume: 20,000 m^3		Depth: 2 m Surface area: 1 ha (10,000 m^2) Volume: 20,000 m^3	Crop scenario specific
DA/VC [b]	5 m^2/m^3 (1.5 acre/acre-ft)		5 m^2/m^3 (1.5 acre/acre-ft)	Crop scenario specific
Degradation Rates	Point Estimates		Point Estimates	Point Estimates [c]
Initial Application Date	Single date		Single date	Single date [d]
EECs Used in Risk Calculations		90th percentile of annual maxima values - peak (instantaneous) - 21-day weighted average - 60-day weighted average	90th percentile of annual maxima values - peak (instantaneous) - 21-day running average - 60-day running average	Distribution of annual maxima - peak - 21-day running average - 60-day running average

[a] Assumes 10 % of pesticide applied to the field runs off

[b] Drainage area (m^2) to volume capacity (m^3) (e.g., the Level I model is 100,000 $m^2 \div (2\ m \times 10{,}000\ m^2)$)

[c] Model is being written to accommodate a choice between using deterministic values or accounting for variability and/or uncertainty in the pesticide fate inputs (e.g., soil aerobic metabolism).

[d] An approach for incorporating a range of dates is under development.

represent the percent of an exposed population that will be affected. The distribution of joint probability functions provides estimates of the uncertainty in the risk estimates.

For the estimate of chronic risks, a distribution of exposure concentrations (annual maxima 21-day or 60-day running averages for invertebrates and fish, respectively) is compared to a chronic measurement endpoint. The risk analysis for chronic effects provides information only on the probability that the chronic endpoint assessed will be exceeded, not on the magnitude of the chronic effect expected. The assessment then proceeds to outline the consequences of the potential effects.

A comparison of the deterministic Level I and probabilistic Level II components are provided in Tables 4-1 and 4-2 along with a comparison Level II model (Version 2.0) from the 2001 pilot model (Version 1.0). Key features of the Level I model include a fixed volume water body fate model, national standard values for drainage area and surface water size ratio, and use of the lowest effects data for a group (e.g., freshwater fish). Highlights of the Level II model include a varying-volume water body fate model, region-specific values for drainage area and surface water size ratios, and use of distribution of effects with a species sensitivity distribution (i.e., generic fish and invertebrate species).

3. Software Package

EPA is developing a software tool that will facilitate execution of the exposure simulation, using an exposure module based on the Agency's PRZM model (used here as a run-off model) linked with the VVWM. A toxicity data analysis module calculates measurement endpoints and species sensitivity distributions. The effects and exposure data are integrated using a two-dimensional Monte Carlo analysis in the probabilistic risk module, yielding estimates of the probability and magnitude of effects to aquatic organisms, as well as estimates of uncertainty associated with those predictions.

Table 4-2. Level I and II Aquatic Risk Assessment Acute Effects Components

Structure		Level I, Tier I and II	Level II, Version 1.0 and 2.0
Acute Effects	Concentration-Response Model	Not restricted (e.g., probit, moving average, binomial)	At least one species, within a group (freshwater fish, freshwater invertebrate, saltwater fish, saltwater invertebrate), with a concentration- response probit slope and intercept model fit
	Effect Endpoint	Median lethal concentration (96-h LC_{50})[(a)]	Full concentration-response relationship[(a)]
	Species Evaluated	Lowest species LC_{50} (EC_{50}) within a group (freshwater fish, freshwater invertebrates, saltwater fish, saltwater invertebrates)	Species-sensitivity distribution (5th, 50th, and 95th generic species LC_{50} [(a)]) for each group
Chronic Analysis	Concentration-Response Model	Tests designed for hypothesis testing—concentration-response curve not calculated	
	Effect Endpoint	No observable adverse effect (NOAEC) for hatching success and survival and growth of larvae for fish (includes reproduction if fish life cycle test conducted), and survival, reproduction and growth in invertebrates.	
	Species Evaluated	Lowest species NOAEC within a group	Species-sensitivity distribution (5th, 50th, and 95th generic species NOAEC) for each group—if data is too limited to develop a species sensitivity distribution individual species NOAECs are evaluated

[(a)] For invertebrates, includes effects such as immobilization in daphnia where the effect is considered as a surrogate for mortality (i.e., includes median effect concentration (EC_{50})). Also for some invertebrates, like daphnia, use 48-h results.

C. A Varying Volume Water Body Model with Daily Parameter Variations for Pesticide Risk Assessments

1. Introduction

An important objective of OPP is to estimate pesticide exposure in surface waters resulting from pesticide applications to agricultural fields. In order to meet this objective, OPP currently uses a small, static standing water body scenario in order to estimate aquatic exposure concentrations. A previous SAP (2001) suggested that this water body model could be improved by allowing volume to vary according to weather conditions which may impact day-to-day concentrations. This section discusses a proposed varying volume water body model (VVWM) that incorporates this SAP suggestion as well as several other modifications to better characterize surface water concentration variability.

In performing pesticide aquatic exposure assessments, OPP currently uses two models–PRZM and EXAMS– in series. PRZM (Carsel et al., 1997) is used to simulate pesticide applications to agricultural fields and its subsequent transport off the field by runoff and erosion. PRZM uses daily historical meteorological data from the particular region of the country for which a risk assessment is being made and calculates daily runoff and spray drift fluxes from "standard" fields over a simulation period (typically about 30 years). These standard fields are parameterized such that they represent particular crops and regions of the United States (e.g., corn grown in Ohio). The receiving water body has historically been simulated with the EXAMS model (Burns, 1985), which reads in the daily pesticide loadings from PRZM and calculates resulting daily concentrations. EXAMS uses the same meteorological data as PRZM, but processes the data into calendar month averages before making allowances for meteorological-dependent properties such as water temperature, photolysis potential, and volatilization potential. EXAMS, however, does not make allowances for potential variations in volume as may occur during periods of drought or excessive runoff and precipitation.

A proposed modification to the water body model has been developed which allows volume to vary according to meteorological (hydrologic) conditions. This modification is demonstrated to have a more significant effect on concentration than many of the other standard meteorologically varying properties currently considered in EXAMS. The proposed new surface water fate model also allows parameters to vary on a daily basis, which is more in line with the input meteorological data than is the current fate model, which only varies on a monthly basis. In addition, the proposed model uses an analytical solution, rather than numerical methods as used in EXAMS, which contributes in part to much shorter runtimes for the new model. The faster speed will have important benefits to refined aquatic risk assessments that use Monte Carlo techniques.

Although OPP uses two scenarios–one for ecological assessments (small, lentic surface water body) and one for drinking water assessments (reservoir)–the modifications that follow are only examined in regards to the ecological scenario. The ecological and reservoir scenarios differ greatly in the scale of the drainage area considered and the dimensions and volume of the

surface water body evaluated. For ecological assessments, the scenario consists of a small fixed-volume surface water body, whereas a larger fixed-volume reservoir is simulated for human drinking water assessments. The smaller ecological surface water scenario will likely be the more volume sensitive of the two. The proposed model has potential for adaptation for use in larger water bodies, but that is not evaluated here.

2. Current Ecological Surface Water Scenario and Model

The conceptual model of the ecological surface water body is a 2-compartment model, comprising a benthic and a littoral zone, and is defined by a set of "standard" parameters that describe it's physical characteristics. For current pesticide surface water assessments, EXAMS (a multi-compartment model) is used in a 2-compartment mode as a means of simulating this conceptual model. Specific physical characteristics of the ecological surface water body are given in Table 4-3 and define the *current standard scenario.* (This table is discussed later in the context of comparison with the proposed changes to the model.) The implementation of EXAMS along with this current standard scenario is used currently to estimate exposure concentrations for ecological risk assessments and will be referred to as the *current EXAMS-based model* throughout this document.

The current standard scenario represents a small, lentic surface water body located at the edge of a pesticide-treated field and is intended to represent a vulnerable exposure scenario. The current dimensions of the water body, which are 1 ha area by 2 m deep, were chosen in accordance with USDA guidance on construction of a permanent small pond or embayment (e.g., irrigation, fire protection, watering cattle, fish and wildlife) given a 10-ha watershed in central Georgia (USDA, 1982). In the current Level I and II (Version 1.0) RRA models, this same water body size is applied uniformly across the U.S. This constant volume characteristic, in essence, means that inflow is assumed to be exactly balanced by evaporative losses. Because EXAMS was constructed with a steady-state hydrology assumption, EXAMS requires that volume be fixed and thus cannot simulate drought or wet conditions. Additionally, EXAMS can only vary parameters such as wind speed and temperature (and the associated degradation or dissipation rates) on a calendar-month basis, whereas input data is delivered on a daily basis. Thus, EXAMS does not take full advantage of the available daily input in a way that could characterize daily variations in weather-dependent processes such as volatilization and metabolic degradation. These issues have lead to proposed changes in the model.

3. Varying Volume Surface Water Body Model (VVWM)

The proposed VVWM is conceptually similar to the current EXAMS-based model in that both are 2-compartment models driven by first-order processes. The proposed VVWM differs from the current model in that it allows for volume changes on a daily basis, depending on runoff, precipitation, or evaporation. The proposed model also allows for temperature, wind speed and pesticide-dissipation processes to vary on a daily basis, which is more in line with the available meteorologic and hydrologic input data. In addition, it is proposed that the characteristics of the water body (depth, surface area, and associated drainage area) be scenario

Table 4-3. Parameters and standard values used in the current EXAMS-based model. Parameters are defined in the EXAMS user manual.

EXAMS parameter	Units	Current Ecological Scenario Value
PRBEN	—	0.5
PCTWA	—	137
BULKD	g/ml	1.85
FROC	—	0.047
CHARL	m	1.05
DSP	m^2/hr	3.00×10^{-5}
AREA	m^2	10,000
VOL_1	m^3	20,000
VOL_2	m^3	500
$DEPTH_1$	m	2
SUSED	mg/L	30
CHL	mg/L	0.005
DOC_1	mg/L	5.0
DOC_2	mg/L	5.0
LAT	degrees	34
BNMAS	g/m^2	0.006
$BNBAC_1$	—	—
$BNBAC_2$	cfu/100g	37
$BACPL_1$	cfu/ml	1
$BACPL_2$	—	—
DFAC	—	1.19
WIND	m/s	Metfile
STFLO	m^3/hr	0
TCEL	°C	Monthly average

specific, such that the water body characteristics are consistent with the associated regional-specific PRZM field scenario. This latter proposal will be discussed in detail in Section E.

The VVWM is conceptualized in Figure 4-2 and consists of two zones—a littoral zone and a benthic zone. Each individual zone is completely mixed and at equilibrium with all phases within the individual zone, with equilibrium within each zone described by a linear isotherm. The two zones are coupled by a turbulent-mixing first-order mass-transfer process. Figure 4-2 also shows that the water volume may vary due to inputs of precipitation and runoff and by outputs of evaporation and overflow.

For this proposed model, the mathematical conceptualization of the water body is formed using daily piecewise solutions. The water body volume is assumed to be constant over the duration of a day, but it is allowed to vary from day to day. In this way, an analytical solution can be retained for the daily concentrations. The assumption of daily variability is consistent with the input data for these models. For example, the runoff, rainfall, and evaporation input data are 24-hour totals, so water volume can never be more accurate than a daily value. Since EXAMS can only change system properties (e.g., temperature, flows) on a calendar-month basis, the proposed VVWM offers an improvement that can take advantage of the higher resolution input data.

All individual dissipation processes (e.g., metabolism, hydrolysis, volatilization) are represented as first-order in concentration, as described later. This representation is the same for both the current EXAMS-based model and the VVWM. For the VVWM, on any given day, the mass of a pesticide in the surface water system is described by two differential equations. Equation 4-1 represents a mass balance on the littoral zone and equation 4-2 represents a mass balance on the benthic zone.

$$m_{sed\_1}\frac{ds_{sed\_1}}{dt} + m_{bio\_1}\frac{ds_{bio\_1}}{dt} + m_{DOC\_1}\frac{ds_{DOC\_1}}{dt} + v_1\frac{dc_1}{dt} = -Qc_1 - QC_{sed}s_{sed\_1} - QC_{bio}s_{bio\_1} - QC_{DOC}s_{DOC\_1} - \alpha\left(c_1 - c_2\right) - v_1\mu_{photo}c_1 - v_1\mu_{bio\_a1}c_1 - v_1\mu_{hydr}c_1 - v_1\mu_{vol}c_1 - m_{sed\_1}\mu_{bio\_sed1}s_{sed\_1} - m_{bio\_1}\mu_{bio\_biota1}s_{bio\_1} - m_{DOC\_1}\mu_{bio\_DOC1}s_{DOC\_1} \quad (4\text{-}1)$$

$$m_{sed\_2}\frac{d_{sed\_2}}{dt} + m_{bio\_2}\frac{ds_{bio\_2}}{dt} + m_{DOC\_2}\frac{ds_{DOC\_2}}{dt} + v_2\frac{dc_2}{dt} = -v_2\mu_{bio\_a2}c_2 - v_2\mu_{hydr\_2}c_2 + \alpha\left(c_1 - c_2\right) - m_{sed\_2}\mu_{bio\_sed2}s_{sed\_2} - m_{bio\_2}\mu_{bio\_biota2}s_{bio\_2} - m_{DOC\_2}\mu_{bio\_DOC2}s_{DOC\_2} \quad (4\text{-}2)$$

where,

c_1 = aqueous concentration of pesticide in littoral zone, [kg/m^3]
c_2 = aqueous concentration of pesticide in benthic zone, [kg/m^3]
C_{sed} = concentration of suspended sediment in littoral zone = m_{sed_1}/v_1 [kg/m^3]
C_{DOC} = concentration of dissolved organic carbon (DOC) in littoral zone = m_{DOC}/v_1, [kg/m^3]
C_{bio} = concentration of biota in littoral zone = m_{bio_1}/v_1 [kg/m^3]
m_{sed_1} = mass of suspended sediment in littoral zone, [kg]
m_{DOC_1} = mass of DOC in littoral zone, [kg]
m_{bio_1} = mass of suspended biota in littoral zone, [kg]
m_{sed_2} = mass of sediment in benthic zone, [kg]
m_{DOC_2} = mass of DOC in benthic zone, [kg]
m_{bio_2} = mass of biota in benthic zone, [kg]
s_{sed_1} = sorbed pesticide concentration on suspended sediment in littoral zone, [kg/kg]
s_{DOC_1} = sorbed pesticide concentration on suspended DOC in littoral zone, [kg/kg]
s_{bio_1} = sorbed pesticide concentration on suspended biota in littoral zone, [kg/kg]
s_{sed_2} = sorbed pesticide concentration on benthic sediment, [kg/kg]
s_{DOC_2} = sorbed pesticide concentration on benthic DOC, [kg/kg]
s_{bio_2} = sorbed pesticide concentration on benthic biota, [kg/kg]
v_1 = volume of water in littoral zone on the specific day, [m^3]
v_2 = volume of water in benthic zone, [m^3]
Q = volumetric flow rate of water out of littoral zone, [m^3/s]
α = 1st order littoral-to-benthic mass transfer coefficient, [m^3/s^{-1}]
μ_{photo} = 1st order photolyisis 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 littoral zone, [s^{-1}]
μ_{bio_sed1} = 1st order sediment-sorbed metabolic degradation rate coefficient in littoral zone, [s^{-1}]
μ_{bio_biota1} = 1st order biota-sorbed metabolic degradation rate coefficient in littoral zone, [s^{-1}]
μ_{bio_DOC1} = 1st order DOC-sorbed metabolic degradation rate coefficient in littoral zone, [s^{-1}]
μ_{bio_a2} = 1st order aqueous-phase metabolic degradation rate coefficient in benthic zone, [s^{-1}]
μ_{bio_sed2} = 1st order sediment-sorbed metabolic degradation rate coefficient in benthic zone, [s^{-1}]
μ_{bio_biota2} = 1st order biota-sorbed metabolic degradation rate coefficient in benthic zone, [s^{-1}]
μ_{bio_DOC2} = 1st order DOC-sorbed metabolic degradation rate coefficient in benthic zone, [s^{-1}]
μ_{hydr_1} = 1st order hydrolysis rate coefficient in littoral zone, [s^{-1}]
μ_{hydr_2} = 1st order hydrolysis rate coefficient in benthic zone, [s^{-1}]

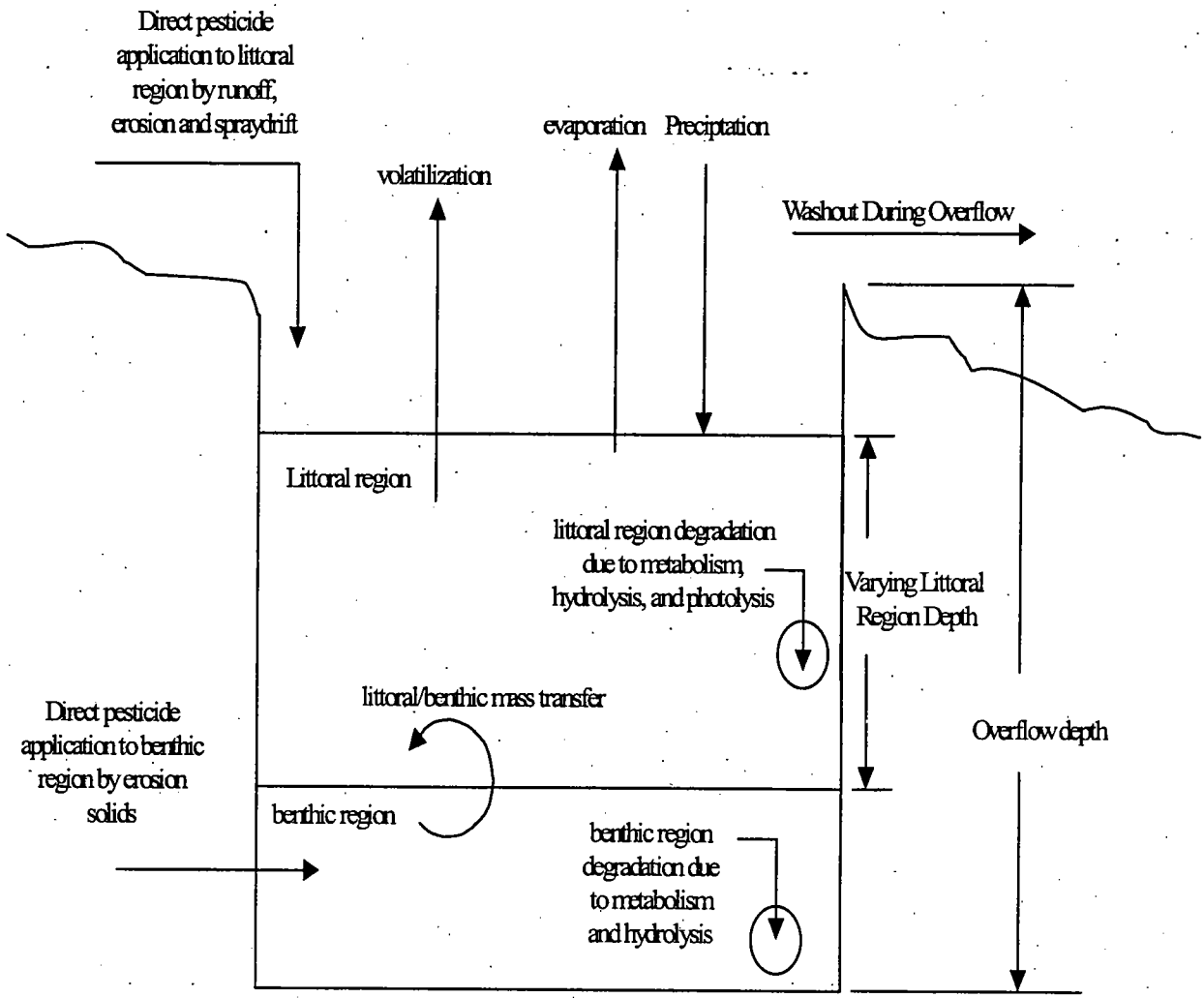


Figure 4-2. Conceptualization of the Varying Volume Water Body Model

All parameters in the above equations, except for the pesticide-specific parameters, have been assigned standard values for use in the current EXAMS-based model when simulating the ecological scenario. These standard system values are listed in Table 4-4. For many of these values, there is no documentation on how they were chosen or how representative they are of national waters. One focus of future work is to review these values to ensure that they meet the intent of the ecological surface water scenario, develop more region-specific values, and document the selection process. Table 4-5 is provided to aid in comparing some of the parameter definitions used in EXAMS with those of the proposed VVWM. Changes to the parameter definitions in the proposed VVWM reflect an effort to use more intuitive descriptions that will help users understand the modeling approach. Table 4-3 lists the values of the EXAMS parameters for the current model.

In both the current EXAMS-based model and the proposed VVWM, the following assumptions are made: (1) suspended matter in the littoral zone is of negligible volume, (2) hydrolysis, photolysis, and volatilization act only on dissolved pesticide species, (3) because of data limitations described later, the rate coefficient for biological metabolism is the same for both dissolved and sorbed forms of pesticide within a single zone (e.g., $\mu_{bio\_1} = \mu_{bio\_a1} = \mu_{bio\_sed1} = \mu_{bio\_DOC1} = \mu_{bio\_biota1}$, and $\mu_{bio\_2} = \mu_{bio\_a2} = \mu_{bio\_sed2} = \mu_{bio\_DOC2} = \mu_{bio\_biota2}$; *where* $\mu_{bio\_1\ and}\ \mu_{bio\_2}$ are the overall metabolism rates in the respective zones), (4) the hydrolysis rate coefficient in the benthic zone is the same as that in the littoral zone, (5) linear isotherm equilibrium exists within each zone among all sorbed species. With these assumptions, equations 4-1 and 4-2 can be rewritten in a simpler form as follows:

$$\frac{dc_1}{dt} = -\Gamma_1 c_1 - \Omega\Theta\left(c_1 - c_2\right) \tag{4-3}$$

$$\frac{dc_2}{dt} = -\Gamma_2 c_2 + \Omega\left(c_1 - c_2\right) \tag{4-4}$$

where,

$$\Gamma_1 = \frac{Q}{v_1} + \left(\mu_{photo} + \mu_{hydr} + \mu_{vol}\right)\left(f_{w1}\right) + \mu_{bio} \tag{4-5}$$

$$\Gamma_2 = \mu_{bi} + f_{w2}\mu_{hydr} \tag{4-6}$$

$$\Omega = \frac{\alpha}{\left(m_{sed\_2}K_{sed\_2} + m_{bio}K_{bio\_2} + m_{DOC\_2}K_{DOC\_2} + v_2\right)} \tag{4-7}$$

Table 4-4. Parameter values for the current EXAMS-based model in terms of the VVWM definitions of the parameters.

Parameter	Unit	Current Value	Notes
v_1	m^3	20,000	Littoral volume
v_2	m^3	249.8	Aqueous benthic volume[a]
A	m^2	10,000	Surface area, calculated (v_1/d_1)
d_1	m	2.0	Littoral depth
d_2	m	0.05	Benthic depth
m_{sed_1}	kg	600	Based on suspended solids concentration of 30 mg/l (see C_{sed_1})
m_{bio_1}	kg	8.0	Based on biota concentration of 0.4 mg/l
m_{DOC_1}	kg	100	Based on DOC concentration of 5 mg/l
f_{oc}	—	0.04	Fraction of organic carbon (littoral and benthic region zone)
m_{sed_2}	kg	6.752×10^5	[b]
m_{bio_2}	kg	0.0600	[c]
m_{DOC_2}	kg	1.249	[d]
pH		7	
C_{CHL}	mg/L	0.005	Chlorophyll concentration in littoral zone
C_{DOC}	mg/L	5	DOC concentration in littoral zone
C_{sed_1}	mg/L	30	Suspended solids concentration in littoral zone
C_{bio}	mg/L	0.4	Biomass concentration in littoral zone
D	m^2/s	8.33×10^{-9}	Sediment dispersion coefficient
Δx	m	1.025	Benthic/littoral boundary layer thickness
V_{T2}	m^3	500	Total volume of benthic zone ($d_1 A$)

[a]calculated from: (*VOL2*)(*BULKD*)(1-100/*PCTWA*) (see Table 4-5)
[b]calculated from: (*BULKD*)(*VOL2*)(100000)/*PCTWA* (see Table 4-5)
[c]calculated from: (*BNMAS*)(*AREA*)(0.001) (see Table 4-5)
[d]calculated from: (*DOC*)(v_2)/1000 (see Table 4-5)

Table 4-5. VVWM parameter equivalents to EXAMS parameters[a]

VVWM		Expressed in terms of EXAMS parameters[b]
Parameter	**Unit**	
m_{sed_1}	kg	$(SUSED)(VOL_1)\left(10^{-6}\frac{kg}{mg}\right)\left(10^{3}\frac{L}{m^3}\right)$
m_{sed_2}	kg	$\left(\frac{BULKD}{PCTWA/100}\right)(VOL_2)\left(10^{6}\frac{ml}{m^3}\right)\left(10^{-3}\frac{kg}{g}\right)$
v_1	m^3	VOL_1
v_2	m^3	$(VOL_2)(BULKD)\left(1-\frac{100}{PCTWA}\right)$ [c]
Q	m^3/s	$(STFLO)/(3{,}600$ s/hr)
μ_{A1}	s^{-1}	$(KBACW_1)(BACPL_1)/(3{,}600$ s/hr)
μ_{S1}	s^{-1}	$(KBACW_2)(BACPL_1)/(3{,}600$ s/hr)
μ_{A2}	s^{-1}	$\frac{(KBACS_1)(BNBAC_2)}{\left(\frac{PCTWA}{100}-1\right)}\left(10^{-2}\frac{100g}{g}\right)\left(\frac{1}{3600}\frac{hr}{s}\right)$
μ_{S2}	s^{-1}	$\frac{(KBACS_2)(BNBAC_2)}{\left(\frac{PCTWA}{100}-1\right)}\left(10^{-2}\frac{100g}{g}\right)\left(\frac{1}{3600}\frac{hr}{s}\right)$
	s^{-1}	$\frac{(AREA)(DSP)}{(CHARL)(VOL_2)}$
K_{sed_1}	m^3/kg	$(KOC)(FROC)(10^{-3}\ m^3/L)$
K_{sed_2}	m^3/kg	$(KOC)(FROC)(10^{-3}\ m^3/L)$

[a] Except for pesticide-specific parameters (e.g., KOC, $KBACW_1$, $KBACW_2$, $KBACS_1$, $KBACS_2$), see Table 4-3 for standard values used for the EXAMS parameters.
[b] Subscripts 1 and 2 refer to littoral compartment and benthic compartments, respectively.
[c] Assumes that the density of water is 1,000 kg/m^3

$$\Theta = \frac{\left(m_{sed\_2}K_{sed\_2} + m_{bio\_2}K_{bio\_2} + m_{DOC\_2}K_{DOC\_2} + v_2\right)}{\left(m_{sed\_1}K_{sed\_1} + m_{bio\_1}K_{bio\_1} + m_{DOC\_1}K_{DOC\_1} + v_1\right)} \quad (4\text{-}8)$$

where f_{w1} and f_{w2} are the fractions of solute in the aqueous phase within the littoral and benthic zones, respectively, as defined by:

$$f_{w1} = \frac{v_1}{\left(m_{sed\_1}K_{sed\_1} + m_{bio\_1}K_{bio\_1} + m_{DOC\_1}K_{DOC\_1} + v_1\right)} \quad (4\text{-}9)$$

$$f_{w2} = \frac{v_2}{\left(m_{sed\_2}K_{sed\_2} + m_{bio\_2}K_{bio\_2} + m_{DOC\_2}K_{DOC\_2} + v_2\right)} \quad (4\text{-}10)$$

and where K_{sed_1}, K_{bio_1}, K_{DOC_1} are the linear isotherm partitioning coefficients for suspended sediments, biota, and DOC in the littoral zone, respectively, and K_{sed_2}, K_{bio_2}, K_{DOC_2} are the linear isotherm partitioning coefficients for sediments, biota, and DOC in the benthic zone, respectively (all with units of m^3/kg).

The term f_{w1} varies on a daily basis depending on the volume of the water body (v_1), as described below in *Daily Piecewise Calculations* (Section C5). For the VVWM, the mass of sediment, biota, and DOC is assumed to remain constant. Although this assumption may not be exactly correct, it is expected to have little impact on the model output and simplifies modeling efforts. Significant sorption to these species only occurs at extremely high partitioning coefficient values, as shown later.

Given a set of initial conditions, equations 4-3 and 4-4 completely describe the VVWM. These equations show that there are four parameters that influence the concentration: Γ_1, Γ_2, Ω, and Θ. The term Γ_1 is the effective overall dissipation rate in the littoral zone [s^{-1}]; Γ_2 is the effective overall degradation rate in the benthic zone, [s^{-1}]; Ω is a mass transfer coefficient describing transfer between the benthic and littoral zones, [s^{-1}]; and Θ is the ratio of solute holding capacity in the benthic zone to that in the littoral zone, [dimensionless]. The sections that follow describe the details of the components of these equations and discusses differences and similarities with current EXAMS-based model.

a. Solute Holding Capacity Ratio (Θ)

The solute holding capacity ratio (Θ) is the ratio of solute holding capacity in the benthic zone to the solute holding capacity in the littoral zone, as defined by equation 4-8. For the current EXAMS-based model simulations, all of the parameters in equation 4-8 that describe the physical characteristics of the water bodies (i.e., masses and volumes) are set to the values given in Table 4-4. For the proposed VVWM, these parameters would be scenario specific, and v_1

would vary according to hydrologic inputs for a given scenario; this proposal is discussed later in Section E. The individual partitioning coefficients for the media (K_{sed}, K_{bio}, and K_{DOC}) used in equation 4-8 are generally not directly measured for a pesticide assessment (as they are not part of the Code of Federal Regulation 40, part 158 test guidelines). Partitioning coefficients (K_d) are typically available for pesticide sorption to agricultural soils, and these values could be (and sometimes are) used for model input for K_{sed}. The VVWM is currently written to accept only K_{oc} values as input.

The partitioning coefficient for sediment is directly proportional to K_{oc} for many organic compounds. The constant of proportionality is the amount of organic carbon in the sediment, which is set to a standard value (see Table 4-4). The fraction of organic carbon in sediment is assumed to be the same in the littoral and benthic zones, and thus the littoral and benthic sediment partitioning coefficients (K_{sed_1} and K_{sed_2}, respectively) can be determined from:

$$K_{sed\_1} = K_{sed\_2} = f_{oc} K_{oc} \left(0.001 \frac{\mathrm{m^3/kg}}{\mathrm{ml/g}} \right) \tag{4-11}$$

where,

K_{oc} = organic carbon partitioning coefficient, [ml/g]
f_{oc} = fraction of organic carbon in sediment [unitless], assumed to be the same for benthic and littoral sediment

Note that the units of the coefficients in equations 4-1 to 4-10 are all given in the Systeme Internationale (SI) form. The SI convention will be maintained throughout this section. However, for some fundamental parameters such as K_{oc}, usually presented in units of ml/g, the common unit and the SI conversion factor will be provided.

The partitioning coefficients for DOC are determined from the default empirical relationships described in the EXAMS documentation (Burns, 2000). The standard water bodies incorporate the notion from Burns (2000) that benthic DOC has higher partitioning characteristics than littoral DOC. The equations for K_{DOC_1} (littoral) and K_{DOC_2} (benthic) given by Burns (2000) and adopted for the VVWM are:

$$K_{DOC\_1} = (0.2114)(K_{oc}) \left(0.001 \frac{\mathrm{m^3/kg}}{\mathrm{ml/g}} \right) \tag{4-12}$$

$$K_{DOC\_2} = (K_{oc}) \left(0.001 \frac{\mathrm{m^3/kg}}{\mathrm{ml/g}} \right) \tag{4-13}$$

The partitioning coefficients for biota are also determined from default empirical relationships described in the EXAMS documentation. These relationships are given by the following:

$$K_{bio\_1} = K_{bio\_2} = 0.436\left(\frac{K_{oc}}{0.35}\right)^{0.907}\left(0.001\frac{\mathrm{m^3/kg}}{\mathrm{ml/g}}\right) \qquad (4\text{-}14)$$

By inserting equations 4-11 through 4-14 into equation 4-8 and with substitution of the specific values from Table 4-4 into equation 4-8, the solute holding capacity can be written such that it is only a function of K_{oc}. The value of Θ as a function of K_{oc} for the current EXAMS-based model is presented in Figure 4-3. The point where Θ is equal to 1 represents the K_{oc} for which the solute capacity in the benthic zone is equal to that in the littoral zone. For the ecological surface water, equal capacities occur at a K_{oc} of 730 ml/g. Of course, the littoral and benthic zones are not at equilibrium, so the actual distribution of solute will not be evenly split between benthic and littoral zones at these K_{oc} values. These K_{oc} values and the figure, however, give some insight into how the solute can potentially be distributed within these systems.

It is also of interest to examine the relative significance of the individual media within each zone with regard to the distribution of solute among them. Figure 4-4 shows the relative capacities of the individual media (aqueous and sorbed to biota, DOC, and suspended sediment) within the littoral zone as a function of K_{oc}. Only the water phase is significant for K_{oc} values up to 10,000 ml/g. For K_{oc} values up to 100,000, biota partitioning is not significant, and at a K_{oc} value of 100,000 the combined capacities of all sorbed species amounts to less than 20 percent of the total littoral zone capacity. DOC and suspended sediments are shown to have nearly equal capacities for solute for the current EXAMS-based standard water bodies.

Figure 4-5 shows the relative solute holding capacities of the individual media components in the benthic zone. In the benthic zone, partitioning to DOC and biota is not significant at any K_{oc} value. The relative fractions for the benthic DOC and biota are on the order of 10^{-7}–10^{-5} for the K_{oc} range shown, and thus cannot be seen in Figure 4-5. At a K_{oc} of about 9 ml/g, solute is evenly distributed between the pore-water-dissolved fraction and the sediment-sorbed fraction. At K_{oc} values above 1,000 ml/g, the vast majority of solute in the benthic zone is sorbed to sediment.

b. Effective Littoral Zone Dissipation (Γ_1)

The overall dissipation rate in the littoral zone (Γ_1), as defined in equation 4-5, 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.

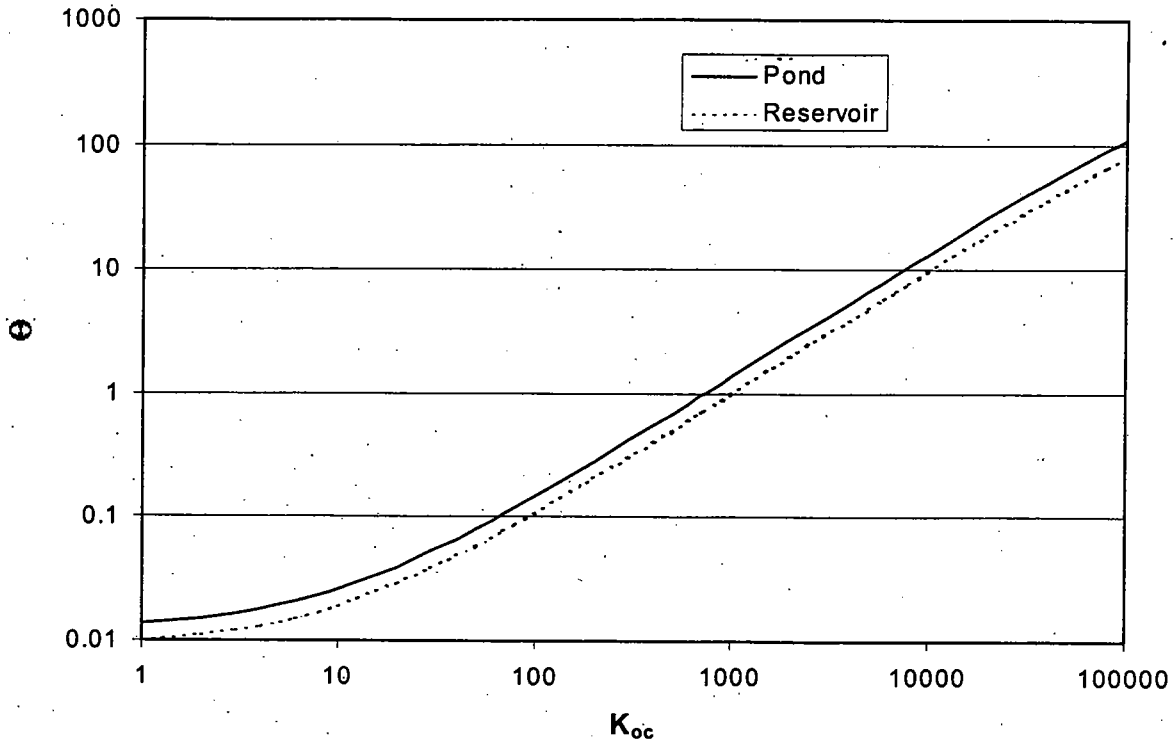


Figure 4-3. Solute holding capacity as a function of K_{oc} for the current (EXAMS-based) model. (The reservoir is another scenario used for drinking water assessments and is not considered here.)

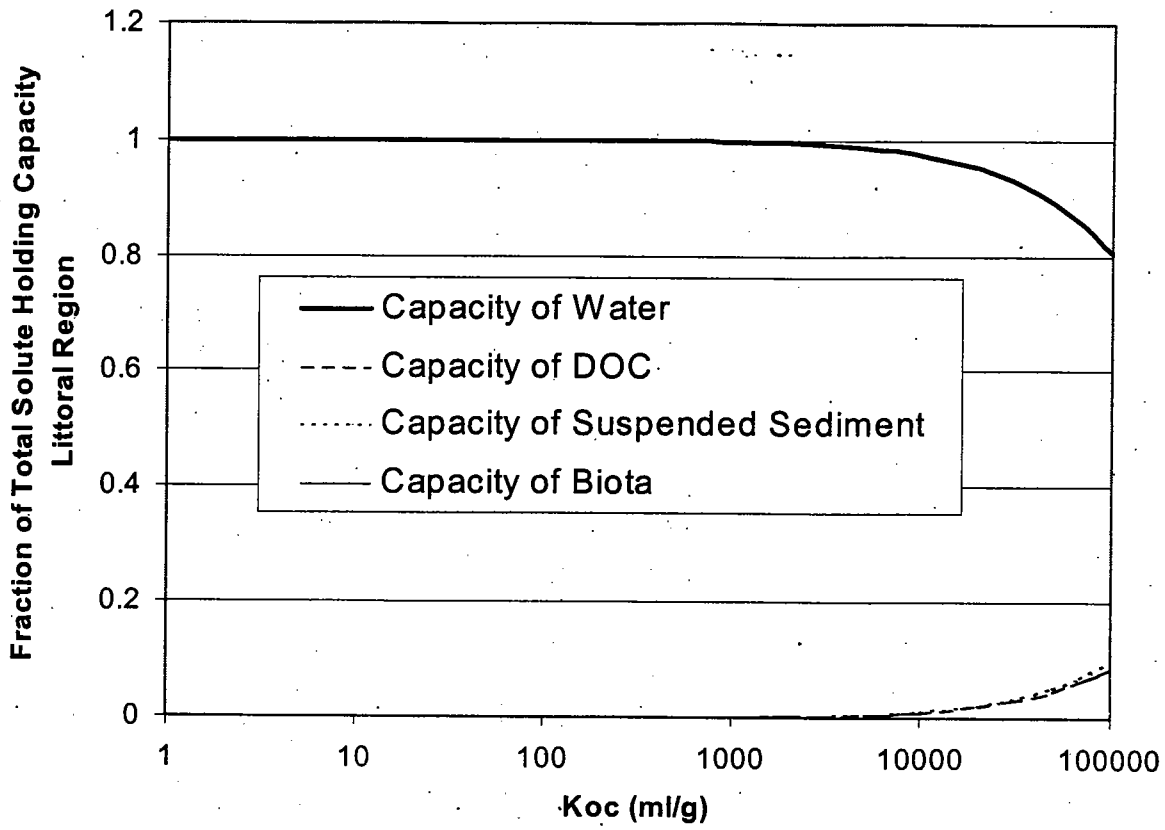


Figure 4-4. Relative solute holding capacity of individual components in the littoral zone.

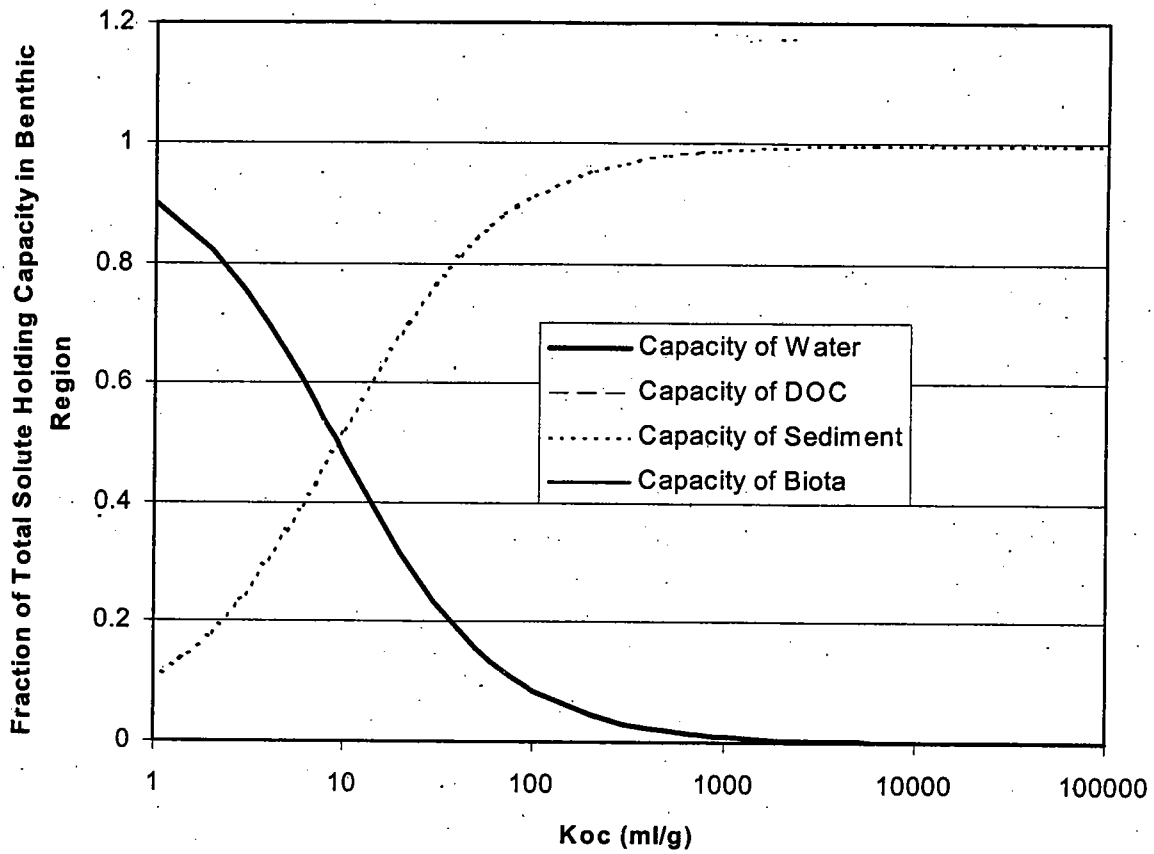


Figure 4-5. Relative solute holding capacity of individual components in benthic region

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

The first term in equation 4-5, Q/v_1, represents the effective first-order dissipation rate due to the flow moving pesticide out of the water body. Flow out of the water body only occurs if meteorological conditions produce enough water inflow to cause the water body to overflow (see *Daily Piecewise Calculations* below). The washout term acts on all forms of pesticide (both aqueous dissolved and sorbed to suspended matter), as is apparent from equation 4-1. This means that settling of suspended solids is not explicitly considered in the VVWM, and pesticide in both dissolved and suspended sorbed forms can flow out of the system.

The current EXAMS-based ecological model does not allow for overflow, while the proposed VVWM does (the current EXAMS-based reservoir model also allows overflow). An example of how overflow will affect pesticide dissipation is given in Figure 4-6. This figure shows the effective dissipation half-life due to washout of a pesticide for a water body with the current EXAMS-based model's dimensions (Table 4-4) and for a range of typical annual average runoff flow rates as determined from standard field scenarios with a field size of 10 ha (the OPP current standard). This figure provides an idealized perspective of the potential long-term effect of the proposed washout addition. Short term effects will be quite variable since washout is calculated on a daily basis. During overflow events, effective dissipation half-life may differ greatly from these long-term averages.

(2). Metabolism (μ_{bio_1})

In the registration process of pesticides, an estimate of the aqueous degradation rate for the pesticide 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 20-25 °C. These tests generally do not differentiate between degradation occurring on the dissolved forms and sorbed forms of the pesticide; an overall degradation rate is generally all that is available. Therefore, the VVWM (as well the current model) treat sorbed-phase and aqueous-phase degradation rates as the same, which makes both equal to the overall rate.

In both the current (EXAMS-based) model and the VVWM, the temperature of the water body is allowed to vary, and thus (when no data are available on temperature effects on metabolism) OPP has adopted a standard method for temperature adjustments to the aqueous-phase aerobic metabolic rate as follows:

$$\mu_{bio\_1} = \mu_{25} \times 2^{\left(\frac{T-T_{ref}}{10}\right)} \qquad (4\text{-}15)$$

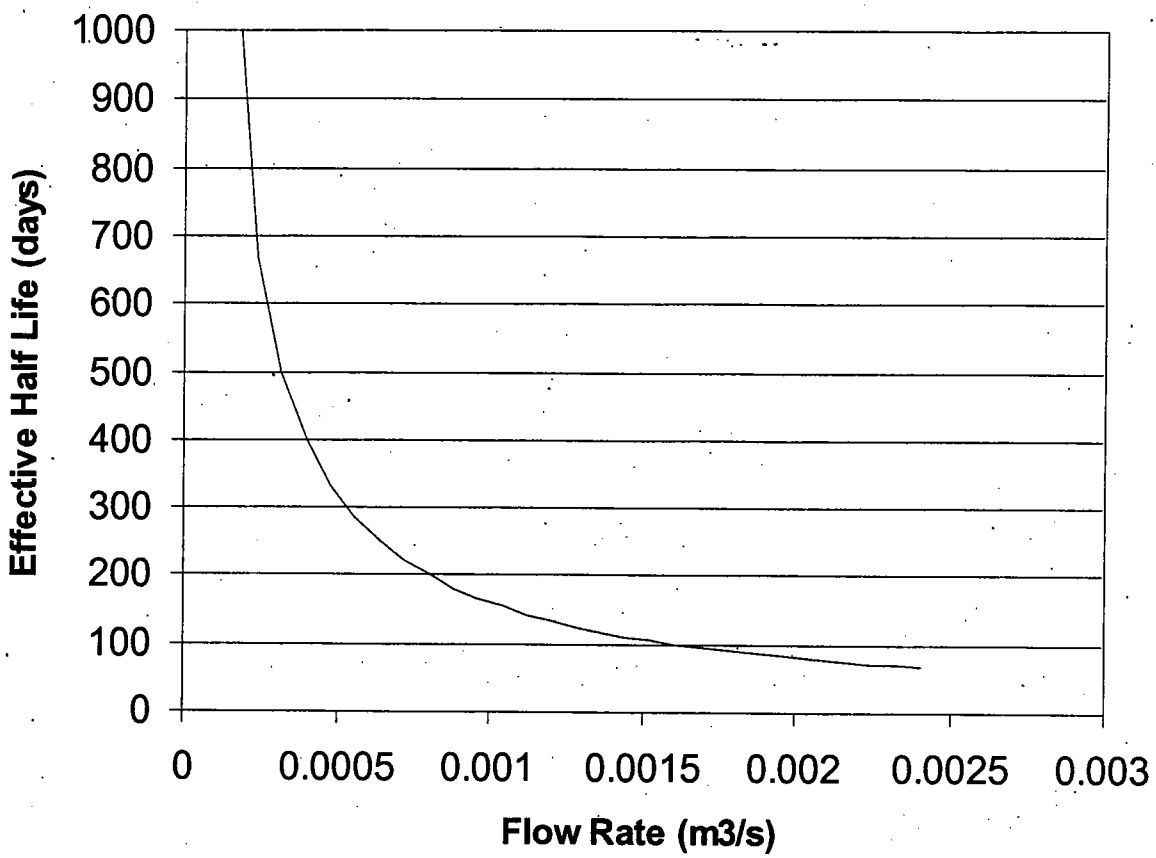


Figure 4-6. Effective half-life of pesticide due to washout in a water body as currently parameterized (1 ha area by 2 m deep). Range of flow rates represents the typical range of flow rates under current standard field size (10 ha).

where,

μ_{25} = laboratory measured aerobic metabolism rate at 25 °C, [s^{-1}]
T = temperature of simulated water body, [°C]
T_{ref} = temperature at which laboratory study was conducted, [°C].

This temperature modification doubles the degradation rate for every 10 degree rise in temperature, and halves the degradation rate for every 10 degree decrease. In EXAMS and the VVWM air temperature is taken from the meteorological data that corresponds to the crop/location scenario being simulated. Because EXAMS can only deal with calendar-month temperature values, the current (EXAMS-based) model uses the average air temperature of the current calendar month. However, since physical processes do not follow a 12-month calendar and since water body temperatures generally lag air temperatures, the proposed VVWM uses the previous 30-day average temperature for any given day; thus adjustments are made daily. Such a modification is not possible in EXAMS, but is easily implemented in the proposed solution described later.

(3). Hydrolysis (μ_{hydr_1})

The hydrolysis rate for a pesticide is directly obtained from experimental measurements, as supplied by pesticide registrant data submissions. The current standard water bodies are modeled at a constant pH of 7 (Table 4-4). Therefore, the effective hydrolysis rate is the experimentally determined overall hydrolysis rate from tests conducted at pH of 7. (Note that this is not just the neutral hydrolysis rate coefficient, but rather implicitly includes acid and base hydrolysis). In a subsequent section, scenario-specific pH values are proposed. Unlike the temperature modifications to metabolism rate, temperature adjustments of hydrolysis rates are not made because temperature-dependent characterizations are not generally made available for the registration process, and a standard adjustment approach for temperature effects on hydrolysis has not been adopted. Therefore, the hydrolysis rate is taken as

$$\mu_{hydr\_1} = \mu_{overall,\,pH=7} \tag{4-16}$$

where,

$\mu_{overall,\,pH=7}$ = laboratory-measured overall hydrolysis rate at pH=7, [s^{-1}]

In both the current EXAMS-based model and the VVWM, it is assumed that hydrolysis acts only on dissolved species. Therefore, the effective hydrolysis rate is reduced by the factor f_{wl}, as defined in equation 4-9 and implemented in equation 4-5. The factor f_{wl} represents the fraction of total pesticide that is present in dissolved aqueous form, as previously described.

(4). Photolysis (μ_{photo})

Photolysis rates are derived from standard laboratory tests following EPA-approved protocol. These tests are designed to estimate the photodegradation rate for near-surface

conditions at a specific latitude and under clear-sky conditions. The methods given in the EXAMS documentation (Burns, 1997, 2000) to account for latitude adjustments, light attenuation, and cloud cover on photolyis are used within the VVWM. These adjustments are implemented as follows:

$$\mu_{photolysis} = f_{lat} f_{cloud} f_{atten} \mu_{measured} \quad (4\text{-}17)$$

where,

f_{lat} = latitude adjustment factor, [unitless]
f_{cloud} = cloudiness adjustment factor, [unitless]
f_{atten} = attenuation factor to absorption, [unitless]
$\mu_{measured}$ = measured near-surface photolysis rate coefficient at reference latitude and clear atmospheric conditions, [sec^{-1}]

Currently, cloudiness does not affect the current standard water bodies, as f_{cloud} is set to a value of 1. The factor is included here for purposes of formality and because this factor may be considered in future versions of the standard water bodies.

The latitude of the standard water bodies may vary, depending on the desired location in where a pesticide assessment is to be made. The effect that latitude has on incident light is accounted for by a latitude adjustment factor (f_{lat}). The latitude adjustment described in the EXAMS documentation (Burns, 2000) is adopted for use within the VVWM. Full details of the reasoning behind the factor can be found in the EXAMS documentation, and only the resulting equation is given here. The latitude adjustment is

$$f_{lat} = \frac{191700 + 87050\cos(0.0349 \times L_{sim})}{191700 + 87050\cos(0.0349 \times L_{ref})} \quad (4\text{-}18)$$

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) for EXAMS has also been adopted for the VVWM. Full details of the reasoning behind the factor are given in the EXAMS documentation, and the resulting equation is

$$f_{atten} = \left[\frac{1 - \exp\left[-(D_{fac})(d_1)a\right]}{(D_{fac})(d_1)a} \right] \quad (4\text{-}19)$$

where,

D_{fac} = EXAMS-defined distribution factor default value of 1.19, [unitless]
d_l = depth of littoral zone, [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

$$a = 0.141 + 101[C_{CHL}] + 6.25[C_{DOC}] + 0.34[C_{Sed}] \quad (4\text{-}20)$$

where C_{DOC} and C_{sed} have been previously defined under equation 4-1, and C_{CHL} is the chlorophyll concentration [mg/L] in the littoral zone. Standard values for C_{DOC}, C_{sed}, and C_{CHL} are given in Table 4-4. With these standard values, $a = 42.096\ m^{-1}$. Therefore, for the ecological scenario, $f_{atten} = 0.009981$.

With the above considerations, the effective photolysis rate, only depends upon the laboratory-measured photolysis rate, the latitude of the water body, and the reference latitude of the measured photolysis rate. The effective photolysis rate can be written in terms of these parameters. For the ecological scenario, the effective rate is

$$\mu_{photo} = \left[\frac{1913 + 868.8\cos(0.0349 \times L_{sim})}{191700 + 87050\cos(0.0349 \times L_{ref})}\right](\mu_{measured}) \quad (4\text{-}21)$$

Temperature effects on photoysis are not considered in the VVWM except that photolysis is not allowed to occur if the water temperature is ≤0 °C (as with the current EXAMS-based model). Temperature effects are not considered is because temperature-dependent data are not typically supplied with pesticide registration submissions, and a standard adjustment for temperature effects on photolysis has not been adopted.

The above equations show that for a water body at a latitude of 34 degrees, and with a reference laboratory latitude of 0 degrees, the effective aqueous-phase photolysis rate in the current EXAMS-based model is 124 times lower than the measured laboratory rate. In addition, as with hydrolysis, photolysis is assumed to act upon only dissolved forms of the pesticide; therefore, the overall effective hydrolysis rate is further reduced by the factor f_{wl} in equation 4-5.

For the VVWM, the assumption is made that the overall photolysis rate does not change as the water depth changes. This simplification is made in part because the mass of light-interfering material is assumed not to change with volume changes, and, therefore, would have an opposing effect to the depth changes. More importantly, photolysis is a relatively minor

variable in most risk assessments in surface waters with depths and suspended matter quantities similar to those in the standard ecological scenario for all chemicals except those with near-surface photolysis rates on the order of hours. However, modifications to the code to incorporate depth-dependent photolysis should be rather minor and are being considered.

(5). Volatilization ($\mu_{volatilization}$)

EXAMS and the VVWM 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. The VVWM uses all of the volatilization default assumptions described in the EXAMS documentation. The overall volatilization rate coefficient may be expressed as

$$\mu_{vol} = \frac{(A)(k_{vol})}{v_1} \tag{4-22}$$

where,

A = surface area of littoral zone, [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:

$$\frac{1}{k_{vol}} = \frac{1}{k_w} + \frac{1}{\left(\frac{H}{RT}\right)k_a} \tag{4-23}$$

where,

k_w = liquid-phase resistance, [m/s]
k_a = gas-phase resistance, [m/s]
H = Henry's law constant, [m^3atm/mol]
R = universal gas constant, [8.206 x 10^{-5} m^3atm/mol/K]
T = temperature, (°K)

The VVWM uses the EXAMS methods 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

$$k_w = k_{O_2}\sqrt{\frac{32}{MW}} \tag{4-24}$$

where,

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

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 originally used in EXAMS will be used. For wind velocities (u_{wind}) less than 5.5 m/s, the relationship used is

$$k_{O_2} = \left(4.19 \times 10^{-6}\right)\left(\sqrt{u_{wind,10m}}\right)\left(1.024^{(T-20)}\right) \tag{4-25}$$

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

$$k_{O_2} = \left(3.2 \times 10^{-7}\right)\left(u_{wind,10m}\right)^2\left(1.024^{(T-20)}\right) \tag{4-26}$$

where,

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

Wind speeds are read from meteorological files in which wind speed is given from measurements 10 m above the surface. A general relationship between wind speed and height is

$$\frac{u_1}{u_2} = \frac{\log\left(z_1/z_0\right)}{\log\left(z_2/z_0\right)} \tag{4-27}$$

where z_0 is the boundary roughness height which is assumed to be 1 mm (0.001 m). 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 using Equation 4-27at 0.1 m is

$$u_{0.1} = \frac{\log\left(0.1/0.001\right)}{\log\left(10/0.001\right)} u_{10} = 0.5u_{10} \tag{4-28}$$

The gas phase resistance (k_a) is referenced to water vapor resistance and an empirical relationship that 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:

$$k_{a,H_2O} = 0.00005 + (0.0032)(u_{0.1}) \quad (4\text{-}29)$$

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 gas phase resistance of a pesticide is related to the exchange rate of water by:

$$k_a = \left(k_{a,H_2O}\right)\left[\frac{D_a}{D_{a,H_2O}}\right]^{\alpha} \quad (4\text{-}30)$$

where 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 VVWM (as well as EXAMS) uses 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):

$$\frac{D_a}{D_{a,H_2O}} \cong \left[\frac{18}{MW}\right]^{0.5} \quad (4\text{-}31)$$

Substituting equation 4-31 into equation 4-30 gives:

$$k_a = \left(k_{a,H_2O}\right)\left[\frac{18}{MW}\right]^{0.5} \quad (4\text{-}32)$$

The resulting relationship is:

$$k_a = \left[0.00005 + (0.0032)(u_{0.1})\right]\left(\sqrt{\frac{18}{MW}}\right) \quad (4\text{-}33)$$

The Henry's Law coefficient (H) is generally not available for pesticide registration, and in such cases, it is approximated from vapor pressure and solubility. The Henry's Law coefficient is not adjusted for temperature as this information is not supplied with pesticide registration submissions, and a standard temperature adjustment factor has not been adopted at this time. The resulting relationship is:

$$H = \frac{(vp/760)}{(sol/MW)} \qquad (4\text{-}34)$$

where,

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

In the proposed VVWM, wind speed varies on a daily basis; in the EXAMS construct average monthly wind speed varies on a monthly basis. The effect that wind speed has on the effective volatilization half-life is given in Figure 4-7 for the current EXAM-based model. The figure shows that wind speed variations will have an increasingly more dramatic effect as Henry's Law coefficient is reduced. The use of daily wind speeds in the proposed VVWM will likely have significant short-term implications (acute concentrations) for compounds with a low Henry's Law coefficient.

Temperature has little effect on compound volatilization in the current EXAMS-based model or the VVWM. The effect of temperature on effective volatilization half-life is shown in Figure 4-8, which shows that volatilization as developed in the models is only a very weak function of temperature. This is primarily because volatilization data as a function of temperature is not supplied with the pesticide registration submissions and a standard to address the influence that temperature has on the Henry's Law coefficient has not been adopted. It is assumed that Henry's Law coefficient is constant with respect to temperature changes. This is an area that should receive future attention.

3. Effective Benthic Zone Dissipation (Γ_2)

The overall benthic degradation, as defined in equation 4-6, is affected only by biodegradation and hydrolysis. As with the littoral zone, it is assumed that biodegradation in the benthic zone affects all forms of pesticide (both dissolved and sorbed forms) and that hydrolysis affects only aqueous dissolved forms (see equation 4-6 and definition of f_{w2}).

a. Benthic hydrolysis (μ_{hydr_2})

In both the current EXAMS-based model and the VVWM, the pH of the entire system (benthic and littoral) is held at a constant pH of 7, although a subsequent section will suggest using scenario-specific pH values. Benthic hydrolysis is assumed to occur at the same rate as hydrolysis in the littoral zone, and the previous discussion of hydrolysis in the littoral zone applies for the benthic zone. These assumptions result in the following relationship:

$$\mu_{hydr\_2} = \mu_{hydr\_1} \qquad (4\text{-}35)$$

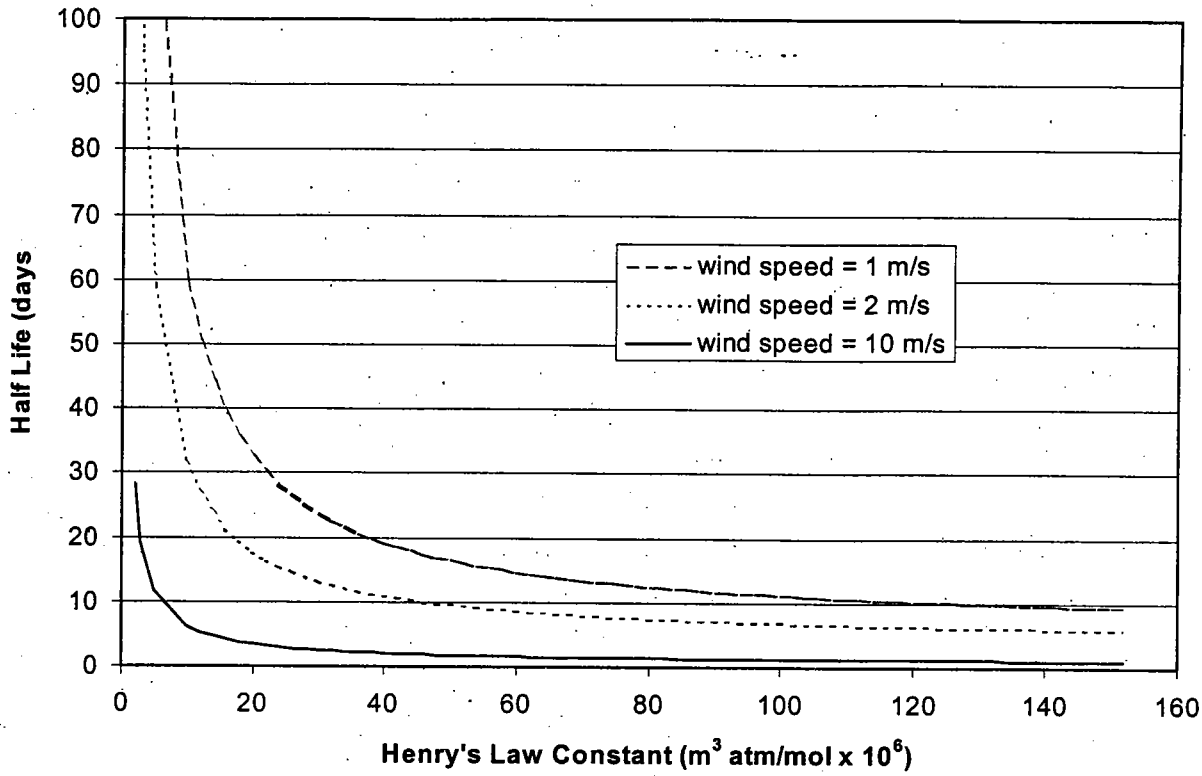


Figure 4-7. Effect of Henry's Law Coefficient and wind speed (measured at 6m) on effective volatilization half-life of aqueous phase. *MW* = 100, Temp = 25 °C.

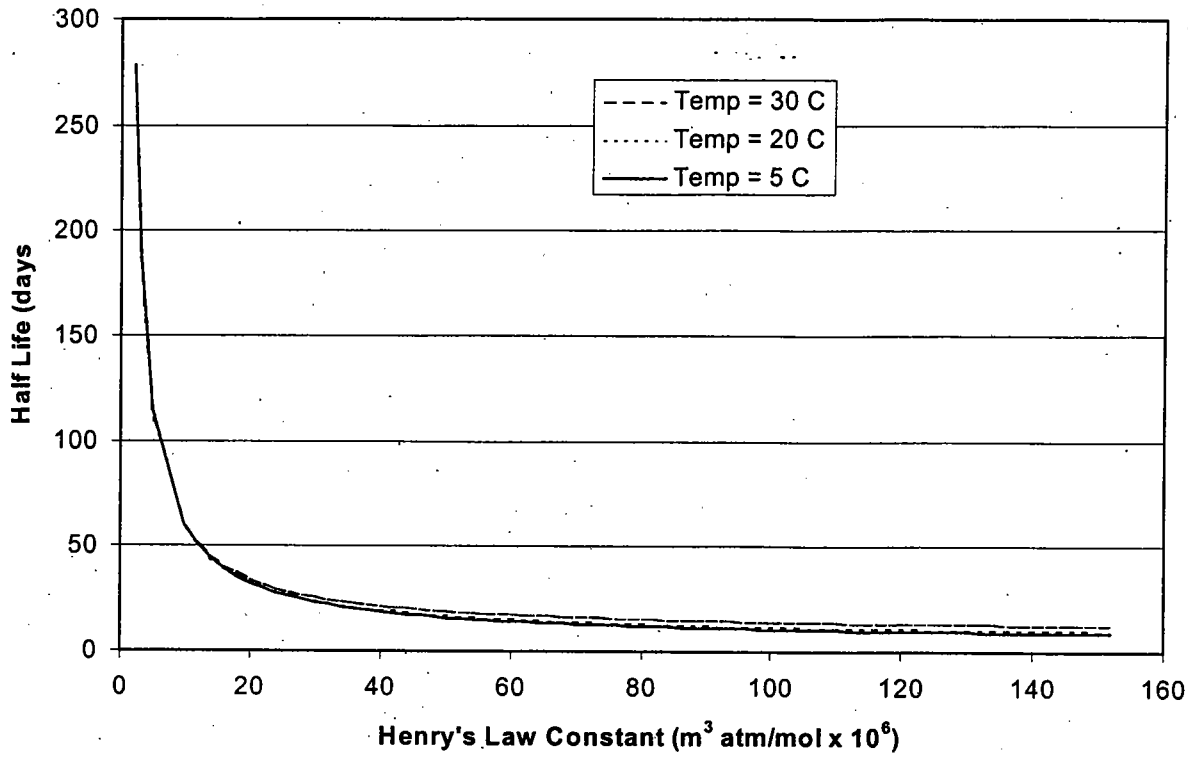


Figure 4-8. Effect of Henry's Law Coefficient and temperature on effective volatilization half-life of aqueous phase for the current (EXAMS-based) model. The lack of temperature sensitivity is a result of not considering the effect of temperature on Henry's Law Coefficient. Wind speed = 1 m/s, *MW*=100.

b. Benthic Metabolism (μ_{bio_2})

In the standard water bodies, benthic metabolism is assumed to occur under anaerobic conditions. Therefore, anaerobic metabolism rates are derived from laboratory tests following standard EPA-approved protocols. These studies are typically conducted in aqueous/sediment systems at 20–25 °C. As with littoral metabolism, it is assumed that sorbed-phase degradation occurs at the same as aqueous-phase degradation. Temperature effects on metabolism are accounted for in an identical manner as for the littoral zone (see previous discussion on littoral metabolism), yielding the following equation:

$$\mu_{bio\_2} = \mu_{measured} \times 2^{\left(\frac{T-T_{ref}}{10}\right)} \qquad (4\text{-}36)$$

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].

4. Mass Transfer Coefficient (Ω)

The mass transfer coefficient (Ω), as defined in equation 4-7, is best thought of as an overall coefficient that includes all means of pesticide exchange between the littoral and benthic zones. 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 (namely α). The parameter α 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 (as EXAMS does) 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.

For the VVWM, the α term is based upon parameters and assumptions given in the EXAMS documentation. In order to understand this parameter, some background is worthwhile. In essence (although not explicitly presented as such), EXAMS uses a boundary layer model to exchange pesticide mass between the littoral zone and the benthic zone. EXAMS defines a parameter, *DSP*, which represents a Fickian-type dispersion coefficient through benthic sediment. This dispersion coefficient acts on the total concentration within the benthic zone. This transfer is approximated as occurring under steady state conditions across a boundary layer of constant thickness. The rate of mass change in the benthic zone can then be expressed as

$$\frac{dM_2}{dt} = (A)\left(\frac{D}{\Delta x}\right)\left(\Re\, C_{T1} - C_{T2}\right) \qquad (4\text{-}37)$$

where,

M_2	=	total pesticide mass in benthic zone
A	=	area of benthic/littoral interface [m^2]
D	=	effective overall dispersion coefficient in benthic media (includes both sorbed and dissolved phases), [m^2/s]; *DSP* in EXAMS
Δx	=	thickness of boundary layer, [m]
$\Re$	=	total partition coefficient for total concentrations [unitless]
C_{T1}	=	total concentration in littoral zone [kg/m^3]
C_{T2}	=	total concentration in benthic zone [kg/m^3]

The total concentration in the littoral and benthic zone can be expressed respectively as:

$$C_{T1} = \frac{c_1\left(v_1 + \sum\left(m_1 K_{d1}\right)\right)}{V_{T1}} \qquad (4\text{-}38)$$

$$C_{T2} = \frac{c_2\left(v_2 + \sum\left(m_2 K_{d2}\right)\right)}{V_{T2}} \qquad (4\text{-}39)$$

where c_1 and v_1 are the aqueous phase concentration and the aqueous volume, as previously defined under equation 4-1; $\Sigma(m1K_{d1})$ and $\Sigma(m_2K_{d2})$ are short-hand notation for the sum of all products of solid masses and the respective K_ds (sediment, biota, DOC) presented under equation 4-1 for the littoral and benthic zones, respectively; V_{T1} and V_{T2} are the total volumes of the littoral zone and benthic zone, respectively, which include both the water and the solids volumes. The total pesticide mass in the benthic zone can be expressed as:

$$M_2 = c_2\left(v_2 + \sum\left(m_2 K_{d2}\right)\right) \qquad (4\text{-}40)$$

The total partitioning coefficient is defined as the ratio of C_{T2} to C_{T1} when the benthic zone is at equilibrium with the littoral zone:

$$\Re = \frac{C_{T2}}{C_{T1}} \qquad \text{(when littoral and benthic zones are at equilibrium)} \qquad (4\text{-}41)$$

By substituting the definitions for C_{T1} and C_{T2} and recognizing that at equilibrium $c_1 = c_2$, the following results:

$$\Re = \left(\frac{\left(v_2 + \sum\left(m_2 K_{d2}\right)\right)}{\left(v_1 + \sum\left(m_1 K_{d1}\right)\right)}\right)\left(\frac{V_{T1}}{V_{T2}}\right) \tag{4-42}$$

Substituting equations 4-38 to 4-42 into equation 4-37, yields the following:

$$\frac{dM_2}{dt} = (A)\left(\frac{D}{\Delta x}\right)\left(\frac{\left(v_2 + \sum\left(m_2 K_{d2}\right)\right)}{V_{T2}}\right)\left(c_1 - c_2\right) \tag{4-43}$$

Comparing equation 4-43 with equation 4-2, we can see that

$$\alpha = (A)\left(\frac{D}{\Delta x}\right)\left(\frac{\left(v_2 + \sum\left(m_2 K_{d2}\right)\right)}{V_{T2}}\right) \tag{4-44}$$

and that Ω, is:

$$\Omega = \frac{(A)(D)}{\left(V_{T2}\right)(\Delta x)} \tag{4-45}$$

where,

D = overall littoral to benthic dispersion coefficient, [8.33 x 10^{-9} m^2/s]
Δx = boundary layer thickness, [m], (1.02 m for current EXAMS-based ecological scenario)
A = surface area, [m^2], (10,000 m^2 for current EXAMS-based ecological scenario)

D in the above equation is set to a constant (see Table 4-4) for both the current EXAMS-based model and the VVWM. The value of D was originally chosen to be on the order of Fickian-type dispersion coefficients in sediments, as observed in field studies reported in the EXAMS documentation. Although equation 4-44 implies a mechanistic meaning to α, it is a difficult endeavor to adequately transform Fickian-type dispersion coefficients into first-order mass transfer coefficients for finite volume compartments. It is equally difficult to define a boundary layer thickness, especially where there is both sediment and aqueous mixing. OPP guidance for the current EXAMS-based model suggests that the boundary layer thickness be equal to the distance between the center of the littoral zone and the center of the benthic zone; however, the actual boundary layer thickness is a difficult parameter to estimate and likely has more to do with benthic animal life than littoral zone depth. This is especially true in light of the

statements made in the EXAMS manual that suggest use of benthic dispersion coefficients from Vanderborght and Wollast (1977), since the dispersion coefficients of Vanderborght and Wollast (1977) have little to do with the depth of littoral zone. As an additional note, Schwarzenbach et al. (1993) used a boundary thickness of 0.5 cm in their analysis of PCB transport in Lake Superior, although a somewhat different conceptual model was used.

Attempting to model the benthic mass transfer parameter as a function of littoral zone depth would be purely speculative at this point, consequently the boundary thickness was kept constant at the current EXAMS-based model value for the proposed VVWM, even though the appropriateness of the value is unknown. This is an area that could use further exploration.

5. Daily Piecewise Calculations

Because an analytical solution was chosen, the model is solved in a daily piecewise fashion, in which the volume of the littoral zone changes at the beginning of the day and remains constant for the duration of that day. This is consistent with the available input data (e,g, flow, precipitation) which are daily totals. Mass is conserved in the littoral zone by recalculating a new beginning day concentration with consideration for this volume change.

a. Volume Calculations

The volume of the littoral zone aqueous phase is calculated from daily runoff, precipitation, and evaporation. For any day, the volume is calculated as:

$$v_1 = v_0 + R + P - E - S \qquad \text{for } 0 < v_1 < v_{max} \qquad (4\text{-}46)$$

where,

v_0 = the aqueous volume of the previous day, [m^3]
R = daily runoff into the water body, [m^3]
P = daily direct precipitation on water body, [m^3]
E = daily evaporation of runoff, [m^3]
S = daily seepage, [m^3] (0, neglected)

Daily runoff is taken from the PRZM model output. Daily precipitation and evaporation are taken from the associated meteorological file. Like the current EXAMS-based model, seepage is not considered in the proposed VVWM. If the newly calculated volume (v_1) is greater than v_{max}, then the volume for the day is set to v_{max}, and the excess water is used in the calculations for washout. Appropriate values for the parameter v_{max} will be discussed in a later chapter. The minimum water volume is obviously zero, but should be set to some minimum to prevent numerical difficulties associated with calculations involving infinity and zero. There also may be some practical physical lower boundary that may be appropriate for a minimum volume such as those associated with soil water holding capacity, water tables, base inflow,

and/or for some ponds refilling practices of pond owners. This is an area that needs to be further explored.

6. Daily Initial Pesticide Conditions

For any given day the initial pesticide concentrations for the littoral and benthic zones are determined by the daily pesticide mass inputs from PRZM and spraydrift and the previous day's pesticide residue. PRZM gives daily outputs for pesticide mass associated with aqueous-phase runoff and for pesticides associated with erosion solids. In both the current EXAMS-based model and the VVWM, all pesticide in aqueous-phase runoff and half of the pesticide associated with the erosion solids are delivered to the littoral zone, and the remaining half of the solids-associated pesticide is delivered to the benthic zone (this is specified by the PRBEN variable in EXAMS). Spray drift is delivered solely to the littoral zone on the day of pesticide application to the field. For the VVWM, there is an instantaneous volume change at the beginning of the day due to hydrologic conditions (see *Volume Calculations* above), and the concentration of any residual pesticide in the littoral zone is adjusted accordingly. The daily initial pesticide concentrations in the littoral and benthic zones, upon addition of new pesticide inputs, can then be expressed as:

$$C_{10} = \left(\frac{f_{w1}}{v_1}\right)\left[\left(M_{runoff} + 0.5M_{erosion} + M_{drift}\right) + \left(\frac{v_{1,prior}}{f_{w1,prior}}\right)\left(C_{10,prior}\right)\right] \tag{4-47}$$

$$C_{20} = \left(\frac{f_{w2}}{v_2}\right)\left(0.5M_{erosion}\right) + C_{20,prior} \tag{4-48}$$

where,

M_{runoff} = mass of pesticide entering water body via runoff, [kg], from PRZM
$M_{erosion}$ = mass of pesticide entering water body via erosion, [kg], from PRZM
M_{drift} = mass of pesticide entering water body via spray drift, [kg]
$C_{10,prior}$ = aqueous concentration in littoral zone before new mass additions, [kg/m^3]
$C_{20,prior}$ = aqueous concentration in benthic zone before new mass additions, [kg/m^3]
$v_{1,prior}$ = the littoral volume from the previous day, [m^3]
$f_{w1,prior}$ = f_{w1} from the previous day

7. Analytical Solution

Equations 4-3 and 4-4 along with the initial conditions represent the two equations describing the VVWM. These equations are in the form of

$$\frac{dc_1}{dt} = Ac_1 + Bc_2 \tag{4-49}$$

$$\frac{dc_2}{dt} = Ec_1 + Fc_2 \qquad (4\text{-}50)$$

where,

$A = -\Gamma_1 - \Omega\Theta$
$B = \Omega\Theta$
$E = \Omega$
$F = -\Gamma_2 - \Omega$

The coupled simultaneous linear ordinary differential equations 4-49 and 4-50 with initial conditions $c_1(0) = c_{10}$ and $c_2(0) = c_{20}$ have the solution

$$c_1 = X_1 e^{\lambda_1 t} + Y_1 e^{\lambda_2 t} \qquad (4\text{-}51)$$

$$c_2 = X_1 \frac{(\lambda_1 - A)}{B} e^{\lambda_1 t} + Y_1 \frac{(\lambda_2 - A)}{B} e^{\lambda_2 t} \qquad (4\text{-}52)$$

where,

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

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

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

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

Average concentrations which are used for chronic assessments can be determined over any time interval in which all parameters remain constant. In the case of the proposed VVWM, parameters change on a daily basis, so the time interval would by 1 day. The average concentration over any time interval is

$$C_{1,avg} = \frac{X_1}{r_1(t_2 - t_1)} e^{\lambda_1 t 2} + \frac{Y_1}{r_2(t_2 - t_1)} e^{\lambda_2 t 2} - \frac{X_1}{r_2(t_2 - t_1)} e^{\lambda_1 t 1} - \frac{Y_1}{r_2(t_2 - t_1)} e^{\lambda_2 t 1} \qquad (4\text{-}53)$$

where,

$C_{l,avg}$ = average littoral concentration [kg/m^3] from time t_1 to t_2
t_1 = time at beginning of the interval [s^{-1}], (zero for the VVWM at each new day)
t_2 = end of the time interval considered [s^{-1}], (86,400 seconds for the VVWM)

For multiple day averages the individual daily results from equation 4-53 are averaged over the relevant time period.

8. Testing and Comparison of Solution with EXAMS

Individual processes of the analytical solution were tested by comparing the output of the proposed VVWM with that of EXAMS (see Section D). For these tests, a constant volume condition was imposed on the proposed VVWM so that only the processes common to both models could be tested. Individual processes were tested by either zeroing out all other dissipation or making them insignificant, and using a single initial aqueous-phase input (see Section D). An example of a test of an individual process is given in Figure 4-9 for the case of volatilization. In this example, it is clear that the volatilization process is captured and the analytical solution is correctly formulated. Other processes–hydrolysis, photolysis, metabolism, and benthic mass transfer–were tested in a similar manner with similar results. Combined processes with multiple inputs including spraydrift, erosion, and runoff as read from PRZM output files were also tested (see Section D). An example of such a test is given in Figure 4-10, which shows excellent agreement with EXAMS, and further verifying the proper formulation of the processes within the proposed VVWM. A detailed discussion of the approaches and methods used for testing the proposed VVWM and a discussion of the effect of incorporating the VVWM in place of EXAMS on pesticide EECs for the Level II refined risk assessment are provided in Section D.

9. Summary

A new surface water model (VVWM) to estimate pesticide concentrations has been developed to improve the pesticide risk assessment process. For the most part, individual processes (e.g., metabolism, photolysis, volatilization) in the proposed VVWM are based on the same equations as in the current EXAMS-based model. The proposed VVWM differs from EXAMS in ways that were intended to improve upon the characterization of temporal variability, improve upon hydrologic balances, and to increase the speed at which computations are made. Some of the differences between the current EXAMS-based model and the proposed VVWM are summarized in the following:

1. The proposed VVWM changes parameter values on a daily basis (e.g., temperature, wind, flow), corresponding to the daily input data from the meteorological file and from PRZM. EXAMS changes parameters only on a calendar-month basis, using calendar month averages for the values.

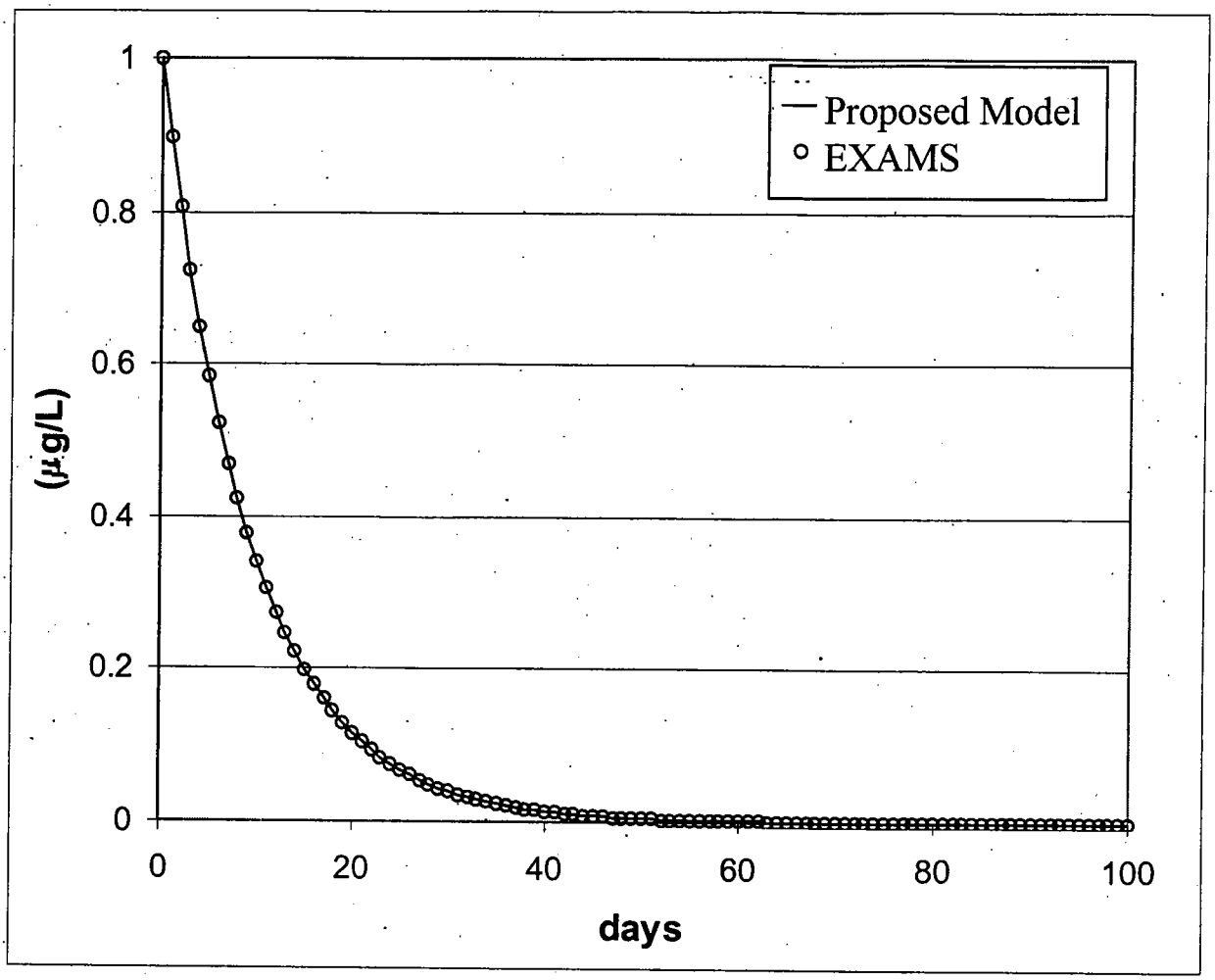


Figure 4-9. Comparison the volatilization mechanisms of the proposed VVWM and EXAMS for conditions of pesticide solubility = 100 mg/L, MW = 100, vapor pressure = 0.1 torr, K_{oc} = 1 mL/g, wind speed = 1 m/s, temperature = 25 °C, and an input mass of 0.02 kg to the littoral zone. A constant volume condition was used for the proposed VVWM.

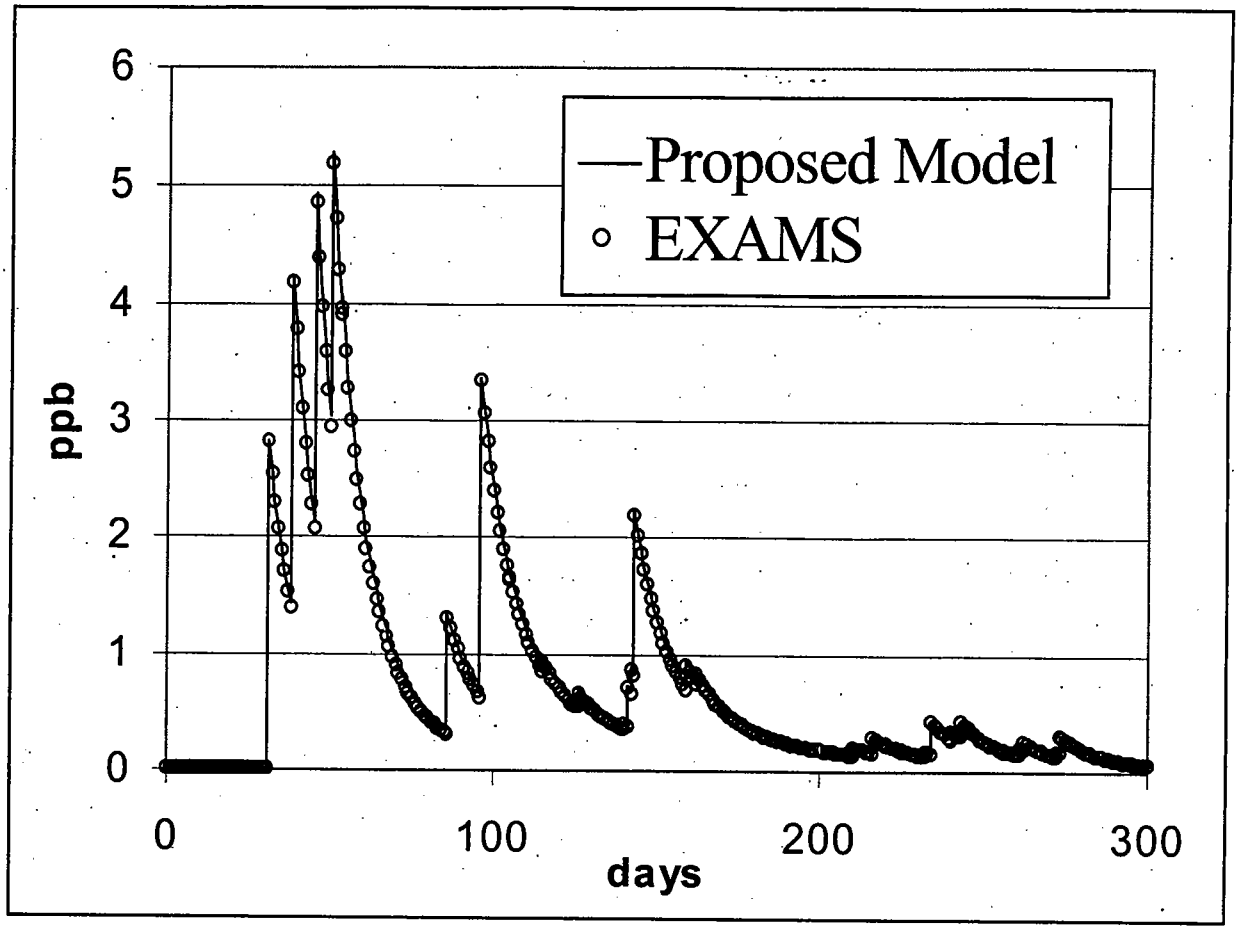


Figure 4-10. Comparison of proposed VVWM with EXAMS for the conditions of $MW = 100$, solubility = 100 mg/L, vapor pressure of 0.01 torr, aerobic half-life of 10 days, anaerobic half-life of 100 days, K_{oc} of 100 mL/g, wind speed of 1 m/s, temperature of 25 °C, and arbitrarily selected PRZM input fluxes. A constant volume condition was used for the proposed VVWM.

2. The proposed VVWM can implement daily changes in temperature, which are based on the preceding 30-day average air temperature, thereby simulating the temperature lag of water bodies with air temperature. EXAMS only makes changes on a calendar-month basis, and water body temperatures therefore do not lag the air temperature (and could actually lead air temperature) .

3. The VVWM considers variations in the water volume due to hydrologic inputs; EXAMS does not.

4. The VVWM is solved analytically and is specifically designed to solve the 2-compartment surface water conceptual model. An informal comparison on a modern computer showed that results from a 36-year simulation are produced nearly instantaneously with the VVWM program, while the same simulation run by EXAMS takes around 10 seconds. This increase in speed can be quite significant for a 10,000-run Monte Carlo simulation.

5. At this time, the proposed VVWM does not calculate the formation and decline of degradates; only the parent compound is considered.

D. Testing and Evaluation

1. Introduction

As discussed in Section C, a varying volume surface water model is proposed for use in the aquatic Level II RRA approach. The Level II RRA exposure modeling tool consists of a graphical user interface (GUI) shell (RRA shell), which launches PRZM and the VVWM. Similar to the GUI shell used to launch PRZM and EXAMS (PE4 shell), the RRA shell allows the user to enter pesticide-specific fate data (e.g., K_{oc}, soil aerobic half-life), application information, and to select a standard crop scenario (e.g., local or regional soil hydrology, soil characteristics and crop characteristics) and associated meteorological file. The RRA shell reads the standard crop scenario file and corresponding meteorological file, generates the PRZM input files, and launches PRZM. PRZM-simulated daily runoff and pesticide loadings are used as inputs into the VVWM and the results are stored for use in the risk calculation module of the aquatic Level II RRA tool. Quality assurance/quality control (QA/QC) measures conducted to document that the RRA shell performed as designed are described in this section. Additionally, the individual processes of the analytical solution in the VVWM and combined processes with multiple inputs (spray drift, erosion, runoff) were tested for correct solutions and to demonstrate the consistency and differences between the VVWM and the fixed-volume surface water model (EXAMS) used in Level I. The approaches and methods used to perform these tests and demonstrations and the associated results are described in this section. Figure 4-11 provides a flow chart of the aquatic Level II RRA exposure modeling approach as compared to the Level I approach.

2. Methods and Approaches

a. QA/QC Testing

The aquatic Level II RRA exposure model including, the VVWM, was tested by comparing components of the model that are consistent with current exposure tools and models (PE4 shell, PRZM/EXAMS) used at Level I. The QA/QC process consisted of four parts: (1) testing the RRA shell PRZM input and output files against the PE4 shell; (2) running all standard crop scenarios with the RRA shell; (3) verifying that the VVWM dissipation algorithms are consistent with EXAMS, and (4) testing the volume and associated overflow and hydrologic chemical washout algorithms in VVWM.

RRA Shell for Launching PRZM Using the same input parameters, PRZM was launched from both the PE4 shell and the RRA shell. The resulting PE4 and RRA shell PRZM input and output files were compared to ensure that the RRA shell correctly reads input values, and launches and runs PRZM correctly.

RRA Shell Reading of Scenario and Metfiles All standard crop scenarios and corresponding meteorological (met) files (as of October 2002) were used to run the RRA shell to ensure that the inputs from these files were read correctly. Error messages were evaluated to

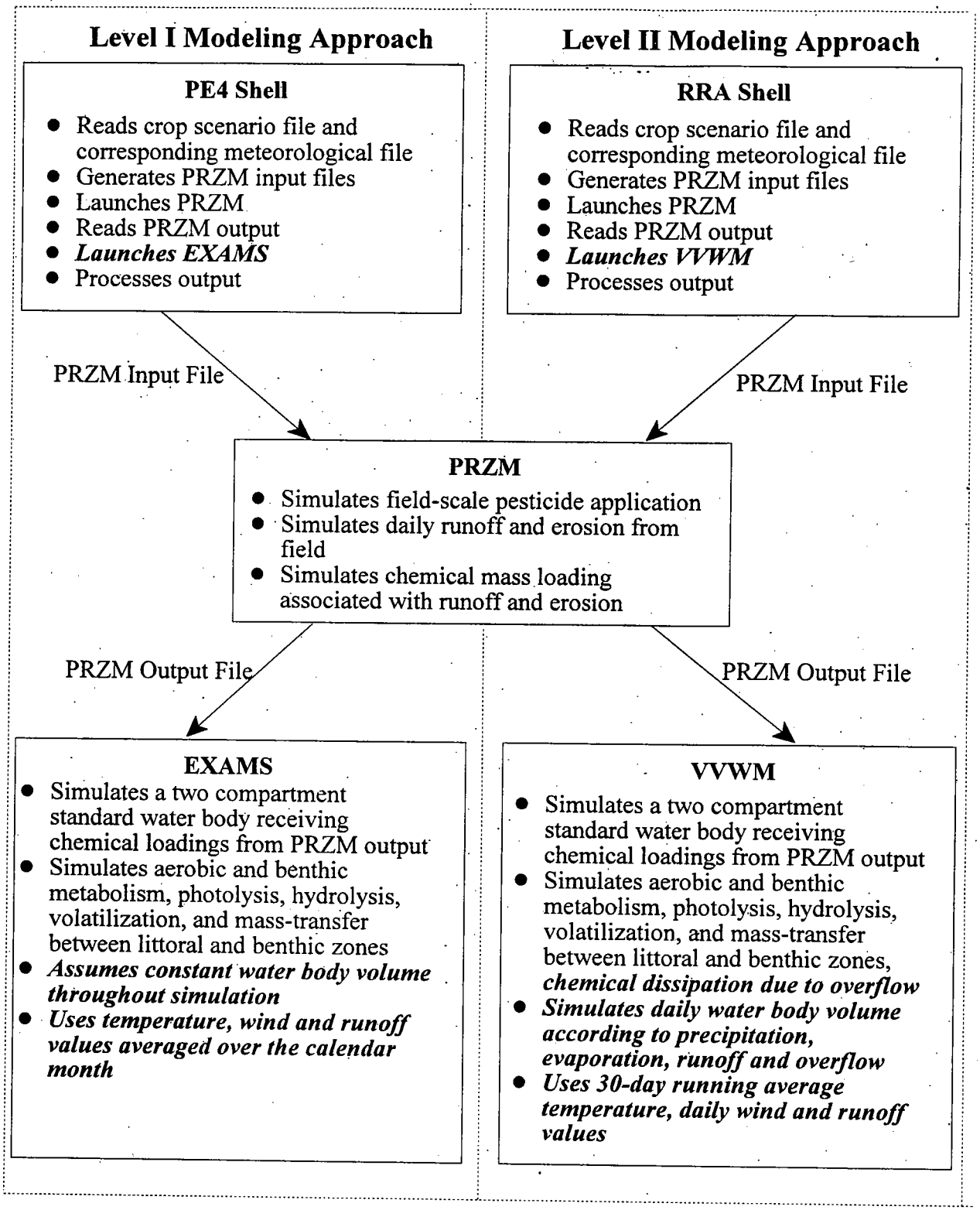


Figure 4-11. Flow chart of Level II exposure modeling approach compared to Level I. Differences between the two are noted in italics.

identify compatibility problems with the RRA shell and specific crop scenarios and/or met files. The PRZM input and output files were also visually inspected to identify any errors with the runs. If errors were detected, appropriate modifications were made to the RRA shell code, the crop scenarios and/or the metfiles.

VVWM Chemical Dissipation Algorithms To verify that the dissipation algorithms in the VVWM are consistent and provide the same solutions as EXAMS, VVWM and EXAMS were run using the same PRZM input, holding the volume of the water body in the VVWM constant and equal to the standard water body volume in EXAMS (20,000 m^3) and setting the washout parameter to zero. Since temperature is calculated differently in each model, it was also set constant. Each chemical dissipation process (aerobic metabolism, benthic metabolism, hydrolysis, photolysis, and volatilization) were tested individually by setting all other rates to zero.

VVWM Volume and Overflow Algorithms The volume and associated overflow algorithms in the VVWM were verified by reproducing the calculations in a spreadsheet. Net flow was calculated by summing runoff (PRZM output) and precipitation (metfile) and then subtracting evaporation (metfile). Water body volume was calculated by adding the net flow to the volume of the previous day. If the new volume exceeded the maximum volume, it was then set to the maximum value and the excess was used to calculate overflow and chemical washout. The rate of dissipation due to washout was calculated from the excess water volume divided by the maximum water body volume.

b. Evaluation of the RRA Level II Exposure Model

The potential outcomes of using a varying volume water body model on estimated exposure concentrations (EECs) were evaluated by comparing model output from EXAMS to output from VVWM for a number of simulations. For this analysis, a combination of two scenarios - one representing a high rainfall area (FL sugarcane) and another representing a low rainfall area (CA almond) - and two chemicals - a short-lived chemical (ChemA) and a long-lived chemical (ChemB) - were used in the simulations. Chemical-specific input parameters used for the simulations for ChemA and ChemB are listed in Table 4-6. For the initial assessment, the standard ecological surface water modeling scenario of a 10 ha field draining into a 1 ha by 2 m deep water body (20,000 m^3) was used. Additionally, for the VVWM simulations a maximum overflow depth was arbitrarily set at 3 m and a minimum depth was arbitrarily set at 0.01 m (to avoid numerical difficulties with calculations involving zero). Table 4-7 summarizes the field and water body size variables for the EXAMS and the VVWM simulations.

Table 4-6. Input Parameters for Short-lived Chemical, ChemA, and Long-lived chemical, ChemB

	ChemA	ChemB
K_{oc}	487	422
Soil degradation (d)	11.25	7,118
Aquatic degradation (d)	4.10	3,824
Benthic degradation (d)	—[a]	1,640
Hydrolysis (d)	40.0	—[a]
Photolysis (d)	2.04	—[a]
Molecular weight	263	368
Vapor pressure (torr)	9.6e-6	3.0e-8
Solubility (ppm)	600	3.3
Application date (month-day)	4-15	4-15
Application rate (kg/ha)	2.25	0.45
Applications per year	8	14
Interval between applications (d)	14	5
Application efficiency	0.99	0.95
Drift	0.01	0.05
Chemical application method (CAM)	1[b]	2[c]

[a]Stable with respect to the dissipation process
[b]CAM 1 = soil applied
[c]CAM 2 = foliar applied

Table 4-7. Summary of PRZM/EXAMS and PRZM/VVWM Field Area and Water Body Size Variables and Their Values

	PRZM/EXAMS	PRZM/VVWM
Field area (ha)	10	10
Surface area (ha)	1	1
Initial depth (m)	2	2
Maximum depth (m)	n.a.	3
Minimum depth (m)	n.a.	0.01
Initial volume (m^3)	20,000	20,000
Maximum volume (m^3)	n.a.	30,000
Minimum volume (m^3)	n.a.	100

n.a. = not applicable

3. Results

a. QA/QC Testing

RRA Shell for Launching PRZM The RRA shell for launching PRZM was tested against PE4 by comparing the PRZM input and output files generated by each. Differences between the two shells, the reasons for these differences, and necessary modifications were identified and are listed in Table 4-8. Examples of differences include the following:

- PRZM parameter IPSCND (RECORD 17), "condition for disposition of foliar pesticide after harvest", is set automatically to 1 (indicating surface applied) in the RRA shell, this is a user input in the PE4 shell. This parameter may more appropriately be put in the crop scenario files since it is crop specific.
- K_{oc} model for soil adsorption coefficient is always used (RECORDS 20). This may be modified in the future.
- PRZM parameter DWRATE/DSRATE, "dissolved/adsorbed phase pesticide decay rate", has slight differences in significant figures (RECORD 36). Comparison of the PRZM output files demonstrated small (<0.1%) differences in chemical loadings in runoff and erosion attributable to the difference in significant figures in DWRATE/DSRATE (Figure 4-12). This difference is not significant and reflects differences in significant figure between the programming languages (PE4 - Perl, RRA - MATLAB).

RRA Shell Reading of Scenario and Met Files All standard crop scenarios and corresponding metfiles (as of October 2002) were used to test the RRA shell for compatibility. Problems were identified and appropriate modifications to the code and/or scenarios were made (Table 4-9). The RRA shell code was modified to include the following functionality:

1. Allow for multiple crop rotations, pertinent for the MS cotton scenario;
2. Recognize irrigation records, pertinent for a number of CA scenarios; and
3. Set volatilization to zero when wind speed equals zero. This is consistent with EXAMS.

VVWM Chemical Dissipation Algorithms An initial comparison of VVWM and EXAMS output was made and appropriate modifications were made where unwanted disparities existed (Table 4-10). Some differences between the models were recognized as intentional, including the following (see Chapter IV, Section C for more details regarding VVWM):

- EXAMS assumes a monthly average wind speed while VVWM uses a daily wind speed read from the meteorological file.
- EXAMS uses a calendar monthly temperature average while VVWM uses a previous 30 day running average.

Maintaining constant temperature, wind speed, and volume in the VVWM and setting all other rates to zero, each dissipation process designed to be the same as that in EXAMS (aerobic metabolism, benthic metabolism, hydrolysis, photolysis, and volatilization) was compared with

Table 4-8. Identified Disparities Between the PE4 Shell and the RRA Shell for Generating PRZM Input Files and Any Subsequent Modifications Made to Address Issues. (Note: the first two disparities, AFIELD and IRFLAG, have been resolved.)

PRZM Input Record[a]	PE4 Shell	RRA Shell	Modification and/or justification
7-4 AFIELD, area of field	Uses standard for ecological assessments (10 ha)	Read from standard scenario file as 172 ha, the standard for drinking water assessments	RRA shell was temporarily modified to use standard (10 ha) for testing[b]
20-7 IRFLAG, irrigation flag	Read in from scenario	Set to zero in code	RRA shell modified to read irrigation parameters from scenario files
17-2 IPSCND, condition for disposition of foliar pesticide after harvest	User input[c]	Automatically set to 1 (surface applied), the most conservative condition	This may be an input to be added in the scenarios, since it is crop and site specific. Note: this is only pertinent when the chemical application method (CAM) = 2
20-3 KDFLAG, method of calculating adsorption coefficient	Allows user to choose K_d, K_{oc}, or solubility to calculate adsorption	Requires K_{oc} input	This may be modified in the future.
36 DWRATE/DSRATE, aerobic soil decay rate	Depending on the rate, PE4 and RRA shell will generate different significant figures for these parameters		No adjustments made to RRA Shell. Resulting differences (<0.1%) in PRZM output (chemical loading in runoff and erosion) are rounding errors and are not considered significant

[a]PRZM Input Record information found in Section 4 of Carsel et al. (1997).
[b]Propose making field area and water body size values regionally specific (see Section E). The values would be set in the standard scenarios input file rather than the shell programming code.
[c]Choices for IPSCND include 1 = surface applied, 2 = complete removal, 3 = left alone.

Table 4-9. Identified Incompatibilities of Standard Crop Scenarios and Corresponding Meteorological Files with RRA Shell and Subsequent Modifications Made to Address Issues

Scenario/Metfile[a]	Incompatibility	Modification
MS cotton	Unable to read multiple crop rotations; PRZM records 8, 9, 11	Modified RRA Shell to handle multiple crop rotations
CA (multiple crops)	Unable to read irrigation/furrow irrigation; PRZM records 20-7, 27, 28, 29	Modified RRA Shell to handle irrigation including furrow irrigation
CA sugarbeet	Record 9a in scenario formatted wrong	Modified scenario format
OR grassseed	Record 9 in scenario missing value for HTMAX	Modified scenario to include missing value
Metfile 131, 130, 133a, 2, 148	Divide by zero error caused when wind speed is zero in VVWM volatilization sub-routine	Modified VVWM such that volatilization is set to zero when wind speed equals zero, this is consistent with EXAMS

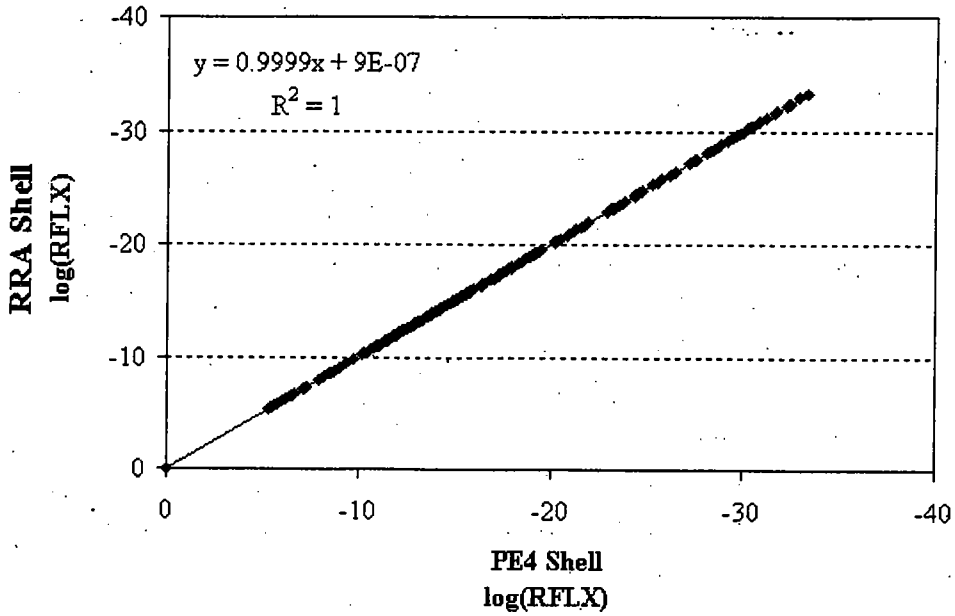
[a]Crop scenarios and metfiles as of October 2002; crop scenarios have since been added and metfiles have been updated.

Table 4-10. Identified Disparities Between VVWM and EXAMS Static Water Body Model While Holding the Volume of the Water Body in VVWM constant and Equal to the Water Body Volume in EXAMS (20,000 m^3) and Subsequent Modification Made to Address Issues

Process	Disparity	Modification and/or justification
Benthic metabolism	Benthic bulk density parameter set to 1,350 kg/m^3 in EXAMS standard water body and 1,300 kg/m^3 in VVWM	Modified VVWM benthic bulk density to 1,350 kg/m^3
Hydrolysis	PE4 shell sets hydrolysis parameter in EXAMS such that hydrolysis occurs in both dissolved and solid phases; VVWM only allows hydrolysis on chemical in the dissolved phase	Modified PE4 shell to only allow hydrolysis for chemical in the dissolved phase
Photolysis	EXAMS sets photolysis to zero when temperature is below zero	Modified VVWM to also set photolysis to zero when temperature is below zero
Volatilization	EXAMS assumes monthly average wind speed while VVWM uses daily wind speed read directly from the met file	Intentional improvement for VVWM[(a)]
Temperature	EXAMS uses the average monthly temperature, VVWM uses a previous 30-day running average	Intentional improvement for VVWM[(a)]

[(a)]See Chapter IV, Section C for details.

A.



B.

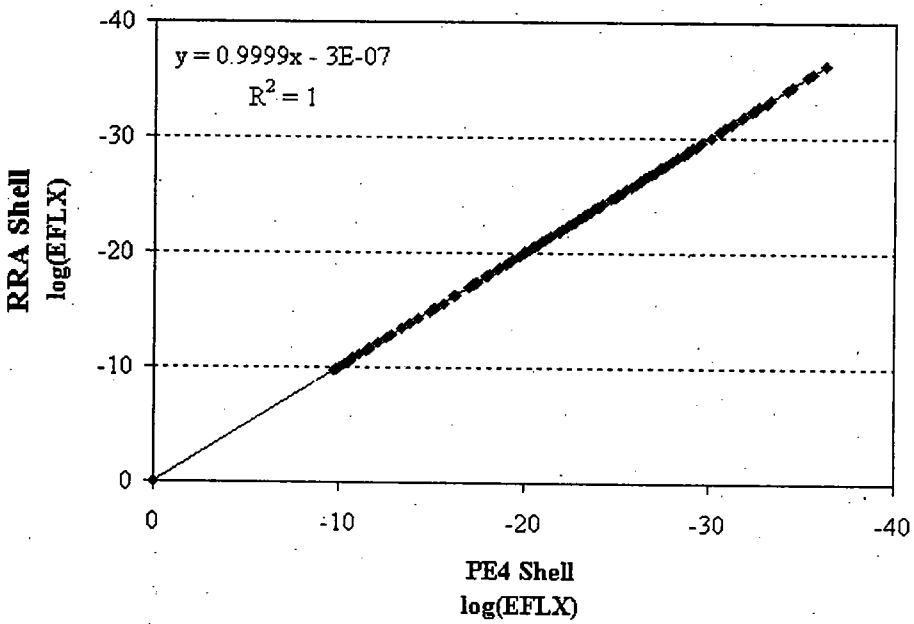


Figure 4-12. RRA shell launched PRZM output compared to PE4 shell launched PRZM output, (a) mass loading in runoff (RFLX) and (b) mass loading in erosion (EFLX). In this example PRZM record 36 was 0.086427 and 0.0864 in the PE4 shell launched and RRA shell launched PRZM input files, respectively.

EXAMS. Results of these comparisons are provided in Figures 4-13–4-17. In all cases the relationship between EXAMS and VVWM daily values were essentially one-to-one ($r^2 \geq 0.999$), demonstrating that the chemical dissipation algorithms in VVWM are consistent with EXAMS.

VVWM Volume and Overflow Algorithms The volume and overflow algorithms in VVWM were verified by reproducing the calculations in a spreadsheet for six scenarios and corresponding meteorological data representing a range of climatic conditions. Calculations in the spreadsheet consistently reproduced the water body volume, overflow and chemical washout results of the VVWM, verifying that the VVWM code performs as designed.

b. Evaluation of the RRA Level II Exposure Model

A total of four EXAMS and VVWM simulations were run to evaluate the effect of the varying volume water body on EECs. Two pesticides, a short-lived (ChemA) and long-lived (ChemB) (Table 4-6), were evaluated under two regional crop scenarios, CA almond and FL sugarcane. This combination was chosen to represent extreme precipitation and evaporation cases for comparison. The FL scenario is characterized by a much higher rainfall, runoff, and lower evaporation relative to the CA scenario. Average yearly net flow under the standard ecological surface water modeling conditions is 61,878 and -5,071 m^3/year for the FL sugarcane and CA almond crop scenarios, respectively, demonstrating very different hydrologic conditions at the two sites.

For this evaluation, the standard field drainage area of 10 ha is used in both the PRZM/EXAMS and the PRZM/VVWM simulations. The initial volume of the water body in the VVWM simulations is set to 20,000 m^3 which is the standard fixed-volume used in the EXAMS simulations. For the arid scenario, CA almond (Figure 4-18), the water body in the VVWM reaches the set minimum volume (100 m^3), essentially going dry almost annually throughout the simulation. This is because there is insufficient runoff and precipitation to balance evaporative losses. Additionally, there are some periods where the water body remains essentially dry for two or more years. As a result of the lower volume in the VVWM as compared to EXAMS, the VVWM predicts much higher daily and annual peak concentrations relative to EXAMS, up to 2 to 3 orders of magnitude higher in some cases. Peak concentrations predicted in VVWM correspond temporally to when the water body goes dry; this is the case for both the short-lived and the long-lived pesticide.

For the high rainfall scenario, FL sugarcane (Figure 4-19), the VVWM predicts lower concentrations relative to EXAMS. Throughout the simulations the varying volume water body is often in overflow conditions (maximum volume = 30,000 m^3) because rainfall and runoff exceed evaporation for a water body of this size with drainage from a 10 ha field. The difference in concentration between EXAMS and VVWM is most pronounced for the long-lived Chem B with peak concentrations predicted in the static EXAMS water body of over an order of magnitude higher that those predicted by the VVWM. In this case chemical washout is a significant source of dissipation. For the short-lived chemical, ChemA, EXAMS also predicts higher concentrations relative to the VVWM, although not to the same extent as the persistent

chemical. EXAMS predicts peak concentrations approximately 1.5–2 times higher than VVWM. In the case of the short-lived chemical, dilution due to the extra storage capacity in the varying volume water body (30,000 m^3) compared to the static water body (20,000 m^3) is the dominant mechanism accounting for the differences in concentration. Dissipation due to washout in the varying volume water body is not expected to dominate over other degradation processes for ChemA.

4. Summary and Conclusions

The QA/QC testing demonstrated that the RRA shell for launching PRZM is comparable to the PE4 shell and is compatible with all standard crop scenarios and metfiles. The testing also demonstrated that the dissipation algorithms in VVWM are consistent with EXAMS and that the volume and washout algorithms are correct and consistent with the approach designed (see Chapter IV, Section C).

Under standard ecological surface water modeling conditions, using a varying volume water body has a significant impact on EECs. Results from side-by-side comparisons of VVWM and EXAMS revealed that EECs are greatly affected by dilution, and dissipation due to washout resulting from seasonal variability or reduction of volume or drying up of the water during periods of drought. Dissipation due to washout can be a dominant process for persistent chemicals in water bodies under high flow conditions.

While a comparison using the ecological modeling standard drainage area, water body size and volume is useful, it does not address the question of whether or not it adequately models the appropriate aquatic resource(s). The evaluation also demonstrates that using a single national standard for drainage area and water body size and using regional-specific meteorological data to calculate water body volume and exposure concentrations needs to be further evaluated in terms of the intent or goals for the aquatic risk assessment. Such an evaluation is conducted in Section E.

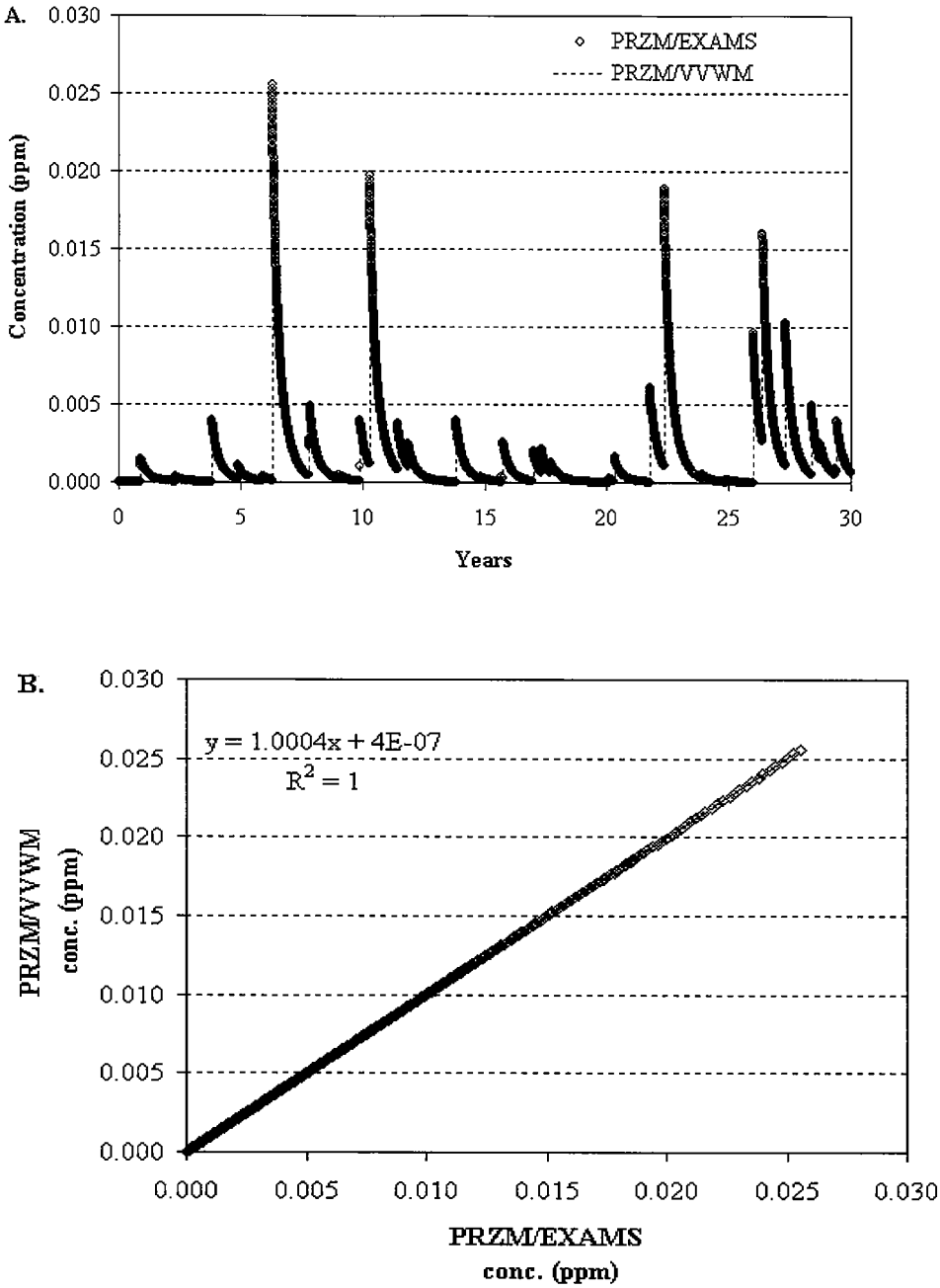


Figure 4-13. RRA Level II Exposure model (PRZM/VVWM) output compared to PRZM/EXAMS exposure model where all transformation processes were set to zero except aerobic metabolism, which was set to an 80 day half-life. (a) times series (b) x-y plot.

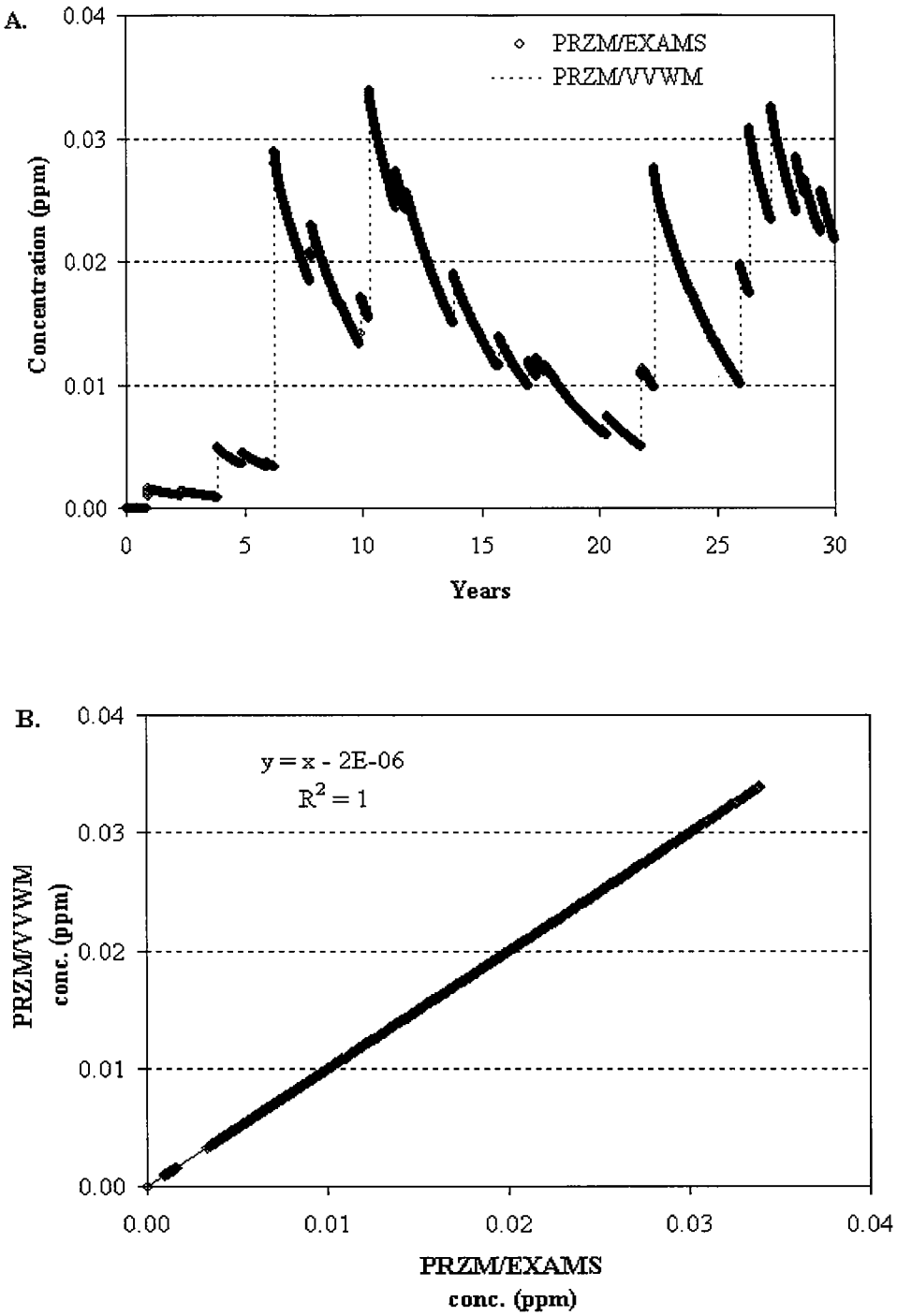


Figure 4-14. RRA Level II Exposure model (PRZM/VVWM) output compared to PRZM/EXAMS exposure model where all transformation processes were set to zero except benthic metabolism, which was set to an 80 day half-life. (a) times series (b) x-y plot.

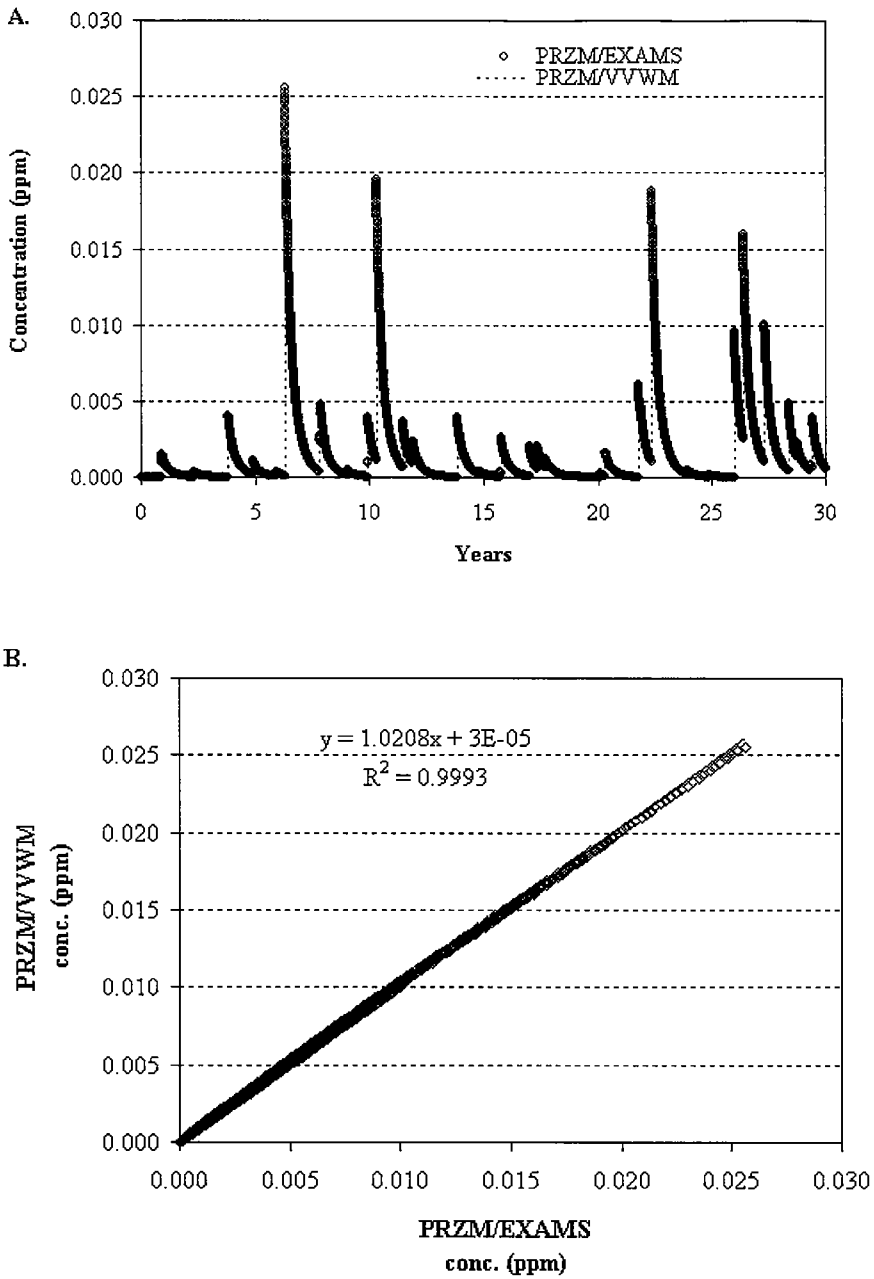


Figure 4-15. RRA Level II Exposure model (PRZM/VVWM) output compared to PRZM/EXAMS exposure model where all transformation processes were set to zero except hydrolysis, which was set to an 80 day half-life. (a) times series (b) x-y plot.

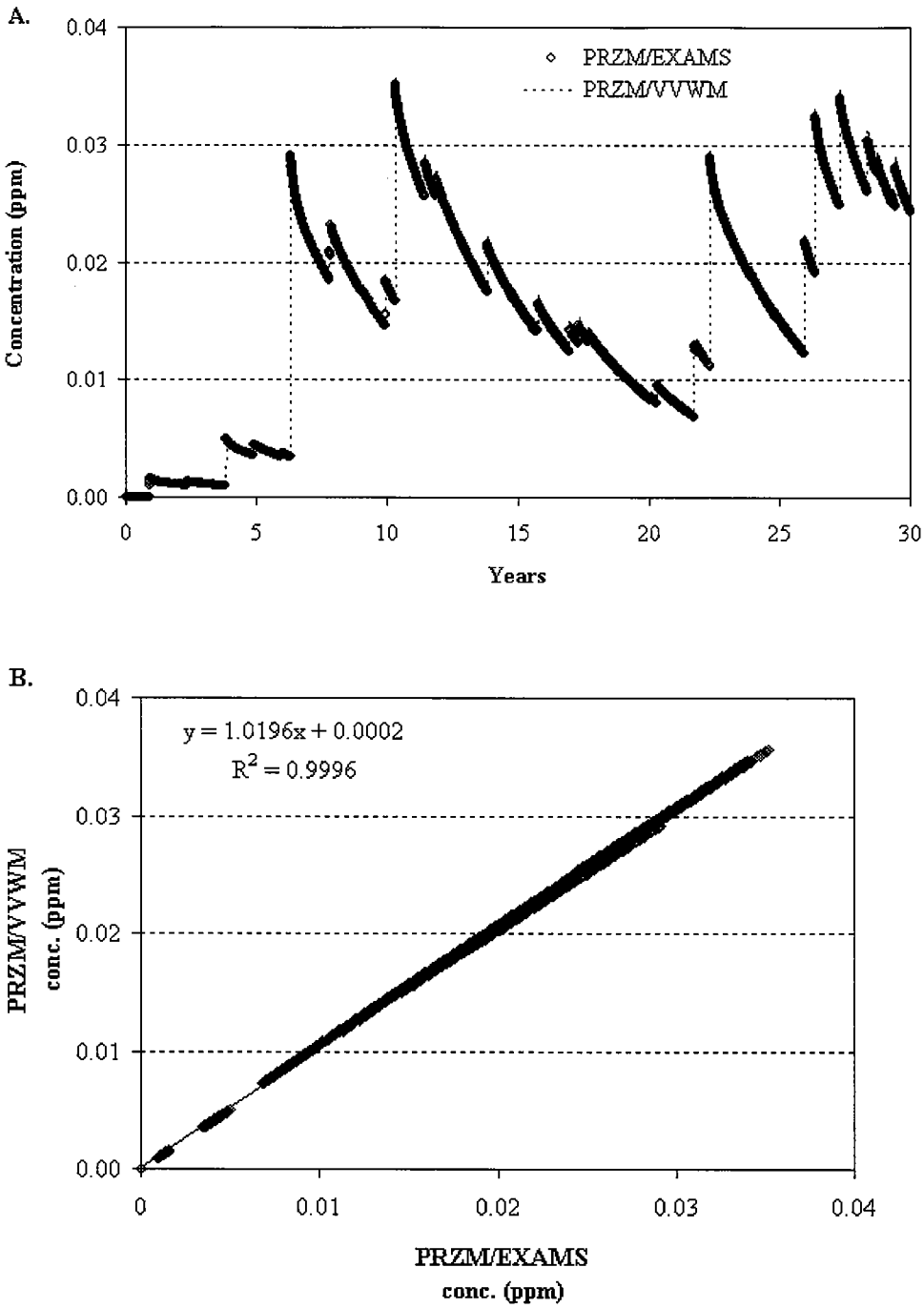


Figure 4-16. RRA Level II Exposure model (PRZM/VVWM) output compared to PRZM/EXAMS exposure model where all transformation processes were set to zero except photolysis, which was set to an 80 day half-life. (a) times series (b) x-y plot.

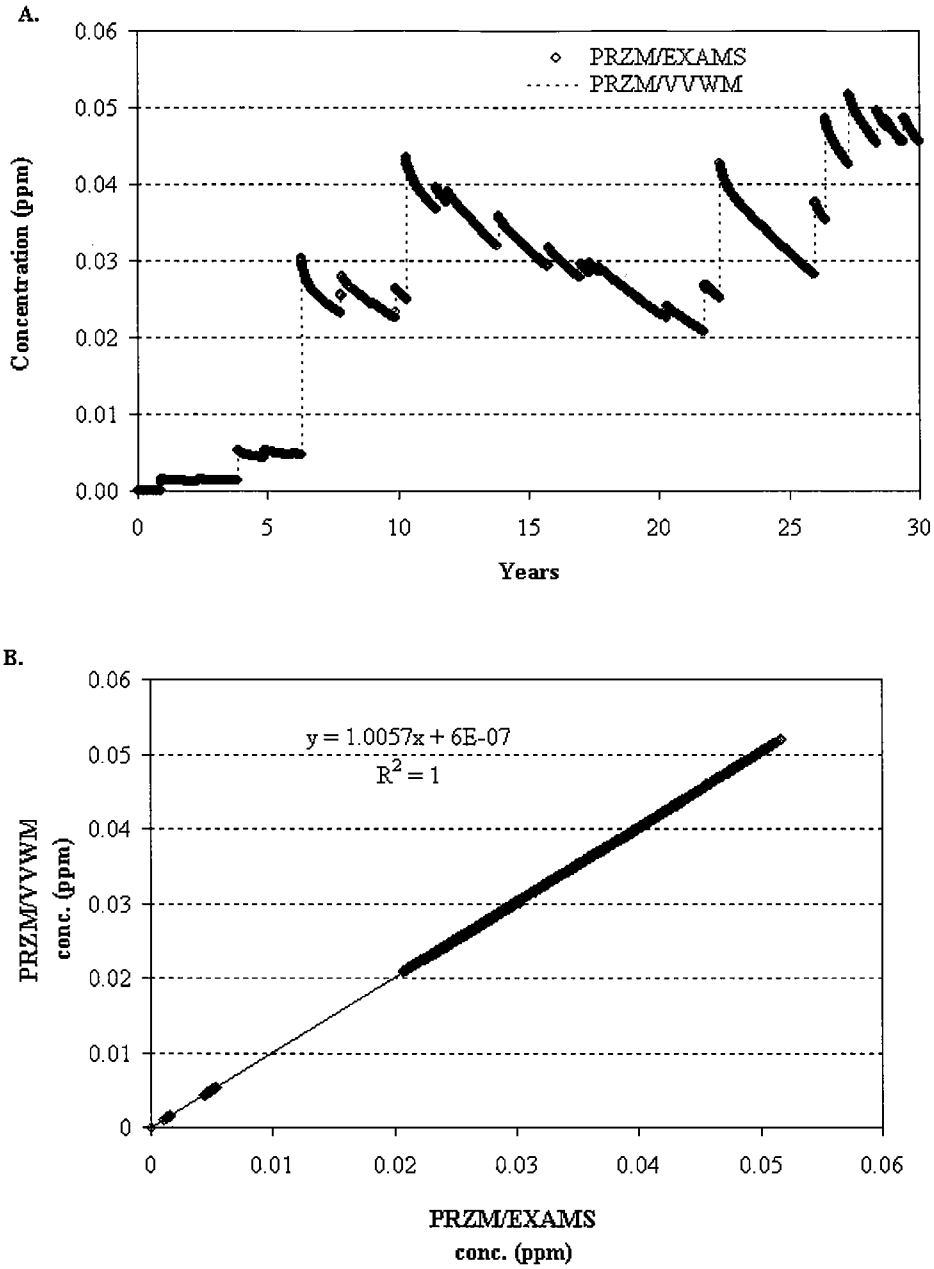


Figure 4-17. RRA Level II Exposure model (PRZM/VVWM) output compared to PRZM/EXAMS exposure model where all transformation processes were set to zero except volatilization, vapor pressure was set to 1e-4 torr. In addition to temperature, wind speed was also kept constant in VVWM. (a) times series (b) x-y plot.

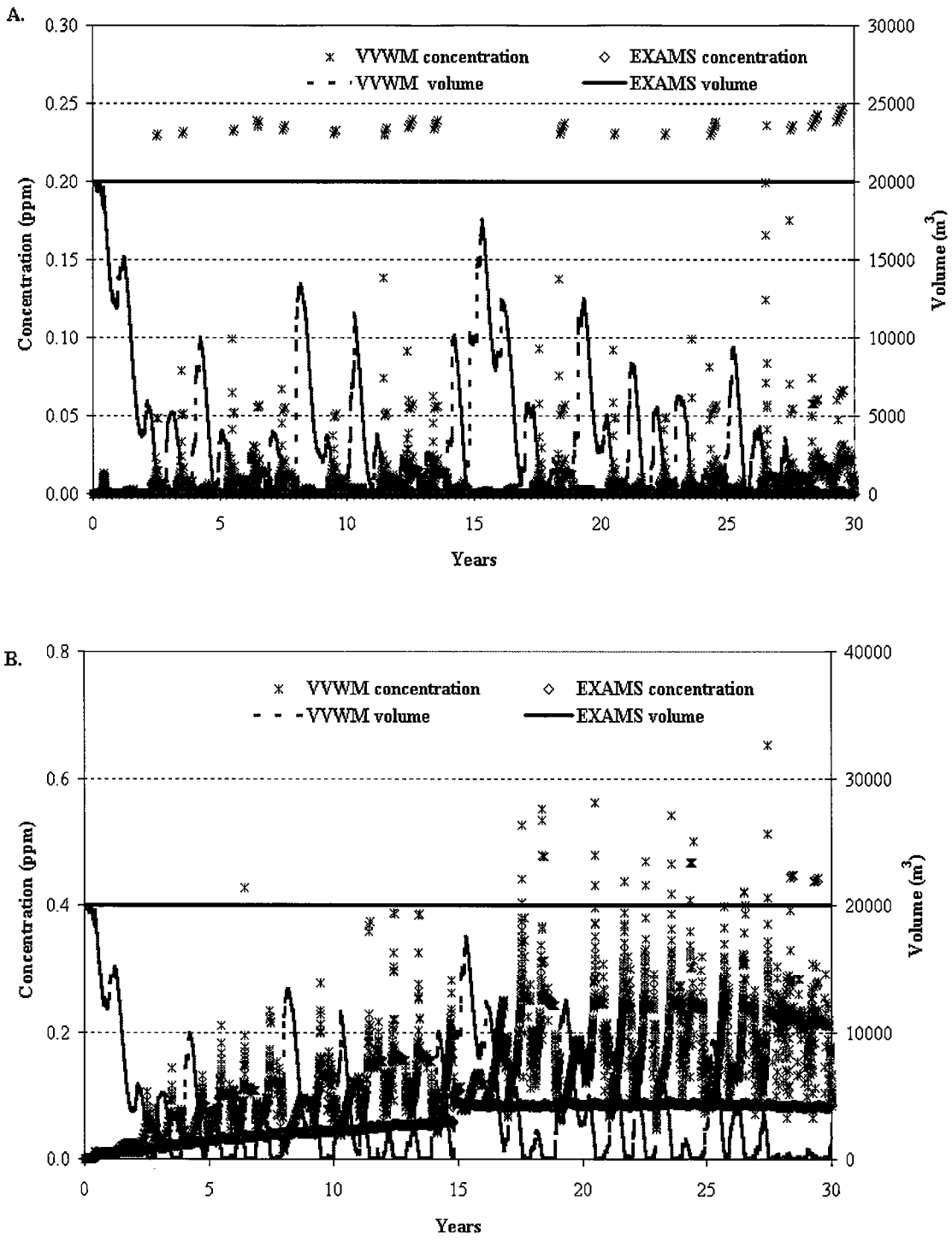


Figure 4-18. EXAMS and VVWM simulated daily concentrations for (a) short-lived ChemA and (b) long-lived ChemB and water body volume for CA almond crop scenario.

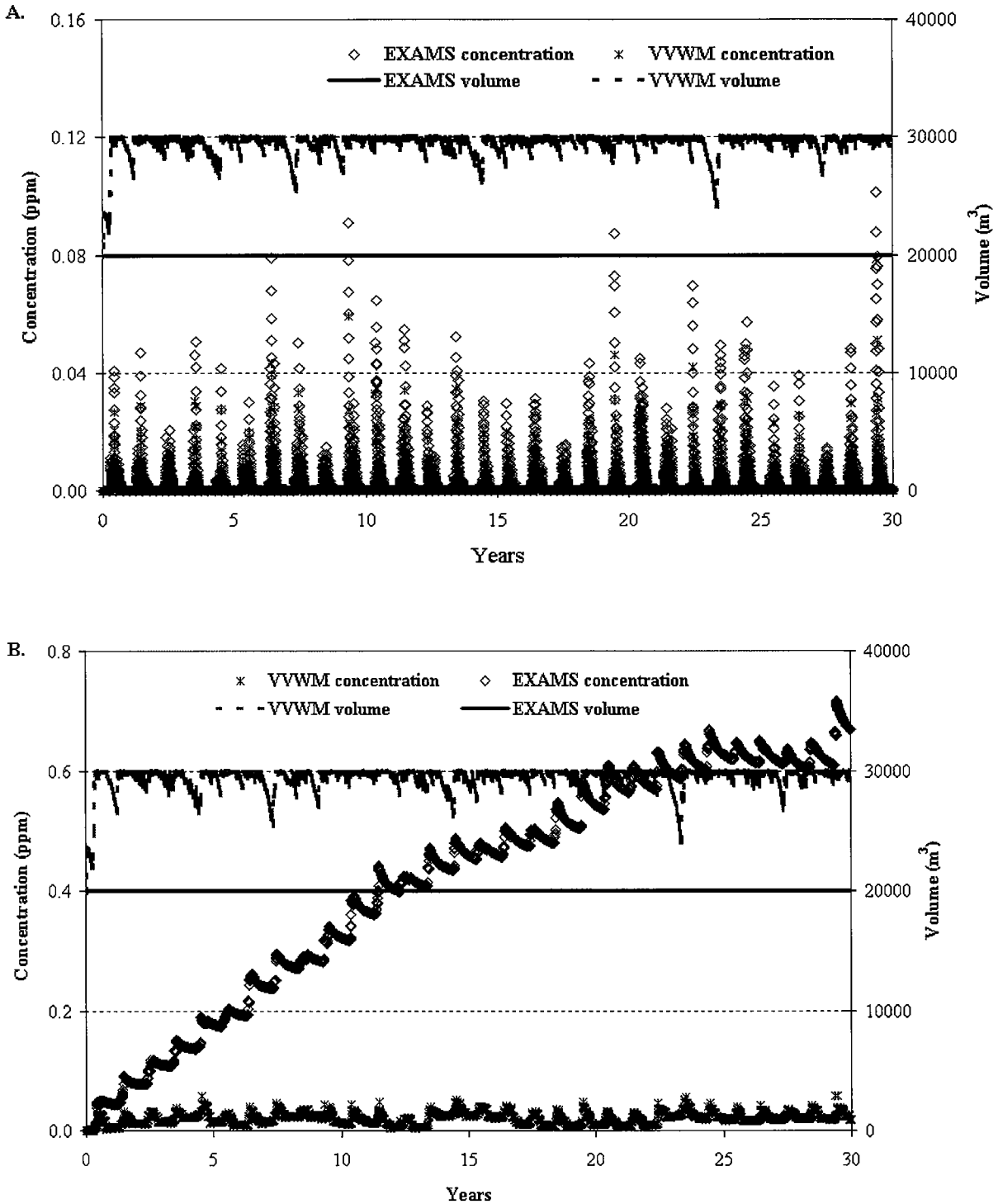


Figure 4-19. EXAMS and VVWM simulated daily concentrations for (a) short-lived ChemA and (b) long-lived ChemB and water body volume for FL sugarcane crop scenario.

E. Development and Evaluation of Scenario-Specific Field Drainage Area and Water Body Size Parameter Conditions

1. Introduction

Incorporation of a surface water model which allows volume to vary according to meteorological and hydrological conditions for a crop scenario has the potential to be more reflective of seasonal variability in both volume and exposure than a fixed-volume model. However, the standard surface water size and volume conditions used for the fixed-volume surface water exposure scenario may not be appropriate for all crop scenarios when a varying volume water model is incorporated. Evaluations of output from the VVWM with standard exposure scenario conditions for high rainfall (FL sugarcane) and low rainfall (CA almond) crop scenarios (Section D) reveal that the standard drainage area to volume capacity conditions are inadequate to balance run-off and precipitation inputs with evaporative losses for all crop scenarios. For the arid crop scenario, CA almond (Figure 4-18), the water body modeled by the VVWM reaches the set minimum volume (100 m^3), essentially going dry almost annually throughout the simulation as a result of insufficient run-off and precipitation to balance evaporative losses. Additionally, there are certain periods of time when it remains dry for two or more years. For the high rainfall crop scenario, FL sugarcane (Figure 4-19), the varying volume water body is often overflowing (throughout the simulation) because rainfall and runoff inputs exceed evaporation for the standard water body.

This section provides an evaluation of drainage area to volume capacity (DA/VC) ratio and water body dimensions appropriate for use in a Level II Exposure model which incorporates a varying volume water body. Before this evaluation is presented, Section E2 discusses the current Level I and Level II Version 1.0 standard surface water exposure scenario and its associated DA/VC ratio and water body dimensions. Following this section is an evaluation of existing sources of data on national and regional DA/VC ratios and associated sizes of surface water bodies (Section E3). Options for using this data to develop crop scenario-specific surface water body size and volume conditions were identified and tested (Section E4). Based on this evaluation as well as the assessment endpoints for the Level II risk assessment paradigm, crop scenario-specific DA/VC ratios and surface water body size values are proposed for use in Level II risk assessments (Section E5).

2. The Current Standard Surface Water Ecological Exposure Modeling Scenario

At Levels I and II (Version 1.0), the surface water ecological exposure modeling scenario is a small, permanent, fixed-volume, standing surface water located at the edge of a pesticide-treated field into which all runoff, soil erosion, and any spray drift from the treated-field is routed. There is no surface water input from non-treated areas to the standard water body and there is no outlet or groundwater seepage. This surface water scenario is a surrogate for aquatic ecosystems supportable at the treated-field scale (e.g., small wetland, pool, or pond). The concept of a field scale aquatic ecosystem as an assessment endpoint at Levels I and II is critical

for a number of reasons. Under real world conditions, typically expect pesticide concentrations to be higher in lower order streams and small wetlands, pools, and ponds adjacent to treated fields than in higher order streams and rivers, and lakes and reservoirs where only a portion of the watershed may be treated. It is assumed that if risk to aquatic populations and communities at this field scale is acceptable, risks in higher order streams and rivers, lakes and reservoirs will be acceptable. The field area selected is small enough to reasonably assume that 100 percent of the field is treated but still large enough to support an aquatic ecosystem from the field runoff alone.

As discussed in Section B of this chapter, the risk assessments conducted at Levels I and II are national or regional assessments in the sense that a given crop scenario (climatology, soil, and cropping practice combination) is used as a surrogate to assess the risk from use of a pesticide on that crop across the U.S. or a given region. Currently, there are four categories of crop scenarios: (1) national—a crop scenario that is a surrogate for that crop nationwide; (2) regional—a crop scenario that is a surrogate for that crop within a region; (3) OP Cumulative —a group of crop scenarios that address cumulative risk from the use of organophosphate pesticides across the nation or within a region; and (4) location specific—crop scenarios that specifically address a crop use in a specific locale. For a standard crop scenario, a soil series that is more vulnerable to soil erosion is selected, based on best professional judgement, from the actual crop growing region represented. Likewise, the dimensions and volume for the surface water exposure model have been standardized for conducting these national/regional assessments. The field size used in the Level I and II (Version 1.0) exposure models is 10 ha (100,000 m^2) and is based on best professional judgement. It represents the largest size of field across the nation that can be assumed to be 100 percent cropped, in the same crop, and treated with a pesticide. The dimensions of the standard water body are 1 ha (10,000 m^2) of area by 2 meters of depth for a total volume of 20,000 m^3. This volume is based on drainage area to unit storage capacity (DA/VC) ratios that are recommended for maintaining small, permanent sources of water in a USDA (1982) pond construction handbook. DA/VC ratios range from ≤ 1 to ≥ 140 acres/acre-ft (≤ 3.3 to ≥ 460 m^2/m^3) across the nation (Figure 4-21a). The DA/VC ratio used as a standard for national or regional assessments is 1.5 acres/acre-ft (5 m^2/m^3; i.e., 100,000 m^2/20,000 m^3). The depth is based on recommended USDA (1982) minimum depths for ponds in various regions across the continental U.S. (Figure 4-20a). The selection of this particular DA/VC ratio and a water body depth of 2 meters as a standard for national/regional assessments is not well documented.

Although the current surface water model does not directly calculate concentrations for lotic systems, a rough estimate of the equivalent flowing waters represented by the exposure scenario water body volume (20,000 m^3) can be determined. The volume of any flowing water (e.g., stream or river) can be estimated by the product of a flow rate (Q) and duration (t). Over a 1-day period, a total volume of 20,000 m^3 can be obtained if the flow rate is 20,000 m^3 per 24 hours, or 8.2 cubic feet per second (ft^3/sec). The 24-hour cycle is consistent with the rainfall data, run-off and dissipation calculations, which are processed in daily time steps in the surface water model. To put this volume (20,000 m^3) in perspective, simulated daily run-off volume, on days with run-off, from a 10 ha field in an arid California crop scenario (CA almond) ranges

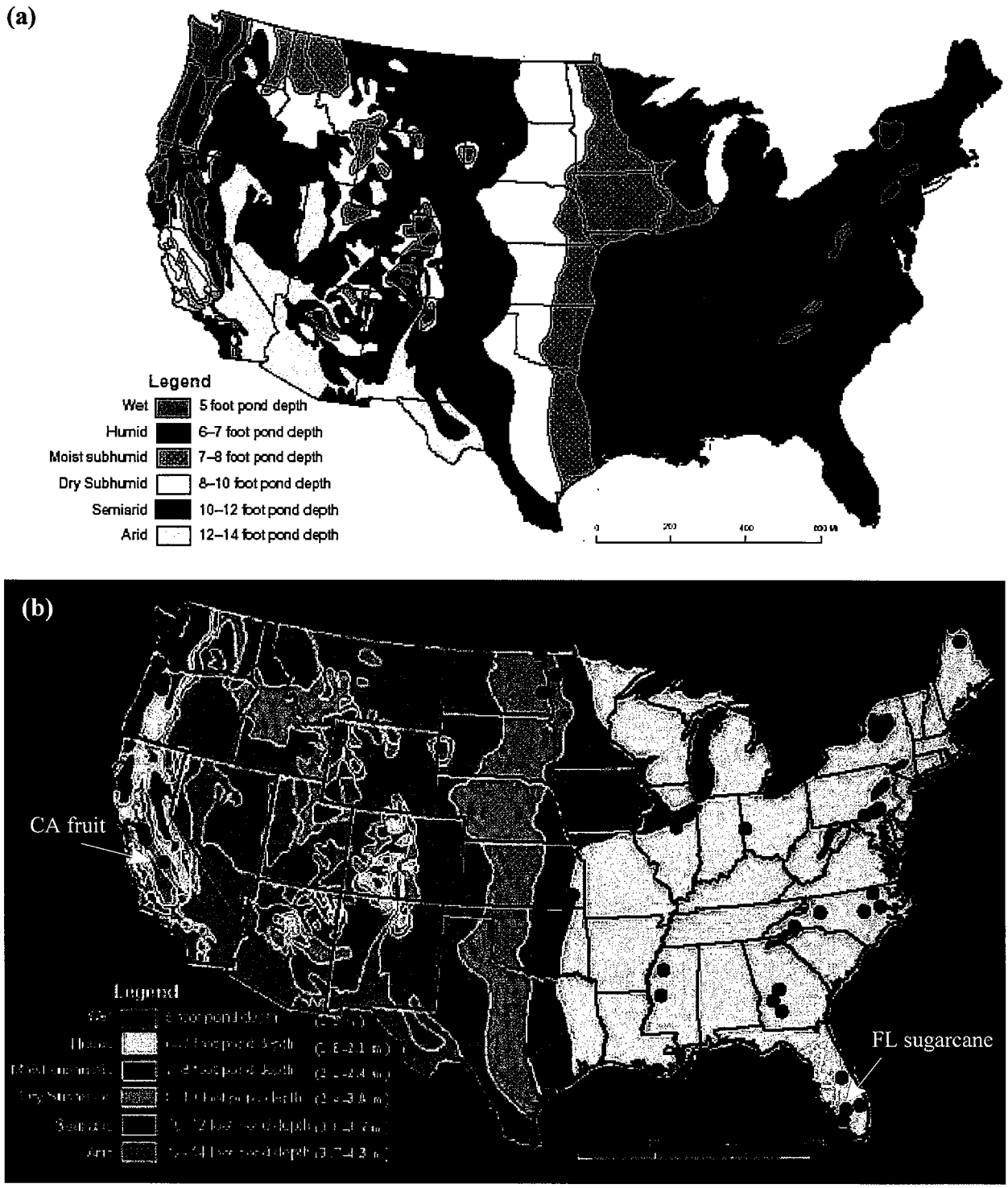


Figure 4-20. (a) USDA recommended minimum depth of water for a small, permanent surface water supply (e.g., pond) in the U.S. (USDA, 1997). (b) Overlay of crop scenarios (county locations) on the USDA minimum depth contour map.

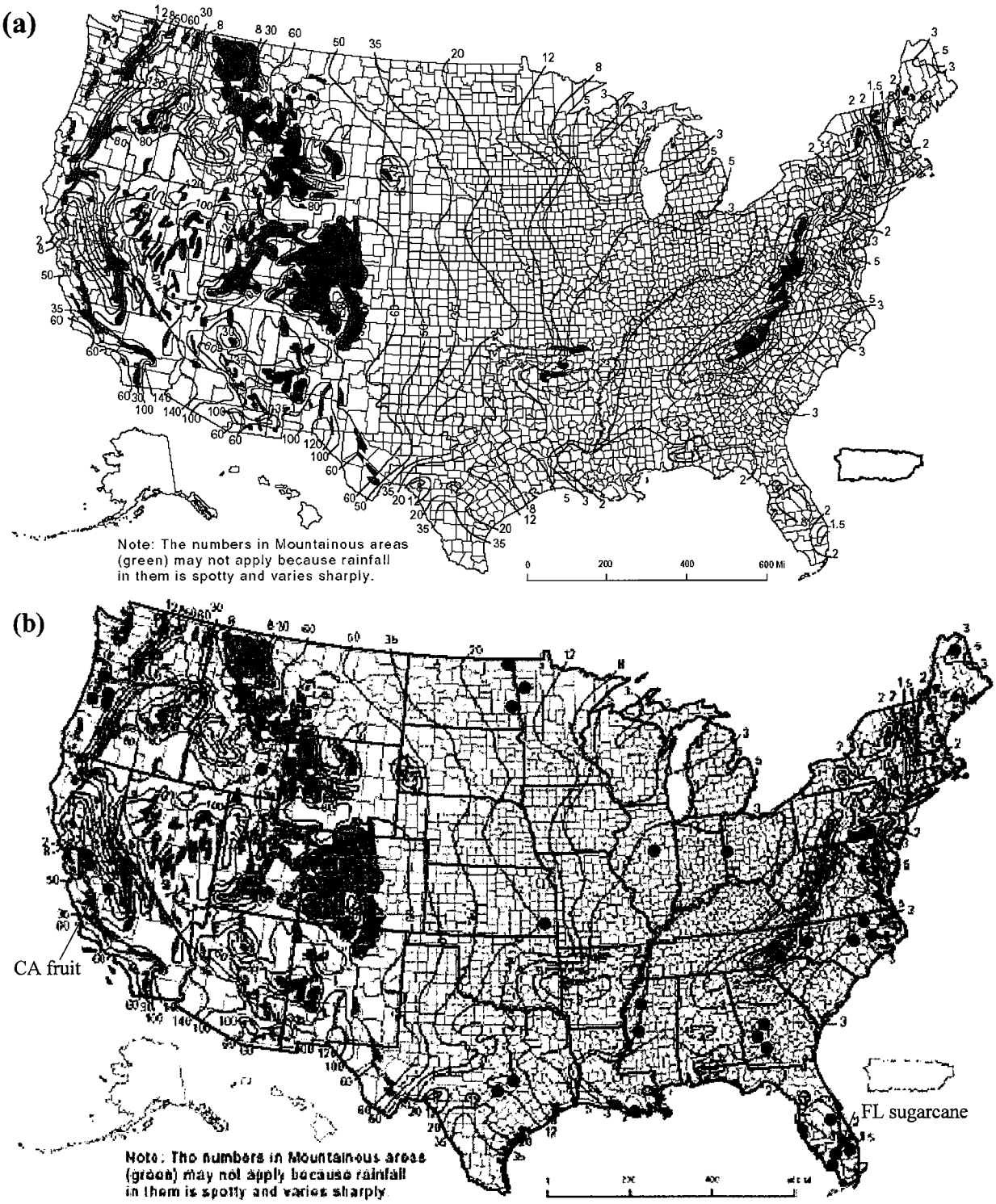


Figure 4-21. (a)USDA guidelines for estimating the size of drainage area (in acres) required for each acre-foot of storage in an embankment or pond (USDA, 1997). (b) Overlay of crop scenarios (county locations) on the USDA drainage area to acre-ft storage map.

from 7.0 m^3 to 5340 m^3, with a median of 111 m^3. In a relatively wet Florida crop scenario (FL sugarcane) run-off volume ranges from 8.0 m^3 to 16,000 m^3 with a median of 1,000 m^3 (Table 4-16). This volume of daily run-off is equivalent to flows of 2.4E-8 ft^3/sec to 2.7 ft^3/sec with a median of 0.05 ft^3/sec for the California site and 3.0E-7 ft^3/sec to 10 ft^3/sec with a median of 0.10 ft^3/sec for the Florida site. The exposure point concentration is simply the weighted average of the concentration in the upstream volume of water (assumed to be 0) and the concentration in the run-off volume. Over a 24-hour period, the concentration in flowing waters can be expected to be the same or lower than that of the standing surface water model for the same volume of water (e.g., 20,000 m^3) because pesticide mass is conserved from day to day in the standing surface water model. However, peak concentrations in flowing water may exceed that of standing water for cases when extreme rainfall yields flashes in run-off to a relatively small volume of flowing water. For example, if total loading to a river were to occur over a 1-hour period following a storm event, the concentration in the river would be 24 times greater than if run-off were distributed uniformly over the entire day.

3. Sources of DA/VC Ratios and Associated Surface Water Body Dimensions

The original source of national DA/VC ratios and surface water depth values used in the development of the current surface water body size, volume and drainage area values is USDA's "Ponds – Planning, Design, Construction" (USDA, 1997). This is a guidance manual for developing and maintaining a permanent water supply (irrigation, recreation, fire protection, livestock, fish production, waterfowl and other wildlife). Other options for obtaining DA/VC ratios and surface water body size estimates, beyond permanent pools or ponds, were explored; however, published national or regional empirical (in-field census) data on DA/VC ratios for small, permanent or ecologically important temporary surface waters were not located. Information is available, though, for drinking water reservoirs (Ruddy and Hite, 1990; USEPA, 1998), that were used to develop the DA/VC ratio used in the OPP drinking water reservoir scenario. The minimum surface water supply included in the DA/VC ratio analysis was 956,000 m^3, and DA/VC ratios ranges from 0.5 to 5,270 m^2/m^3. The applicability of these ratios for the smaller water bodies is unknown. Under the national Landscape Indicators for Pesticides Study (LIPS) program, a census and landscape indicator approach is being explored for a portion of the Midwest. However, the results of this study will not be available for at least 4 to 5 years and, as indicated, will only be applicable for a small portion of the U.S.

The use of digital data was explored as a source of obtaining drainage area and water body surface area and depth on a national or regional scale. Delineation of field drainage area and water body surface area, but not water body depth, can be obtained from national USGS digital data sets including the (1) National Land Cover Data Set, (2) the digital elevation models (DEMs), (3) digital line graph maps (DLGs), derived from digitized topographic map sheets, and (4) aerial photography. Although researchers have a method to estimate drainage area and water surface area, some of the necessary data exist only as partial coverages of the U.S. Values that can be compared and applied on a regional or national basis are not yet derived and the method does not provide estimates of water body volumes.

As described above, there are no new identified sources of DA/VC ratios and associated surface water body size values for small surface waters on a national or regional basis. As a result, approaches for developing crop scenario-specific field drainage area and water body size values were developed and evaluated using the existing USDA DA/VC ratios and water body size information (see section E.4).

4. Development and Evaluation of Field Drainage Area and Water Body Size Conditions for Crop Scenarios

In the VVWM, volume of the littoral zone is calculated from daily run-off, precipitation, and evaporation. Conceptually, the varying volume water body has a fixed surface area that is uniform throughout the littoral and benthic zones and has a littoral depth that varies to accommodate daily net flow. A maximum overflow depth corresponds to the maximum volume, and a minimum depth corresponds to the minimum volume (see Figure 4-2). This section describes approaches for setting field drainage area and water body size conditions that will ensure a run-off scenario that is field scale and consists of a small but relatively permanent (does not go dry for prolonged periods of time) water body for the Level II Exposure Model.

a. Methods

For a specific crop scenario, initial and maximum water body depth (D_0 and D_{max}) was set to the recommended minimum depth of water for maintaining a small, permanent surface water supply (e.g., irrigation, livestock, fish production, waterfowl and other wildlife) at the crop scenario location (county) in the U.S. (Figure 4-20a, b). Where there is a range of minimum values provided in the map legend for a location, no attempt was made to interpolate between them or average them to set D_0 and D_{max} because the distribution of minimum depths for small, permanent pools, wetlands, ponds, and embayments nationally or regionally is not known. Both D_0 and D_{max} were set to the minimum of the range of values in keeping with the objective to have a realistic but protective (high-end) exposure scenario. The field drainage area to water body volume capacity (*DA/VC*) ratio for a specific crop scenario was set to the highest contour value adjacent to the crop scenario location (Figure 4-21a, b).

No attempt was made to determine a national or regional representative depth or a national or regional *DA/VC* ratio based on distributions across a given crop growing area because the tools to calculate them have not been developed yet. An effort is underway to convert the USDA depth and DA/VC maps into digital formats for use with a GIS. These maps can then be overlaid with digital crop maps, which also provide crop density information. Such maps may be used to develop a weighted national or regional crop scenario-specific DA/VC or water body volume. In addition to the development of a digital DA/VC map, there are some crops for which digital maps do not yet exist which will also require development. In the interim, the non-GIS approach described above is being proposed for use in setting crop scenario-specific D_0, D_{max} and *DA/VC* ratio values.

After the crop scenario-specific D_{max} and *DA/VC* ratio was assigned, three options of setting scenario-specific values for the remaining water body parameters (water body surface area, SA; field drainage area, *DA*; and maximum volume capacity, *VC*) were compared. The initial volume, V_0, of the varying volume water body was set equal to *VC* (maximum volume capacity). The options, listed below, were derived from a systematic series of calculations where each remaining parameter (SA, DA, or VC) in turn was set to its current standard scenario value and the other two were calculated based on the relationship between volume, depth and surface area ($VC = D_{max} \times SA$):

1) Set the water body surface area, *SA*, to 1 ha (standard surface water scenario value), derive the value for *VC* by multiplying *SA* and D_{max} (Table 4-11), and obtain the *DA* from the *DA/VC* ratio for this *VC* (Table 4-12);

2) Set the volume capacity, *VC*, to 20,000 m^3 (standard surface water scenario value), derive *SA* by dividing *VC* by D_{max} (Table 4-13), and derive the *DA* from the *DA/VC* ratio (Table 4-14);

3) Set the field drainage area, *DA*, derive the *VC* from the *DA/VC* ratio, and derive *SA* by dividing *VC* by D_{max}. This option was evaluated with *DA* set to 10 (standard surface water scenario value), 20, 40 and 100 ha.

The options were evaluated with both a low rainfall (CA fruit) and high rainfall (FL sugarcane) standard crop scenario and using a short-lived chemical (ChemA) and a long-lived chemical (ChemB). See Table 4-6 for chemical properties. All simulations were run using the same application date and methods.

In addition to the above analyses, which used the minimum value from the depth range for a crop scenario in Figure 4-20b for D_0 and D_{max}, a limited number of simulations were also performed using the average ([minimum + maximum]÷2) and maximum depth range values from Figure 4-20a for the scenario-specific maximum water body depth (D_{max}) to evaluate how large an effect this difference in choice of depth had on results. For these analyses, initial water body depth (D_0) for the varying volume water body was set to the maximum depth (D_{max}), field drainage area (*DA*) was set to 10 ha, maximum volume capacity was derived from the *DA/VC* ratio, and surface area (*SA*) was derived from the maximum depth and volume.

b. Results

Condition Derivation

Using the method described above, the initial and maximum water body depth (D_0 and D_{max}) is 2.4 m for the semi-arid scenario (CA fruit) and is 1.8 m for the humid scenario (FL sugarcane) (Figure 4-20b). Field drainage area to volume capacity ratios (*DA/VC*) are 50 acres/acre-ft for the CA fruit scenario and 3 acres/acre-ft for the FL sugarcane scenario

Table 4-11. Water body volume for a given depth and set surface area of 1 ha (10,000 m^2)

Depth[a] (ft)	Depth[b] (m)	Surface Area (m^2)	Volume[c] (m^3)
5	1.5	10000	15340
6	1.8	10000	18288
6.5	2.0	10000	19812
7	2.1	10000	21336
7.5	2.3	10000	22860
8	2.4	10000	24384
9	2.7	10000	27432
10	3.0	10000	30480

[a] Site-specific depth obtained from Figure 4-20a.
[b] 1 foot = 0.3048 meters
[c] Volume (m^3) = Depth (m) × Surface area (m^2)

Table 4-12. Field drainage area (ha) for a given water body depth and water body volume.

DA/VC Ratio[b] (acre/acre-ft)	Water Body Volume[a] (m^3)								
	20000[c]	15240	18288	19812	21336	22860	24384	27432	30480
1	6.6	5.0	6.0	6.5	7.0	7.5	8.0	9.0	10.0
1.5	9.8	7.5	9.0	9.8	10.5	11.3	12.0	13.5	15.0
2	13.1	10.0	12.0	13.0	14.0	15.0	16.0	18.0	20.0
3	19.7	15.0	18.0	19.5	21.0	22.5	24.0	27.0	30.0
5	32.8	25.0	30.0	32.5	35.0	37.5	40.0	45.0	50.0
8	52.5	40.0	48.0	52.0	56.0	60.0	64.0	72.0	80.0
12	78.8	60.0	72.0	78.0	84.0	90.0	96.0	108	120
20	131	100	120	130	140	150	160	180	200
30	197	150	180	195	210	225	240	270	300
35	230	175	210	228	245	263	280	315	350
50	328	250	300	325	350	375	400	450	500
80	525	400	480	520	560	600	640	720	800

[a] Water body volume obtained from Table 4-11.
[b] Site-specific field area to water body volume capacity ratio obtained from Figure 4-21a.
[c] $\left(1\frac{\text{acre}}{\text{acre}-\text{ft}}\right)\left(0.40469\frac{\text{ha}}{\text{acre}}\right)\left(\frac{1}{1233}\frac{\text{acre}-\text{ft}}{\text{m}^3}\right) = \frac{6.56}{20000}\frac{\text{ha}}{\text{m}^3}$

Table 4-13. Water body surface area for a given initial depth and set water body volume (20,000 m^3).

Depth[(a)] (ft)	Depth[(b)] (m)	Volume (m^3)	Surface Area[(c)] (m^2)
5	1.5	20000	13123
6	1.8	20000	10936
6.5	2.0	20000	10095
7	2.1	20000	9373.8
7.5	2.3	20000	8748.9
8	2.4	20000	8202.1
9	2.7	20000	7290.8
10	3.0	20000	6561.7

[(a)] Site-specific depth obtained from Figure 4-20a.
[(b)] 1 foot = 0.3048 m
[(c)] Surface Area (m^2) = Volume (m^3) ÷ Depth (m)

Table 4-14. Field drainage area for a given depth and set water body volume (20000 m^3).

DA/VC Ratio[(a)] (acre/acre-ft)	Drainage Area[(b)] (ha)
1	6.6
1.5	9.8
2	13.1
3	19.7
5	32.8
8	52.5
12	78.8
20	131
30	197
35	230
50	328
80	525

[(a)] Site-specific field area to water body volume capacity ratio obtained from Figure 4-21a.
[(b)] $\left(x\frac{\text{acre}}{\text{acre}-\text{ft}}\right)\left(0.405\frac{\text{ha}}{\text{acre}}\right)\left(\frac{1}{1233}\frac{\text{acre}-\text{ft}}{\text{m}^3}\right)\left(20000\,\text{m}^3\right) = y$ hectares

(Figure 4-21b). Crop scenario-specific values for the remaining parameter values (*SA*, *VC* and field *DA*) are provided in Table 4-15 for each of the three options.

Comparison of Crop Scenario-Specific Options Using USDA (1997) DA/VC and Depth Guidelines

Simulated daily concentration and water body volume results were used to compare the options for setting field area and water body size parameter values for the varying volume surface water exposure modeling scenario. Simulated daily concentration and volume results for the CA fruit scenario with a long-lived pesticide, ChemB, for all three options are provided in Figures 4-22 and 4-23. The magnitude of water body volume present on any given day differed among the three options, but the temporal volume pattern (i.e., drying out and overflow) did not differ because the same meteorological data set is used for each option for a given crop scenario (Figures 4-22b and 4-23b). Despite affecting the water body volume magnitude, the three options for setting values for drainage area and water body size parameters did not result in meaningful differences in simulated daily concentrations (Figures 4-22a and 4-23a). This was also the case for the three options for the CA fruit scenario with the short-lived pesticide and the FL sugarcane scenario with both the long-lived and short-lived pesticide (simulation results for these are not shown). The PRZM/VVWM calculations, which account for the same simulated daily concentrations among the three options, are discussed below.

Model Calculations PRZM/VVWM

Discounting degradation, the instantaneous daily peak concentration of pesticide X in the littoral zone in the VVWM is calculated as follows:

$$[X] = \frac{X_{mass}}{V} \tag{4-54}$$

where,

[X] = aqueous concentration of pesticide X in the littoral zone, kg/m^3;
X_{mass} = mass of chemical X in the littoral zone, kg; and
V = water body volume of the littoral zone, m^3.

PRZM output for pesticide mass, which feeds the VVWM, is given per unit field area such that:

$$X_{mass} = \left(X_{mass-area}\right)(DA) \tag{4-55}$$

where,

$X_{mass\text{-}area}$ = mass of chemical X per unit field area, kg/ha; and
DA = field drainage area, ha.

Table 4-15. Field drainage area and water body size parameter values for option (1) setting surface area, *SA*, to 1 ha, (2) setting volume capacity, *VC*, to 20,000 m³, and (3) setting field area, *DA*, to 10, 20, 40, and 100 ha for crop scenarios CA fruit and FL sugarcane.

Parameters	CA fruit						FL sugarcane					
	SA[a] (ha)	V_0[b, c] (m³)	DA[d] (ha)				SA[a] (ha)	V_0[b, c] (m³)	DA[d] (ha)			
	1	20000	10	20	40	100	1	20000	10	20	40	100
DA/VC[e] acre/acre-ft	50						3					
D_0[f] (m)	2.4						1.8					
D_{max}[f] (m)	2.4						1.8					
SA (m²)	10000	8202	250	500	1000	2499	10000	10936	5553	11107	22213	55533
V_0 (m³)[c]	24384	20000	609	1219	2437	6094	18288	20000	10156	20312	40624	101559
VC (m³)	24384	20000	609	1219	2437	6094	18288	20000	10156	20312	40624	101559
DA (ha)	400	328	10	20	40	100	18	20	10	20	40	100

[a] Option (1) SA set to current standard, 1 ha, and VC based on $VC = D_{max} \times SA$ and $DA = VC \times DA/VC$ ratio.
[b] Option (2) VC set to current standard, 20,000 m³, and SA based on $SA = D_{max} \div VC$ and $DA = VC \times DA/VC$ ratio.
[c] $V_0 = VC$
[d] Option (3) DA set to current standard, 10 ha, and VC based on $VC = DA \div DA/VC$ ratio and $SA = D_{max} \div VC$.
[e] Field area to volume capacity ratio taken from Figure 4-21b.
[f] Initial, D_0, and maximum depth, D_{max}, taken from the minimum of the range in Figure 4-20b.

Table 4-16. Field area and water body size parameter values derived by setting field area to 10 ha and setting initial and maximum depth to the minimum, average and maximum of the range in Figure 4-20b for crop scenarios CA fruit and FL sugarcane.

Parameters	CA fruit			FL sugarcane		
	Minimum[a]	Average[a]	Maximum[a]	Minimum[a]	Average[a]	Maximum[a]
DA/VC[b] acre/acre-ft	50			3		
DA[c] (ha)	10			10		
D_0[a] (m)	2.44	2.74	3.05	1.83	1.98	2.13
D_{max}[a] (m)	2.44	2.74	3.05	1.83	1.98	2.13
V_0[d] (m³)	609.4			10156		
VC[d] (m³)	609.4			10156		
SA[e] (m²)	249.9	222.1	199.9	5553	5216	4760

[a] Initial, D_0, and maximum, D_{max}, depth set to the minimum, average or maximum depth range for the depth isopleth in Figure 4-20b where the crop scenario is located.
[b] Field area to volume capacity ratio taken from Figure 4-21b for where the given crop scenario is located.
[c] Field area set to the current standard condition of 10 ha.
[d] Initial, V_0, and maximum, VC, volume derived from $V_0 = VC = DA \div DA/VC$ ratio.
[e] Surface area derived from $SA = D_{max} \div VC$.

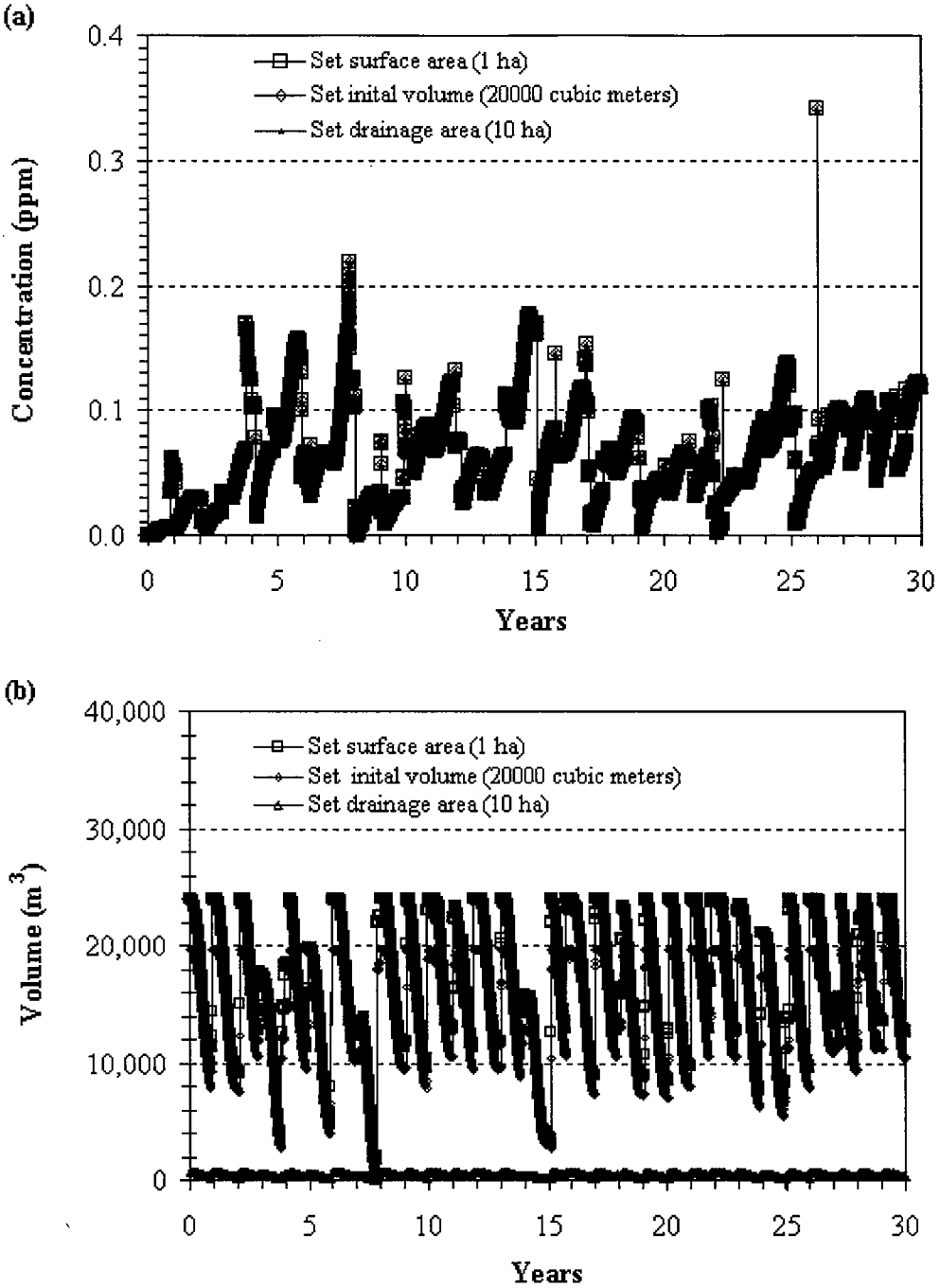


Figure 4-22. The effect of setting water body surface area, initial volume or drainage area on (a) daily concentration and (b) water body volume for ChemB at a semi-arid site corresponding to the CA fruit crop scenario (metfile W93193, DA/VC = 50 acre/acre-ft, $D_0 = D_{max} = 2.4$ m). For surface area of 1 ha, volume capacity = 24,384 m^3 and drainage area = 400 ha. For volume capacity of 20,000 m^3, drainage area = 328 ha and surface area = 8202 m^2. For drainage area of 10 ha, volume capacity = 609 m^3 and surface area = 250 m^3.

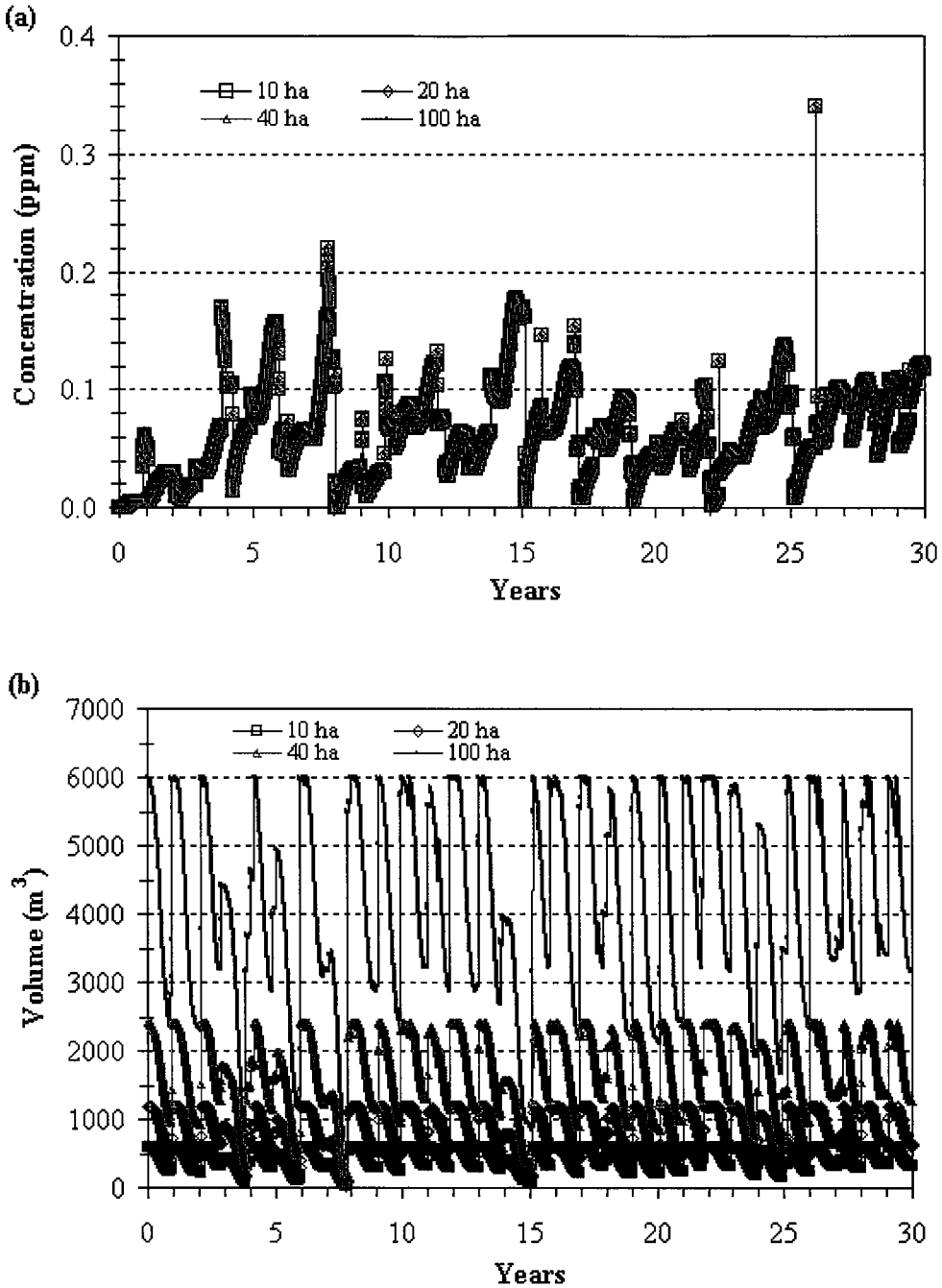


Figure 4-23. The effect of varying drainage areas on (a) daily concentration and (b) water body volume for ChemB in semi-arid site corresponding to standard scenario CA fruit (metfile W93193, DA/VC ratio = 50 acre/acre-ft, and $D_0 = D_{max} = 2.4$ m. For drainage area of 10 ha, volume capacity = 609 m^3 and surface area = 250 m^2. For drainage area of 20 ha, volume capacity = 1219 m^3 and surface area = 500 m^2. For drainage area of 40 ha, volume capacity = 2437 m^3 and surface area =1000 m^2. For drainage area of 100 ha, volume capacity = 6094 m^3 and surface area = 2499 m^2.

The equation for the littoral zone volume is the initial volume plus precipitation and runoff minus evaporation:

$$V = V_0 + (SA)(P - E) + (R)(DA) \tag{4-56}$$

where,

V_0 = initial littoral zone volume, m^3;
SA = water body surface area, m^2;
P = precipitation, m;
E = evaporation, m; and
R = run-off per unit field area, m^3/ha.

Substituting initial volume divided by initial water depth for surface area in equation 4-56 produces the following equation:

$$V = V_0 + \left(\frac{V_0}{D_0}\right)(P - E) + (R)(DA) \tag{4-57}$$

where,

D_0 = initial littoral zone water depth, m.

Simplifying equation 4-57 produces:

$$V = (V_0)\left(1 + \left(\frac{1}{D_0}\right)(P - E)\right) + (R)(DA) \tag{4-58}$$

Substituting equations 4-55 and 4-58 into equation 4-54 produces:

$$[X] = \frac{(X_{mass-area})(DA)}{(V_0)\left(1 + \left(1/D_0\right)(P - E)\right) + (R)(DA)} \tag{4-59}$$

Dividing the numerator and denominator by DA results in:

$$[X] = \frac{(X_{mass-area})}{\left(\left(\frac{V_0}{DA}\right)\left(1 + \left(\frac{1}{D_0}\right)(P - E)\right) + R\right)} \tag{4-60}$$

Since the DA/VC ratio and D_0 are set site-specifically from Figures 4-21b and 4-20b, respectively, varying field drainage area, DA, and water body size parameter values based on the volume and surface area relationship ($VC = D_{max} \times SA$) will affect mass loading (X_{mass}) and water body volume (V) proportionally. In this case concentration of the pesticide, $[X]$, is the same regardless of which option is used to derive the specific parameter values. However, this is only the case when degradation is neglected. Degradation processes that are dependent on water body surface area, such as volatilization, may affect $[X]$. For the CA fruit scenario, however, there was no difference in daily concentration for simulations when the three options for deriving the drainage area and water body size values were compared. In these options, the water body surface area ranged from 250 to 10,000 m^2 (Table 4-15) for both ChemA and ChemB.

Sensitivity of VVWM Results to Maximum Water Body Depth

Simulated daily concentrations and water body volume were used to evaluate the sensitivity of the model to setting the maximum water body depth to the minimum, average, and maximum values of the range of values given in Figure 4-20a. Since field area and maximum volume was the same for all the simulations for each crop scenario, the comparison actually assessed the impact of using a more shallow water body with a proportionally larger surface area rather than a slightly deeper water body with a proportionally smaller surface area (Table 4-16). Simulated daily concentrations and water body volume results for setting the maximum water depth to the minimum, average, and maximum values of the range are provided in Figure 4-24 for the low-rainfall crop scenario, CA fruit, using ChemA and ChemB and in Figure 4-25 for the high-rainfall crop scenario, FL sugarcane, using ChemA and ChemB. For the semi-arid scenario, CA fruit, daily concentrations calculated with the minimum depth from the range resulted, on average, in the highest concentrations followed by those calculated with the average and maximum depth from the range (Figures 4-24a and 4-24b). This corresponds to an inverse relationship between water body volume during dry periods and the volume calculated with the minimum depth from the range resulting in the lowest volumes followed by those with the average and maximum depth from the range (Figure 4-24c). During dry periods, the water body with the largest surface area (shallowest) appears to reach the lowest volume as a result of increased evaporation that causes the pesticide to become more concentrated. Alternatively, during wet periods, the water body with the smallest surface area (deepest) appears to experience greater overflow and consequently a greater amount of dissipation because washout causes the greatest decrease in pesticide concentration. Differences in daily concentrations were more pronounced for the short-lived pesticide (ChemA) relative to the long-lived pesticide (ChemB). The long-lived chemical is more sensitive to dissipation due to washout during overflow conditions than the short-lived chemical. For the semi-arid site, CA fruit, the average percent difference (+/- 1 standard deviation (S.D.)) in daily concentration between the minimum and average depth from the range and between the average and maximum depth from the range was 24.9 ± 11.6% and 20.9 ± 8.7%, respectively, for ChemA and 12.5 ± 5.0% and 10.0 ± 4.1%, respectively, for ChemB.

For the high-rainfall crop scenario, FL sugarcane, daily concentrations calculated using the minimum depth from the range in Figure 4-20b resulted in higher concentrations, on average,

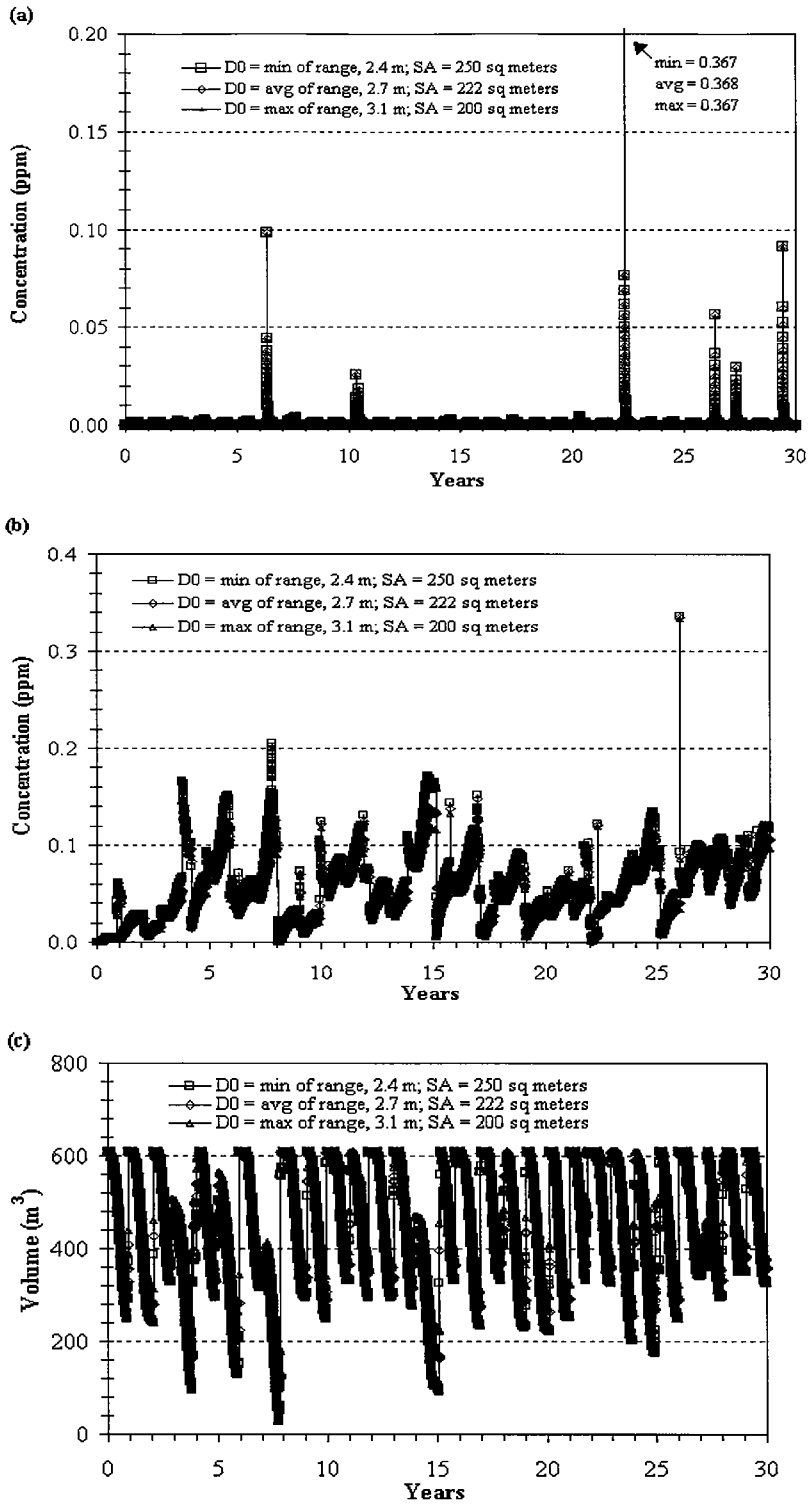


Figure 4-24. The effect of using the minimum (min), average (avg), and maximum (max) initial water body depth (D0) on daily concentration for (a) ChemA and (b) ChemB and (c) water body volume in semi-arid site corresponding to standard scenario CA fruit, metfile w93193.

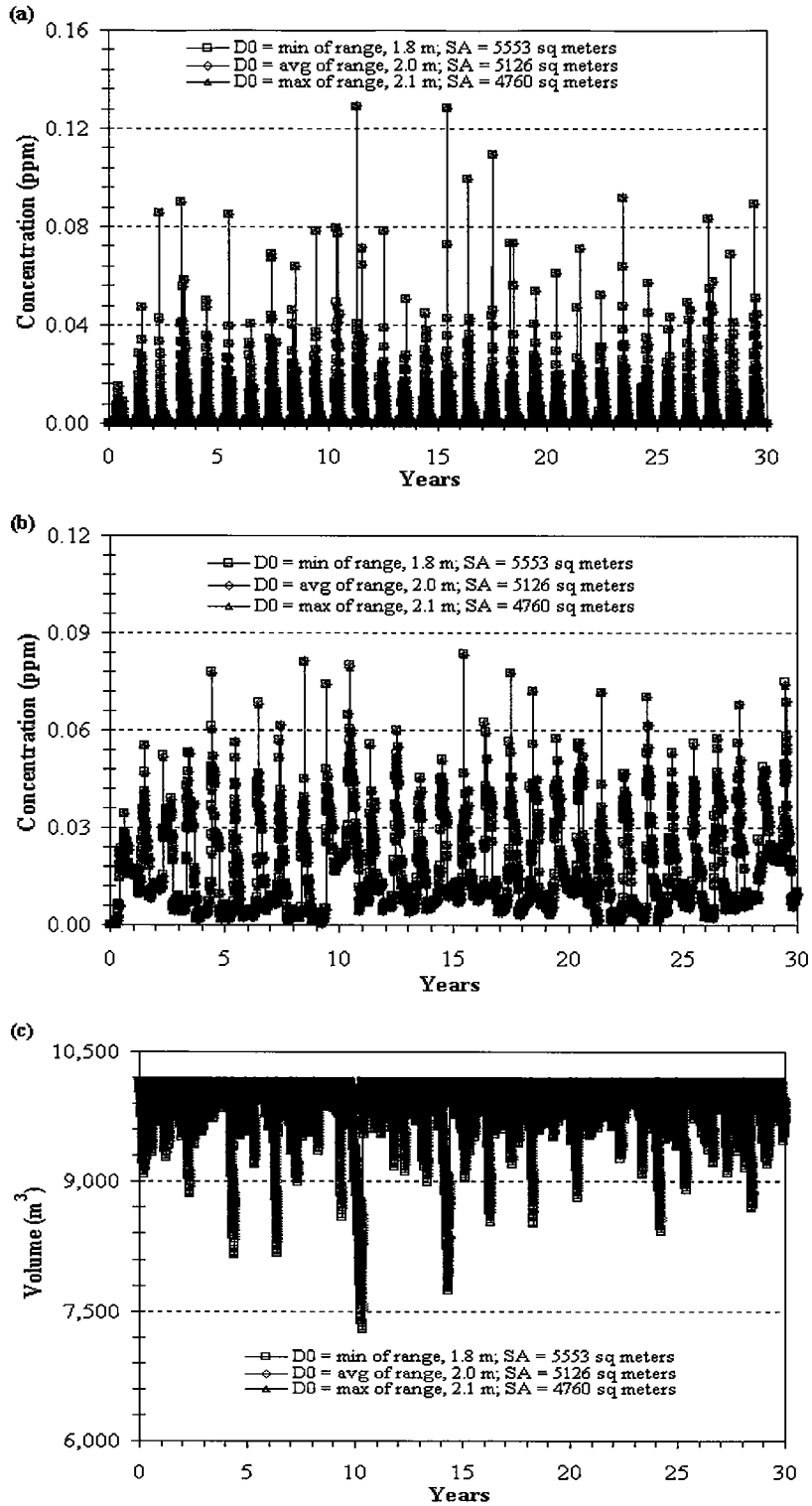


Figure 4-25. The effect of using the minimum (min), average (avg), and maximum (max) initial water body depth (D0) on daily concentration for (a) ChemA and (b) ChemB and (c) water body volume in humid site corresponding to standard scenario FL sugarcane, metfile w12844.

than those calculated using the average and maximum depth from the range for the short-lived chemical (ChemA) (Figure 4-25a). On average, there was little difference in daily concentrations for the long-lived chemical (ChemB) when using the minimum, average, or maximum range value was used as the initial depth (Figure 4-25b), probably because increases in concentration during the dry season for the shallower water bodies were counter-balanced by decreased loses during overflow conditions. The average percent difference (+/- 1 S.D.) in daily concentration between the minimum and average depth from the range and between the average and maximum depth from the range was 4.6 ± 3.0% and 4.2 ± 2.7%, respectively, for ChemA and 2.3 ± 2.4% and 2.1 ± 2.2%, respectively, for ChemB.

5. Proposed Crop Scenario-Specific Field Drainage Area and Water Body Size Parameter Values

Since concentration is not affected by the method of derivation of the water body size parameter values (*SA*, *DA*, *VC*) once the *DA/VC* ratio and D_{max} (D_0) have been set, we propose retaining the standard field area (*DA*) of10 ha for all crop scenarios, and deriving the values for the remaining water body size parameters (*SA*, *VC*) according to the crop scenario-specific *DA/VC* ratio and the D_{max} (Table 4-17). Retaining the standard field area size of 10 ha meets the objective for a field-scale assessment and does not require adjustments for percent crop treated that a larger field size may require. That is, one can reasonably assume that 100% of the field is planted with the same crop, has the same cropping practices, and is treated with a pesticide at the same time. Additionally, PRZM currently uses a single soil series, assigned in the crop scenario, for modeling run-off. While it is recognized that soil series in a field are not homogeneous, it is reasonable to assume soil type conditions are more homogeneous in a 10 ha field than a larger area. The other two options that were evaluated in this exercise result in some crop scenarios with field areas of over 500 acres. Use of these two options would therefore require adjustments to the assumptions that 100% of the field is treated, 100% of run-off from a treated field is routed to the same surface water body, and that a single soil series is present.

Comparison of Standard and Crop Scenario-Specific Simulated EECs and Surface Volume

The impact of using the varying volume water body with proposed crop scenario-specific water body size values (VVWM-scenario specific) versus the standard water body size parameter values (VVVWM-standard; DA = 10 ha; SA = 1 ha; VC = 20,000 m^3) was evaluated using a combination of low-rainfall (CA fruit) and high-rainfall (FL sugarcane) crop scenarios with ChemA and ChemB. Simulated daily concentrations and water volume output for the arid scenario (CA fruit) are provided in Figure 4-26. Using the standard water body parameter values (VVWM-standard) resulted in the water body volume reaching the minimum (i.e., essentially drying out) throughout much of the simulation for the CA fruit scenario (Figure 4-26c). Using the crop scenario-specific values (VVWM-scenario specific), on the other hand, resulted in a volume pattern that was representative of a permanent water body, and captured seasonal variability (Figure 4-26c). For the short-lived chemical (ChemA) and long-lived chemical (ChemB), the VVWM-standard model predicted high peak concentrations when the water body

Table 4-17. Proposed field and water body size parameter values for all standard crop scenarios for the Level II Exposure Model.

Scenario						Metfile			DA/VC[c]	D_{max}[d]	D_{max}	DA[e]	SA[f]	VC[g]
Name	Category[a]	County	MLRA[b]	Latitude	Longitude	Number	Latitude	Longitude	(acre/acre-ft)	(ft)	(m)	(ha)	(m^2)	(m^3)
CA alfalfa	OP, R	San Joaquin	17	37.93	-121.27	w93193	N 36° 47"	W 119° 43"	50	8	2.4	10	250	609
CA almond	OP, R	San Joaquin	17	37.93	-121.27	w23232	N 38° 31"	W 121° 30"	50	8	2.4	10	250	609
CA citrus	OP, R	Fresno	17	36.75	-119.65	w23155	N 35° 25"	W 119° 43"	50	8	2.4	10	250	609
CA corn	OP, R	Stanislaus	17	37.56	-120.99	w23232	N 35° 31"	W 121° 30"	50	8	2.4	10	250	609
CA fruit	OP, R	Fresno	17	36.75	-119.65	w93193	N 36° 47"	W 119° 43"	50	8	2.4	10	250	609
CA grapes	OP, R	San Joaquin	17	37.93	-121.27	w93193	N 36° 47"	W 119° 43"	50	8	2.4	10	250	609
CA sugar beets	OP, R	Fresno	17	36.75	-119.65	w93193	N 36° 47"	W 119° 43"	50	8	2.4	10	250	609
CA tomato	OP, R	San Joaquin	17	37.93	-121.27	w93193	N 36° 47"	W 119° 43"	50	8	2.4	10	250	609
FL cabbage	N	Collier	156B	26.08	-81.40	w12842	N 27° 58"	W 82° 32"	3	6	1.8	10	5553	10156
FL citrus	N	Collier	156A	26.08	-81.40	w12842	N 27° 58"	W 82° 32"	3	6	1.8	10	5553	10156
FL cucumber	N	Collier	156B	26.08	-81.40	w12842	N 27° 58"	W 82° 32"	3	6	1.8	10	5553	10156
FL peppers	N	Collier	155	26.08	-81.40	w12844	N 26° 41"	W 80° 7"	3	6	1.8	10	5553	10156
FL sugarcane	R	Hendry	156A	26.55	-81.17	w12844	N 26° 41"	W 80° 7"	3	6	1.8	10	5553	10156
FL sweet corn	R	Palm Beach	156B	26.64	-80.44	w12844	N 26° 41"	W 80° 7"	2	6	1.8	10	8330	15234
FL tomato	N	Collier	155	26.08	-81.40	w12844	N 26° 41"	W 80° 7"	3	6	1.8	10	5553	10156
FL turf	R	Osceola	156A	28.06	-81.15	w12834	N 29° 11"	W 81° 3"	1	6	1.8	10	16660	30468
GA peaches	N	Peach	133A	32.56	-83.83	w03813	N 32° 42"	W 83° 39"	3	6	1.8	10	5553	10156
ID potato	R	Bingham	13	43.22	-112.40	w24156	N 42° 55"	W 112° 36"	80	10	3.0	10	125	381
IL corn	R	McLean	108	40.49	-88.85	w14923	N 41° 27"	W 90° 30"	5	6	1.8	10	3332	6094
KS sorghum	R	Neosha	112	37.56	-95.30	w13966	N 33° 58"	W 98° 29"	20	7	2.1	10	714	1523
LA sugarcane	R	Terrebonne	131	29.34	-90.84	w13970	N 30° 32"	W 91° 8"	2	6	1.8	10	8330	15234
ME potato	N	Aroostook	146	46.64	-68.59	w14607	N 46° 52"	W 68° 1"	5	6	1.8	10	3332	6094
MN alfalfa	R	Polk	56	47.77	-96.40	w14914	N 46° 54"	W 96° 48"	20	8	2.4	10	625	1523
MN sugar beet	N	Polk	56	47.77	-96.40	w14914	N 46° 54"	W 96° 48"	20	8	2.4	10	325	1523

Scenario						Metfile			DA/VC[c]	D_{max}[d]	D_{max}	DA[e]	SA[f]	VC[g]
Name	Category[a]	County	MLRA[b]	Latitude	Longitude	Number	Latitude	Longitude	(acre/acre-ft)	(ft)	(m)	(ha)	(m^2)	(m^3)
MS corn	R	Tallahatchie	134	33.95	-90.17	w13893	N 35° 3"	W 90° 0"	5	6	1.8	10	3332	6094
MS cotton	N	Yazoo	134	32.78	-90.40	w03940	N 32° 19"	W 90° 5"	5	6	1.8	10	3332	6094
MS soybean	R	Yazoo	134	32.78	-90.40	w13893	N 35° 3"	W 90° 0"	5	6	1.8	10	3332	6094
NC alfalfa	R	Iredell	130	35.81	-80.87	w03812	N 35° 26"	W 82° 33"	2	6	1.8	10	8330	15234
NC apple	R	Henderson	130	35.34	-82.48	w03812	N 35° 26"	W 82° 33"	1	6	1.8	10	16660	30468
NC corn EC	R	Pitt	133	35.59	-77.38	w13722	N 35° 52"	W 78° 47"	5	6	1.8	10	3332	6094
NC corn WC	R	Henderson	130	35.34	-82.48	w03812	N 35° 26"	W 82° 33"	1	6	1.8	10	16660	30468
NC cotton	R	Halifax	133A	36.26	-77.66	w13722	N 35° 52"	W 78° 47"	5	6	1.8	10	3332	6094
NC peanut	N	Pitt	133	35.59	-77.38	w13737	N 36° 54"	W 76° 12"	5	6	1.8	10	3332	6094
NC tobacco	N	Johnson	133A	35.52	-78.37	w13722	N 35° 52"	W 78° 47"	5	6	1.8	10	3332	6094
ND corn	R	Pembina	56	48.77	-97.55	w14914	N 46° 54"	W 96° 48"	20	8	2.4	10	625	1523
ND wheat	R	Cass	56	46.93	-97.25	w14914	N 46° 54"	W 96° 48"	20	8	2.4	10	625	1523
OH corn	N	Darke	111	40.13	-84.62	w93815	N 39° 54"	W 84° 12"	5	7	2.1	10	2856	6094
OR apple	R	Marion	A2	44.91	-122.58	w24229	N 45° 36"	W 22° 36"	2	6	1.8	10	8330	15234
OR berries	N	Marion	A2	44.91	-122.58	w24232	N 44° 55"	W 123° 0"	2	6	1.8	10	8330	15234
OR filberts	N	Washington	2	45.55	-123.09	w24232	N 44° 55"	W 123° 0"	2	5	1.5	10	9996	15234
OR grass seed	OP	Linn	2	44.49	-122.53	w24232	N 44° 55"	W 123° 0"	2	6	1.8	10	8330	15234
OR hops	N	Marion	A2	44.91	-122.58	w24232	N 44° 55"	W 123° 0"	2	6	1.8	10	8330	15234
OR mint	N	Marion	A2	44.91	-122.58	w24232	N 44° 55"	W 123° 0"	2	6	1.8	10	8330	15234
OR snbeans	N	Marion	2	44.91	-122.58	w24232	N 44° 55"	W 123° 0"	2	6	1.8	10	8330	15234
OR swcorn	R	Marion	2	44.91	-122.58	w24232	N 44° 55"	W 123° 0"	2	6	1.8	10	8330	15234
OR wheat	R	Marion	2	44.91	-122.58	w24232	N 44° 55"	W 123° 0"	2	6	1.8	10	8330	15234
OR Xmas tree	OP, L	Benton	A2	44.50	-123.43	w24232	N 44° 55"	W 123° 0"	2	5	1.5	10	9996	15234
PA alfalfa	R	York	148	39.92	-76.63	w14737	N 40° 39"	W 75° 26"	3	6	1.8	10	5553	10156
PA apple	R	Lancaster	148	40.04	-76.25	w14737	N 40° 39"	W 75° 26"	3	6	1.8	10	5553	10156

Scenario						Metfile			DA/VC[c]	D_{max}[d]	D_{max}	DA[e]	SA[f]	VC[g]
Name	**Category**[a]	**County**	**MLRA**[b]	**Latitude**	**Longitude**	**Number**	**Latitude**	**Longitude**	**(acre/acre-ft)**	**(ft)**	**(m)**	**(ha)**	**(m^2)**	**(m^3)**
PA corn	R	Lancaster	148	40.04	-76.25	w14737	N 40° 39"	W 75° 26"	3	6	1.8	10	5553	10156
PA tomato	R	Adams	148	39.87	-77.22	w14737	N 40° 39"	W 75° 26"	3	6	1.8	10	5553	10156
PA turf	R	York	148	39.92	-76.63	w14737	N 40° 39"	W 75° 26"	3	6	1.8	10	5553	10156
TX alfalfa	OP, R	Milam	J-87	30.79	-96.98	w13958	N 30° 17"	W 97° 42"	12	7	2.1	10	1190	2539
TX corn	OP, R	Milam	J-87	30.79	-96.98	w13958	N 30° 17"	W 97° 42"	12	7	2.1	10	1190	2539
TX cotton	OP, R	Milam	86	30.79	-96.98	w13958	N 30° 17"	W 97° 42"	12	7	2.1	10	1190	2539
TX sorghum	OP, R	Milam	J-87	30.79	-96.98	w13958	N 30° 17"	W 97° 42"	12	7	2.1	10	1190	2539
TX wheat	OP, R	Travis	87	30.33	-97.78	w13958	N 30° 17"	W 97° 42"	20	8	2.4	10	625	1523

[a] Crop scenario risk assessment category: N = national; R = regional; OP = OP cumulative; L = local specific

[b] Major Land Resource Area

[c] Field area to volume capacity ratio is set to the maximum value of the isopleth where the crop scenario is located in Figure 4-21b.

[d] Initial, D_0, and maximum, D_{max}, depth is set to the minimum value of the depth range for where the crop scenario is located in Figure 4-20b.

[e] Field area set to 10 ha.

[f] Surface area derived from $SA = D_{max} \div VC$ relationship.

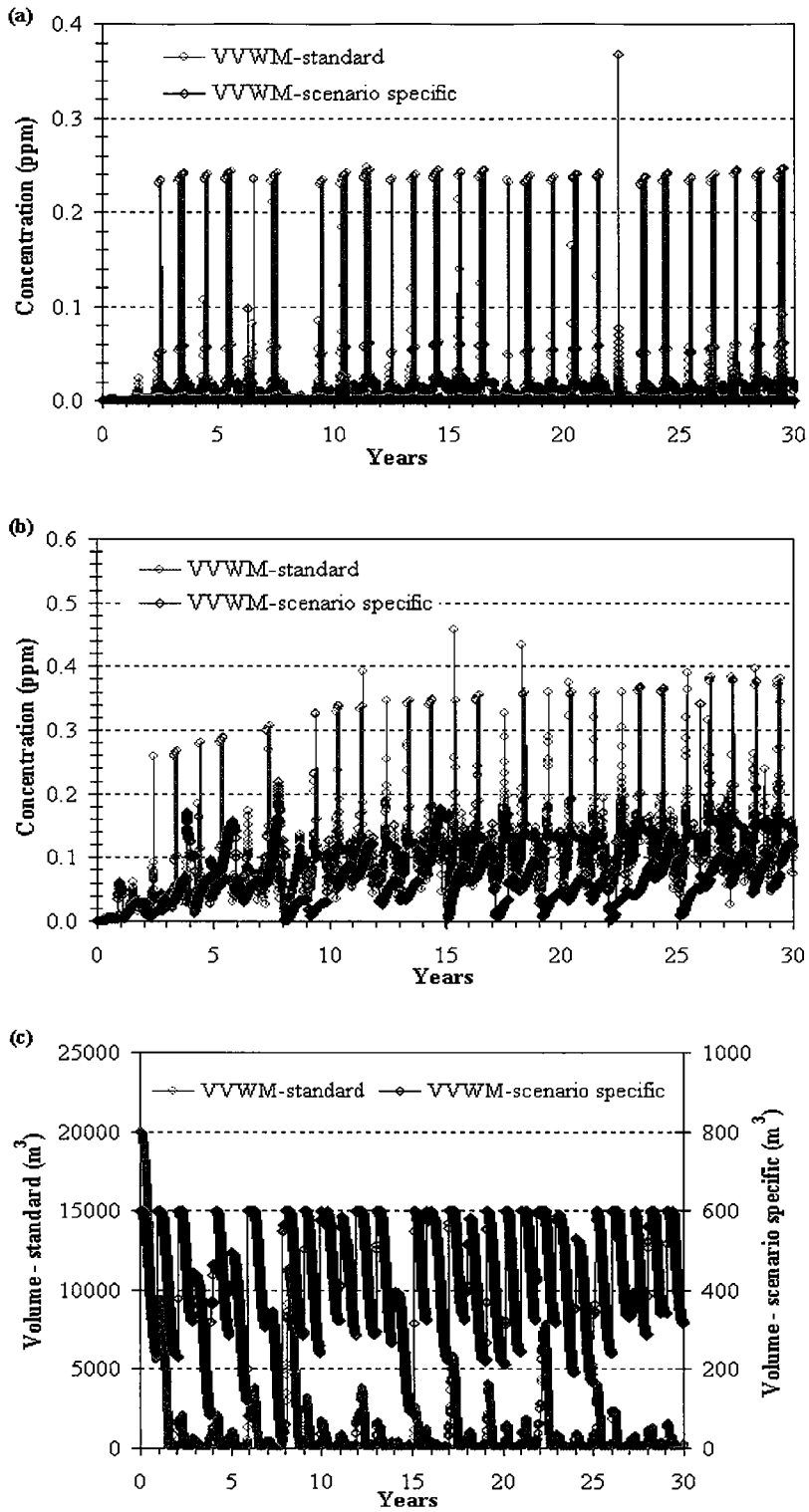


Figure 4-26. Comparison of VVWM using standard water body conditions and VVWM using crop scenario-specific water body conditions for (a) ChemA, (b) ChemB, and (c) volume for CA fruit scenario, met w93193.

volume reached the minimum. When the scenario-specific water body was used, the model predicted peak concentrations that were not associated with the water body going dry.

Simulated daily concentrations and water volume output for the FL sugarcane scenario, with ChemA and Chem B for VVWM-crop specific and VVWM-standard are provided in Figure 4-27. For the FL sugarcane scenario, the VVWM-scenario specific model resulted in lower water body volumes compared to using the standard water body parameter values (VVWM-standard) (Figure 4-27c). This is due to the difference between the standard and crop scenario-specific *DA/VC* ratios, 1.5 compared to 3, respectively. Consequently, the concentrations predicted by the VVWM-scenario specific model are slightly higher than those predicted by the VVWM-standard model for both ChemA and ChemB (Figures 4-27a and 4-27b).

The proposed approach of using DA/VC ratios that are crop scenario-specific rather than the current national standard is more realistic and represents an incremental refinement in exposure modeling for ecological risk assessment. As demonstrated previously, a 1 ha by 2 meter deep surface water fed by runoff from a 10 ha field is inadequate as a national standard for use with a varying volume water body. In addition, development of a single national standard water body dimension for the varying volume model is also inadequate given the large range in DA/VC ratios across the nation.

Simulated daily water volume using the VVWM-scenario specific model approach for each crop scenario is shown in Appendix I. In the CA citrus crop scenario, the water body still goes dry, reaching the default minimum depth of 0.01 m. This crop scenario has less volume than the CA fruit scenario, which is located in the same county with the same soil series, DA/VC ratio, *SA*, and *VC* (V_0), because different metfiles are used for these two scenarios. The metfile used for CA citrus, w23155, is characterized by much higher evaporation relative to precipitation compared to the metfile used for CA fruit, w93193. Over the 30 years of meteorological data, metfile w23155 has approximately 12 times higher evaporation than precipitation whereas metfile w93193 has approximately 6 times higher evaporation than precipitation. Adjustments need to be made to the CA citrus scenario-specific water body to ensure a small, but permanent surface water body is represented.

Comparison of PRZM/EXAMS-Standard Scenario with PRZM/VVWM-Crop Specific Scenario

The impact of using the proposed crop scenario-specific water body size values with the varying volume water body (VVWM-scenario specific) versus the standard water body size parameter values (DA = 10 ha; SA = 1 ha; VC = 20,000 m^3) with the fixed-volume model (EXAMS-standard) was evaluated using a combination of low-rainfall (CA fruit) and high-rainfall (FL sugarcane) crop scenarios with ChemA and ChemB. Simulated daily concentrations and water volume output for the CA fruit and FL sugarcane scenario are provided in Appendix M.

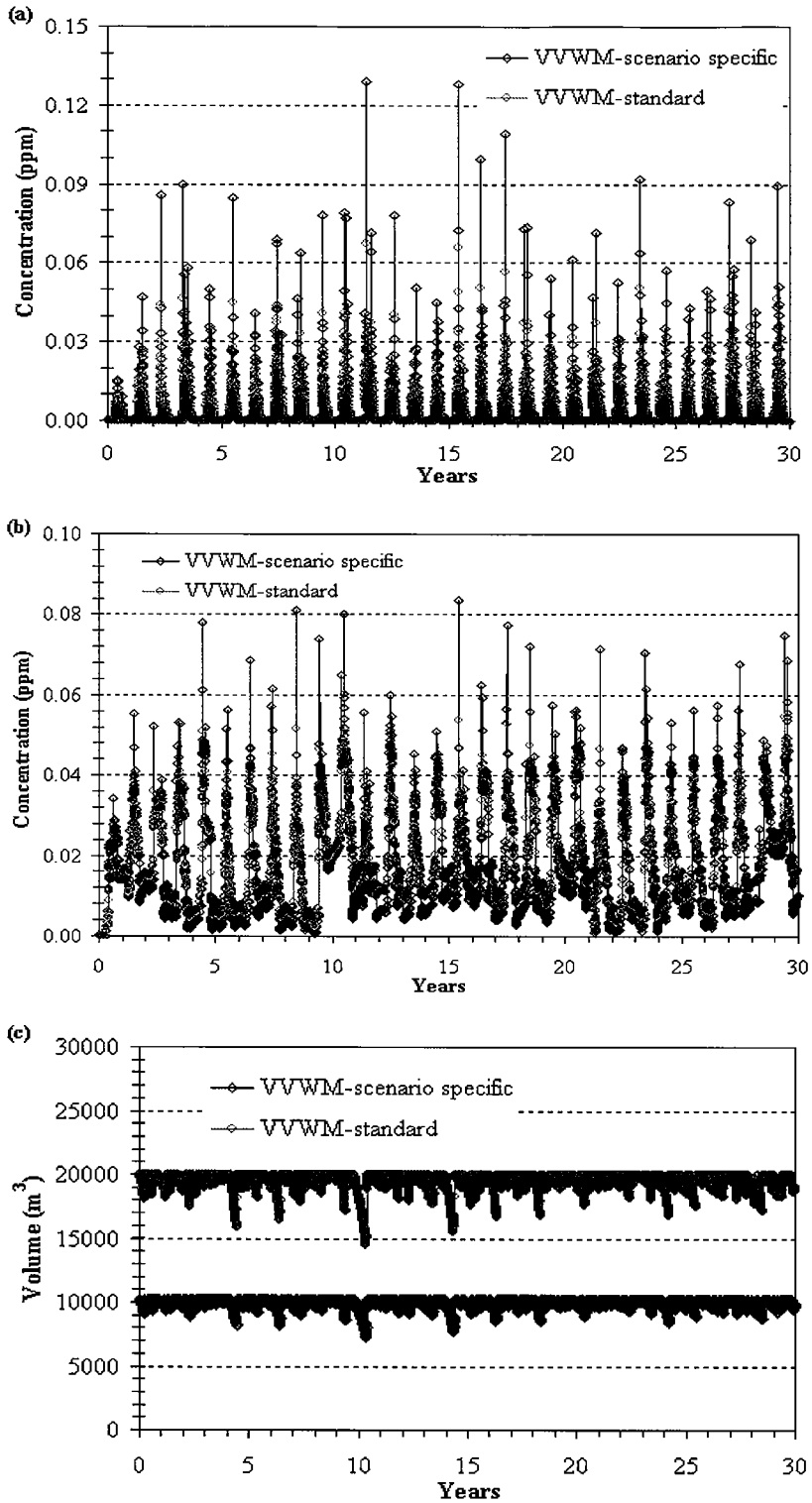


Figure 4-27. Comparison of VVWM using the standard water body conditions, and VVWM using the crop scenario-specific water body conditions for (a) ChemA, (b) ChemB and (c) volume for FL sugarcane.

For the CA fruit scenario, the peak concentrations predicted by the VVWM-crop specific water body model are, often higher than those predicted by the EXAMS-standard. This is reflective of the much higher *DA/VC* ratio used in the scenario-specific model compared to the standard water body scenario, 50 versus 1.5 (see Table 4-17). In the FL sugarcane scenario for short-lived ChemA, the VVWM-scenario specific model predicts higher concentrations than the EXAMS-standard model. This is because the water body volume is smaller in the VVWM-scenario specific model due to the differences in the *DA/VC* ratios and because dissipation due to washout is not a dominant process for short-lived chemicals. Alternatively, for the long-lived ChemB, the EXAMS-standard model predicts much higher concentrations than the VVWM-scenario specific or VVWM-standard models. This is because in the EXAMS-standard model there is no overflow, which is a significant source of dissipation in the varying volume simulations since ChemB is extremely resistant to degradation and the FL sugarcane scenario is characterized by high flow conditions.

Comparison of Daily Surface Water Volume with PRZM Runoff Volume

Minimum, median, and maximum daily run-off volume simulated by PRZM for a 10 ha drainage area for each crop scenario is listed in Table 4-18. The minimum surface water volume and minimum depth that is simulated using the VVWM-crop specific model approach is listed in Table 4-18 for each crop scenario. Maximum run-off volume to maximum surface water volume capacity ranges from 0.22 for the NC apple scenario to 11.4 times for the CA corn scenario. For CA corn, there is at least one rainfall event that replaces the volume in the pond at least 11 times in one day.

Comparison of Proposed Crop Scenario-Specific Water Body Volume with Flowing Waters

As described previously, the volume of the standard surface water body (20,000 m^3) expressed as flow past the field in 24 hours, is equivalent to 8.2 ft^3/sec. The maximum volume capacity and the minimum surface water volume for each crop scenario expressed as an equivalent 24 hour flow past the field is provided in Table 4-18. Under maximum volume conditions represented flow ranges from 0.16 ft^3/sec for the Idaho potato site to 12.5 ft^3/sec for the NC apple and NC corn WC sites. The minimum surface water volume conditions represented as a 24 hour flow ranges from 0.001 ft^3/sec in the CA citrus scenario to 9.9 ft^3/sec in the NC corn WC scenario.

To determine a typical drainage area size for this range of flow, the relationship between drainage area ($miles^2$) and flow rate (ft^3/sec) for U.S. streamflow sites were examined. There are over 1.5 million streamflow sites across the U.S., the District of Columbia, and Puerto Rico that have been monitored by the United States Geological Survey (USGS) (USGS, 2004). In addition to streamflow data, information available for these sites, pertinent to this comparison, include location (i.e., state, latitude, and longitude), drainage area size, and for some sites but not all, elevation. Monthly average daily streamflow values were obtained from the USGS web site for all available locations. The relationship between drainage area (<1000 square miles) and streamflow for a given state during the months of March, April, May, June and August are

Table 4-18. Summary of simulated water volume and depth conditions and runoff volume associated with proposed crop scenario-specific conditions.

Scenario				Simulated Water Body					PRZM Runoff			
				Maximum		Minimum				Volume[i] (m^3)		
Name	Category[a]	County	*DA/VC* Ratio[b] (acre/acre-ft)	Volume[c] (m^3)	24 hr Flow[d] (cfs)	Volume[e] (m^3)	24 hr Flow[f] (cfs)	Depth[g] (m)	N[h]	Min	Median	Max
CA alfalfa	OP, R	San Joaquin	50	609	0.25	225	0.09	0.90	357	1.0	110	2980
CA almond	OP, R	San Joaquin	50	609	0.25	151	0.06	0.60	340	7.0	111	5340
CA citrus	OP, R	Fresno	50	609	0.25	2.5	0.001	0.01	81	0.56	32	2430
CA corn	OP, R	Stanislaus	50	609	0.25	295	0.12	1.18	464	10	200	6920
CA fruit	OP, R	Fresno	50	609	0.25	27.6	0.01	0.11	205	1.0	82	2310
CA grapes	OP, R	San Joaquin	50	609	0.25	17.6	0.007	0.07	198	0.2	90	2500
CA sugar beets	OP, R	Fresno	50	609	0.25	211	0.09	0.84	350	6.0	120	3590
CA tomato	OP, R	San Joaquin	50	609	0.25	211	0.09	0.84	382	1.0	150	3630
FL cabbage	N	Collier	3	10156	4.1	7102	2.9	1.28	897	1.0	500	26400
FL citrus	N	Collier	3	10156	4.1	7099	2.9	1.28	812	0.41	400	25000
FL cucumber	N	Collier	3	10156	4.1	7202	2.9	1.30	921	10	500	26500
FL peppers	N	Collier	3	10156	4.1	7009	2.9	1.26	1023	1.0	800	16000
FL sugarcane	R	Hendry	3	10156	4.1	7309	3.0	1.32	1198	8.0	1000	16000
FL sweet corn	R	Palm Beach	2	15234	6.2	10563	4.3	1.27	1030	9.0	800	16000
FL tomato	N	Collier	3	10156	4.1	7109	2.9	1.28	1033	9.0	800	16000
FL turf	R	Osceola	1	30468	12.5	19062	7.8	1.14	462	1.0	300	9200
GA peaches	N	Peach	3	10156	4.1	3300	1.3	0.59	376	1.0	200	6710
ID potato	R	Bingham	80	381	0.16	217	0.09	1.74	245	1.0	50	1330
IL corn	R	McLean	5	6094	2.5	4882	2.0	1.46	829	0.25	300	12600
KS sorghum	R	Neosha	20	1523	0.62	1204	0.49	1.69	700	8.7	400	8000
LA sugarcane	R	Terrebonne	2	15234	6.2	11735	4.8	1.41	1095	1.0	1000	24700

Scenario				Simulated Water Body					PRZM Runoff			
				Maximum		Minimum				Volume[i] (m^3)		
Name	Category[a]	County	*DA/VC* Ratio[b] (acre/acre-ft)	Volume[c] (m^3)	24 hr Flow[d] (cfs)	Volume[e] (m^3)	24 hr Flow[f] (cfs)	Depth[g] (m)	N[h]	Min	Median	Max
ME potato	N	Aroostook	5	6094	2.5	5397	2.2	1.62	950	0.57	200	13900
MN alfalfa	R	Polk	20	1523	0.62	944	0.39	1.51	313	1.0	110	4900
MN sugar beet	N	Polk	20	1523	0.62	944	0.39	2.90	395	1.0	190	5840
MS corn	R	Tallahatchie	5	6094	2.5	4158	1.7	1.25	814	4.71	430	11900
MS cotton	N	Yazoo	5	6094	2.5	4755	1.9	1.43	1010	7.0	700	15500
MS soybean	R	Yazoo	5	6094	2.5	4416	1.8	1.32	989	0.6	400	11300
NC alfalfa	R	Iredell	2	15234	6.2	12326	5.0	1.48	777	1.0	390	7790
NC apple	R	Henderson	1	30468	12.5	23564	9.6	1.41	655	0.1	300	6730
NC corn EC	R	Pitt	5	6094	2.5	5104	2.1	1.53	884	1.0	300	8780
NC corn WC	R	Henderson	1	30468	12.5	24052	9.8	1.44	853	2.0	370	8200
NC cotton	R	Halifax	5	6094	2.5	5222	2.1	1.57	1088	2.0	300	9610
NC peanut	N	Pitt	5	6094	2.5	4781	2.0	1.43	898	1.0	300	15190
NC tobacco	N	Johnson	5	6094	2.5	4955	2.0	1.49	661	1.0	240	7830
ND corn	R	Pembina	20	1523	0.62	984	0.40	1.57	443	1.0	200	6400
ND wheat	R	Cass	20	1523	0.62	944	0.38	1.51	497	2.0	200	6900
OH corn	N	Darke	5	6094	2.5	5006	2.0	1.75	854	1.0	215	5800
OR apple	R	Marion	2	15234	6.2	9756	4.0	1.17	661	0.27	170	3300
OR berries	N	Marion	2	15234	6.2	10189	4.2	1.22	583	1.0	170	3860
OR filberts	N	Washington	2	15234	6.2	9298	3.8	0.93	743	1.5	200	4600
OR grass seed	OP	Linn	2	15234	6.2	10279	4.2	1.23	605	2.0	151	3910
OR hops	N	Marion	2	15234	6.2	10279	4.2	1.23	696	1.0	200	4300
OR mint	N	Marion	2	15234	6.2	10279	4.2	1.23	756	0.5	200	4600
OR snbeans	N	Marion	2	15234	6.2	10404	4.2	1.25	1505	1.0	300	6200

Scenario				Simulated Water Body					PRZM Runoff			
				Maximum		Minimum				Volume[i] (m^3)		
Name	Category[a]	County	*DA/VC* Ratio[b] (acre/acre-ft)	Volume[c] (m^3)	24 hr Flow[d] (cfs)	Volume[e] (m^3)	24 hr Flow[f] (cfs)	Depth[g] (m)	N[h]	Min	Median	Max
OR swcorn	R	Marion	2	15234	6.2	10304	4.2	1.24	1284	2.0	300	5900
OR wheat	R	Marion	2	15234	6.2	10334	4.2	1.24	880	1.0	200	4600
OR Xmas tree	OP, L	Benton	2	15234	6.2	9100	3.8	0.91	456	1.0	110	3320
PA alfalfa	R	York	3	10156	4.2	7640	3.1	1.38	867	2.0	300	11200
PA apple	R	Lancaster	3	10156	4.2	7604	3.1	1.37	651	1.0	210	10100
PA corn	R	Lancaster	3	10156	4.2	7498	3.1	1.35	515	0.9	220	5090
PA tomato	R	Adams	3	10156	4.2	7640	3.1	1.38	799	2.0	280	11100
PA turf	R	York	3	10156	4.2	7504	3.1	1.35	436	0.1	180	9100
TX alfalfa	OP, R	Milam	12	2539	1.0	1857	0.76	1.56	673	10	400	10800
TX corn	OP, R	Milam	12	2539	1.0	1759	0.72	1.48	712	2.0	400	9800
TX cotton	OP, R	Milam	12	2539	1.0	1744	0.71	1.46	569	2.0	390	8700
TX sorghum	OP, R	Milam	12	2539	1.0	1759	0.72	1.48	701	10	400	9100
TX wheat	OP, R	Travis	20	1523	0.62	1113	0.45	1.78	602	10	400	9900

[a] Crop scenario risk assessment category: N = national; R = regional; OP = OP cumulative; L = local specific

[b] Field area to volume capacity ratio is set to the maximum value of the isopleth where the crop scenario is located in Figure 4-21b.

[c] Initial, V_0, and maximum, VC, volume capacity derived from $VC = DA \div DA/VC$ ratio where DA = 10 ha.

[d] Rough estimate of the flowing waters, represented by these scenario conditions, assuming the initial water body volume (i.e., maximum volume) flowed past the field in 24 hours, Flow (cubic feet per second) = (VC m^3 × 35.315 ft^3/m^3) ÷ (24 hours × 3,600 sec/hour). This is a maximum flow estimate in that the surface water volume decreases seasonally and with long-term drought patterns in the meteorological file.

[e] The minimum volume that the simulated water body reaches using the crop scenario-specific water body values (Table 4-17).

[f] Rough estimate of the flowing waters represented at minimum volume of surface water, assumes the minimum water body volume flows past the field in 24 hours, Flow (cubic feet per second) = (Minimum volume × 35.315 ft^3/m^3) ÷ (24 hours × 3,600 sec/hour).

[g] Minimum surface water depth that the simulated water body reaches. Default programming minimum is 0.01 m.

[h] Number of days with runoff. (Total number of days with and without rainfall--For NC alfalfa, NC apple and NC corn WC (metfile: 03812) there are a total of 9,496 days in a simulation; for all other scenarios there are 10,957 days in a simulation.)

[i] The minimum (Min), median, and maximum (Max) runoff volume predicted by PRZM, given a 10 ha field drainage area, for the designated crop scenario.

presented graphically in Appendix J. Monthly 25th percentile and median mean daily flow rates and the quartile range for these estimates are provided in Appendix K.

6. Summary and Conclusions

While the incorporation of a surface water model, which allows volume to vary according to meteorological and hydrological conditions has the potential to be more reflective of real field conditions and captures seasonal variability, the current standard size and volume conditions are not suitable across all crop scenarios. Crop scenario-specific *DA/VC* ratios and surface water body size conditions reflective of the crop scenario and the level of assessment (national, regional, local) are needed to incorporate a small but permanent varying volume water body into the Level II Exposure model.

Sources of readily available national and regional *DA/VC* ratios and associated size, depth, and volume data for temporary or permanent surface water bodies (e.g., wetlands, pools, and ponds) are very limited and consist essentially of the USDA (1997) guidelines for small, permanent surface waters. There are efforts currently underway to determine *DA/VC* ratios associated with both temporary and permanent small surface water bodies (e.g., wetlands, pools, and ponds), however, this information will not be available, especially on a national or regional basis, in the near future. Options for developing crop scenario-specific field drainage area and surface water body size values using the USDA national/regional *DA/VC* ratio and surface water depth guidelines for small, permanent water supplies were identified. It is preferred that a weighted or distributional approach is used for selecting a crop scenario-specific *DA/VC* ratio and water body depth to reflect its national, regional, or local assessment status, however, the approach has not yet been developed. There is an effort underway to take this type of approach, but in the interim, the *DA/VC* ratio and water body depth values for a given crop scenario will be selected to reflect high-end exposure conditions.

Given a crop scenario-specific DA/VC ratio and water body depth, the options evaluated consisted of a systematic examination of setting surface area, *SA*, maximum volume capacity, *VC* (initial volume, V_0), or field drainage area, *DA*, to its current standard exposure scenario value and calculating the other two values based on the relationship between volume, depth and surface area ($VC = D_{max} \times SA$). The analysis showed that although water body volume is affected by the three options for setting values for drainage area and water body size parameter values (*SA*, *DA*, *VC*), concentration estimates are not influenced once the *DA/VC* ratio and D_{max} (D_0) have been set. Consequently, the proposed approach consists of retaining the standard field area (*DA*) as10 ha for all crop scenarios, and deriving the values for the remaining water body size parameters (*SA*, *VC*) according to the crop scenario-specific *DA/VC* ratio and the D_{max} (Table 4-17).

The analyses performed indicate that the proposed approach is likely to be "high-end" and will not suffer from "drying out", for most crop scenarios. The proposed approach, by retaining the 10 ha field size, does not require additional adjustments to a number of other assumptions to the exposure scenario. Overall, the inclusion of a water body that varies according to hydrologic conditions and a proposed crop scenario-specific water body geometry at Level II is an attempt to

move towards better representation of actual field conditions and should improve aquatic exposure assessments.

For the majority of crop-scenarios, the proposed Level II DA/VC ratios are higher than the national standard used with the fixed-volume model (1.5 acres/acre-ft), which results in higher EECs predicted some of the time for this approach than at Level I. The use of a national standard for the fixed-volume model needs further consideration.

F. Implementation of a Probabilistic Curve Number Method in the PRZM Runoff Model

1. Introduction

The SAP in 2001 recommended that important factors affecting pesticide runoff be considered with regard to their variability among pesticide use sites. Besides the amount of rainfall, the most important factor influencing run-off in EPA's run-off model (PRZM) is the curve number parameter. The curve number method is a frequently misunderstood and possibly misused parameter that was not originally designed for continuous model simulations such as PRZM produces. Thus an investigation of the meaning of the curve number and its effect on model output is a logical place to begin an investigation on the uncertainty and the variability of run-off estimates by PRZM. This section discusses some exploratory work aimed at better characterizing the curve number, which will lead to better characterization of the uncertainty and variability in pesticide runoff estimates.

2. Background

As part of the routine regulatory evaluation of pesticides, the Environmental Protection Agency uses PRZM to estimate pesticide runoff from agricultural fields. PRZM calculates the volume of runoff leaving an agricultural field by the Natural Resources Conservation Service's curve number method (NRCS, 2003). Because the curve number is one of the most sensitive parameters in PRZM, a clear understanding of its origins and its limitations is important in interpreting the meaning of PRZM-generated pesticide transport data.

The curve number method is an empirical runoff estimator, which was developed in the 1940's. It has proved useful because of its simplicity (Ponce and Hawkins, 1996), and in many cases it performs as well as or better than more complex mechanistic runoff models such as those based on Green-Apt infiltration (Wilcox et al., 1990). Although a complete account of the development of the curve number is unavailable (Hjelmfelt, 1991; Ponce and Hawkins, 1996); Rallston and Cronshey (1979) provide some historical insight into its development, and Ponce and Hawkins (1996) made a noteworthy effort at providing a critical review of the method and its limitations and usefulness. The curve number method is "officially" described (although not developed) in the National Soil Conservation Service's National Engineering Handbook (NEH-4) which is undergoing revisions (NRCS, 2003).

The curve number method expresses run-off volume as a function of rainfall volume, hydrologic storage, and initial abstraction as follows:

$$Q = \begin{cases} 0 & \textbf{for } P \le I_a \\ \dfrac{(P - I_a)^2}{P - I_a + S} & \textbf{for } P > I_a \end{cases} \qquad (4\text{-}61)$$

where,

Q = runoff (inches)
P = precipitation (inches)
S = potential retention (inches)
I_a = initial abstraction (inches)

In this equation, the parameter S has been interpreted as representing potential hydrologic storage, or the maximum depth of rainfall that could potentially be abstracted at a site (Ponce and Hawkins, 1996). I_a, which represents the amount of rainfall that does not contribute to runoff, is usually assumed to be equal to 0.2S in order to simplify the equation and eliminate one variable. Thus, equation 4-61 is normally presented as

$$Q = \begin{cases} 0 & \textbf{for } P \leq 0.2S \\ \dfrac{(P - 0.2S)^2}{P + 0.8S} & \textbf{for } P > 0.2S \end{cases} \tag{4-62}$$

In this case, S becomes the single parameter that characterizes the runoff behavior at a site. By definition, S can assume any value from zero to infinity. In order to provide a more convenient parameter than S, NRCS devised the curve number, which is a transform for S that varies from zero to 100:

$$S = \frac{1000}{CN} - 10 \tag{4-63}$$

where,

CN = curve number [unitless].

NRCS has tabulated curve numbers for various types of fields, as shown in Table 4-19. The original rainfall-runoff data sets used for development of the curve number table corresponded to the annual flood series at multiple sites with similar characteristics. The annual maximum data from sites with similar soils and coverage were plotted as runoff versus rainfall, and the curve number that divided the data into two equal parts was taken as the median curve number, and was designated as CN_{II} (Ponce and Hawkins, 1996). The scatter around the plots represents the natural variability of the runoff characteristics and includes both inter-site and intra-site variability. In the original work, it was recognized that there was considerable variability in the curve number, and that even a single watershed may be characterized by different curve numbers from one event to the next. To account for the variability, an upper curve number (CN_{III}) and a lower curve number (CN_I) were associated with each average curve number (CN_{II}), as shown in Table 4-20. The records of the reasoning for how CN_I and CN_{III} were actually derived have apparently been lost (Hawkins, 1978). Curve number developers assumed that some antecedent field condition caused the variability; thus, the subscripts on the

Table 4-19. Runoff Curve Numbers for soil cover complexes and soil groups (Antecedent Runoff Condition II and $I_a = 0.2$)

Land Use	Treatment or Practice	Hydrologic Condition	Soil Group			
			A	B	C	D
Fallow Row Crops	Straight Row	---	77	86	91	94
	Straight Row	Poor	72	81	88	91
	Straight Row	Good	67	78	85	89
	Contoured	Poor	70	79	84	88
	Contoured	Good	65	75	82	86
	Contoured and terraced	Poor	66	74	80	82
	Contoured and terraced	Good	62	71	78	81
Small Grain	Straight row	Poor	65	76	84	88
	Straight row	Good	63	75	83	87
	Contoured	Poor	63	74	83	87
	Contoured	Good	61	73	81	84
	Contoured and terraced	Poor	61	72	79	82
	Contoured and terraced	Good	59	70	78	81
Close-seeded legumes or rotation meadow	Straight row	Poor	66	77	85	89
	Straight row	Good	58	72	81	85
	Contoured	Poor	64	75	83	85
	Contoured	Good	55	69	78	83
	Contoured and terraced	Poor	63	73	80	83
	Contoured and terraced	Good	51	67	76	80
Pasture or Range		Poor	68	79	86	89
		Fair	49	69	79	84
		Good	39	61	74	80
	Contoured	Poor	47	67	81	88
	Contoured	Fair	25	59	75	83
	Contoured	Good	6	35	70	79
Meadow		Good	30	58	71	78
Woods		Poor	45	66	77	83
		Fair	36	60	73	79
		Good	25	55	70	77
Farmsteads		----	59	74	82	86
Roads (dirt) (hard surface)		----	72	82	87	89
		----	74	84	90	92

Table 4-20. Relationship of CN_I CN_{II} and CN_{III}

CN_I	CN_{II}	CN_{III}
100	100	100
87	95	98
78	90	96
70	85	94
63	80	91
57	75	88
51	70	85
45	65	82
40	60	78
35	55	74
31	50	70
26	45	65
22	40	60

curve number are typically referred to as *antecedent runoff condition* (ARC) I, II, or III, or dry, average, or wet conditions, respectively.

The current NEH-4 does not give guidance on selecting the antecedent runoff condition. Curve number users, however, have historically associated the three curve numbers with soil moisture or one of its surrogates (e.g., 5-day antecedent rainfall), even though the original data was not characterized by soil moisture content. Subsequent work has challenged the concept that parameters such as soil moisture or antecedent rainfall are useful predictors of the antecedent runoff condition. Antecedent moisture (or antecedent rainfall) does not account for all of the variability in runoff, and in many cases appears not even to be an important predictor of runoff volume in response to rainfall (Hjelmfelt, 1983; Cronshey, 1983). Specific causes of variations from storm to storm may include seasonal changes in watershed characteristics, temporal and spatial variability in rainfall volume and intensity, temperature and other meteorological effects, physical changes to the field (e.g., tractor tracks, root channels), as well as soil moisture. Because of the combined effect of these and many other unknown factors influencing runoff, single-factor (e.g., moisture) curve number adjustments may be ineffective. For example Kottegoda et al. (2000; see Figure 5 in Kottegoda et al.) showed that the curve number calculated for a basin varies considerably, and has no apparent relationship with antecedent rainfall. In another study, Hawkins (personal communication, 2001) looked at the influence of rainfall intensity, storm distribution, storm duration, and antecedent rainfall on curve numbers and found that none were consistent predictors of curve number variability. For these reasons NEH-4 revision will not include references to antecedent moisture (Hjelmfelt et al., 2001).

3. Probabilistic Treatments of Curve Number

Because of the variability in curve number and because of the difficulties in relating the variability to some causative mechanism, probabilistic treatments of curve number have been proposed (McCuen, 2002; Yulianti and Lence, 1999; Gray et al., 1982; Hjelmfelt et al., 1982; Hjelmfelt, 1991; and Hawkins et al., 1985). A workgroup formed to revise NEH-4 has agreed to incorporate variability in the approach by considering curve number to be a random variable (Hjfelmfelt et al., 2001; van Mullem et al., 2002).

In characterizing the curve number as a random variable, Hjemfelt (1991) and Hawkins et al. (1985) showed that CN_I and CN_{III} can be interpreted as representing the 90^{th} percentile and 10^{th} percentile exceedence probabilities of runoff depth for a given depth of rainfall, while CN_{II} represents the 50^{th} percentile. Hjelmfelt (1991) looked at the 10^{th} and 90^{th} runoff percentiles from 14 watersheds and found that the curve numbers for these events were in good agreement with the CN_I and CN_{III} values, when the CN_{II} values were taken from the 50^{th} percentile. Figure 4-28 is a reproduction of the data from Hjelmfelt (1991) showing that the 10^{th} and 90^{th} percentile runoff exceedences are well characterized by ARC I and III. It should be recognized that these data represent only maximum annual runoff events, and thus do not necessarily represent the variability that would be manifested by an analysis of all events (as in a continuous model discussed below).

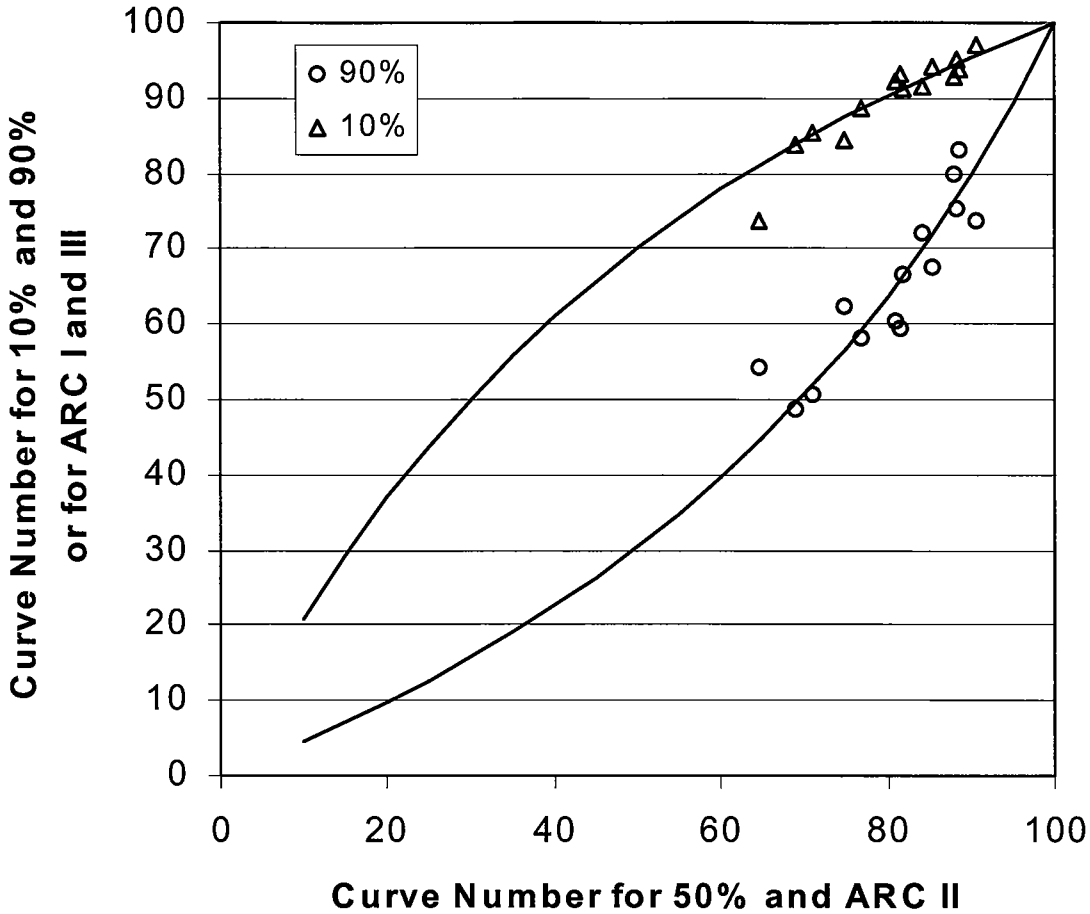


Figure 4-28. Plot of the curve numbers that represent the 10th and 90th percentile exceedence frequencies for 14 watersheds as presented by Hjelmfelt (1991). Rankings were based on the maximum annual events. Lines represent the ARC I and III curve numbers as given in NEH-4.

Since ARC I, II and III appear to be good representations of the 90, 50, and 10 percent cumulative probabilities of the runoff depth for a given rainfall, Hawkins et al. (1985) found that the quantity I_a/S_{II} could be described by a log-normal distribution, with a (natural log space) mean of -1.609 and a standard distribution of 0.67. This is related to the fact that Prob($Q/S_{II}>0$) vs. P/S_{II} for ARC I, II, and III can be fit to a log-normal distribution with these parameters. Thus, instead of treating I_a as a constant fraction of S_{II} (see equation 4-62) and all the variability in possible runoff at a site as embodied in S, the variability in runoff can alternatively be treated as being embodied in variable I_a, with S rather than Ia/S treated as a constant (equal to what is usually thought of as S_{II}). This makes physical sense if S is considered to be an inherent field characteristic (e.g., reflecting the field's average run-off condition), and I_a a surrogate for all potential sources of variability in the amount of rainfall that is not available for runoff (e.g., soil moisture, rain intensity, physical field changes). The idea of randomly choosing an initial abstraction from a distribution will be explored below with regards to implementation in PRZM.

In an application of the random curve number concept, Yulianti and Lence (1999) implemented a variation of a probabilistic curve number procedure. Curve numbers were randomly generated by selecting the inverse of the curve number from a normal distribution in which $1/CN_I$ and $1/CN_{III}$ define the 99.5 percent confidence interval of a mean inverse curve number(S) from a normal distribution. The application was for design storms, which is consistent with the way the curve number was developed.

4. Continuous Simulation Modeling With the Curve Number

The curve number method was derived based upon examination of annual flood event data, and thus is probably most properly used in designs involving single high runoff events (Cronshey, 1983). Contrary to the original design purpose of the curve number, a number of continuous simulation models that use the curve number have been developed, including GLEAMS (Knisel et al. 1994), SWAT (Neitsch et al., 2002), and PRZM (Carsel et al., 1997). Use of the curve number in a continuous simulation mode raises important questions regarding how to define rainfall events, how to define the antecedent conditions, and how to apply the method to precipitation events with much higher than annual return frequency.

Continuous simulation models use the curve number method to process time series of precipitation and generate corresponding time series estimates of run-off. In order to do this, an arbitrary duration of rainfall is typically assumed, corresponding to the time discretization of the model. In the case of PRZM, a rainfall event is defined as the sum of all rainfall that occurs during a calendar day (*i.e.*, from midnight of one day to midnight of the next). Thus, a rainfall that spans 2 days, for example, would be defined as two separate events, and each event would be associated with a different curve number depending on the antecedent condition (described in more detail below). Although widely used in this fashion, the performance of the curve number method in simulating daily runoff has not been extensively investigated.

Because events are discretized into arbitrary 24-hour time units, an antecedent condition must be defined at the start of each new interval. In the case of PRZM, this may cause

conceptual difficulties. For example, PRZM resets soil moisture at the beginning of each time step to field capacity, regardless of how much rain has fallen the previous day. Since PRZM modifies curve numbers based upon soil moisture at the start of each time step, curve numbers could conceivably be underestimated on days in which rain occurred on the previous day. Another issue with continuous simulation models is how well the curve number works for low rainfall events. The curve number was developed based on annual maximum rainfall/runoff events, and rainfall runoff events may not follow the curve number relationship for the full span of possible rainfalls (Hawkins et al., 1985; Hjelmfelt et al., 2001). The variability embodied in CN_I and CN_{III} may also only apply to the high runoff events, and variability in smaller events may be considerably higher, as speculated by McCuen (2002).

In using a continuous curve number method, all these issues should be considered when interpreting the results. The curve number may not provide precise estimates of runoff, but if uncertainty is addressed in the model, more meaningful interpretations could be made. One way to achieve this result is to incorporate the curve number as a random variable that perhaps could be defined by distributions previously described; however, these distributions have not been explored in the context of continuous simulation models. In the work that follows, an attempt has been made to address some of this uncertainty using a modified version of the PRZM model.

5. The PRZM 3.12 Method of Curve Number Implementation

PRZM is the standard model that EPA uses for estimating the amount of pesticide that may be transported in run-off from an agricultural field. PRZM is a continuous simulation model that uses daily weather data to calculate soil moisture and predict run-off (and hence pesticide loading). Soil moisture is calculated on a daily basis and the daily curve number is accordingly adjusted. The current PRZM 3.12 documentation incorrectly states that algorithms used to make curve number adjustments are from Haith and Loehr (1979), as an examination of the PRZM 3.12 code has revealed. There is no indication within the code as to why the PRZM 3.12 code differs from its description in the documentation and no references supporting the PRZM 3.12 method of curve number adjustments (described below) have been found. This does not mean that the PRZM 3.12 method is inappropriate since there is no "correct" or proven method for curve number adjustments and NRCS leaves curve number adjustments to "best professional judgment".

In PRZM 3.12, the curve number under average antecedent runoff conditions (CN_{II}) is a user input, and PRZM determines the low and high antecedent runoff condition curve numbers (CN_I and CN_{III}, respectively) from standard NRCS tables. PRZM calculates the average soil moisture in the top 10 cm of soil at the beginning of the day to make adjustment to the curve number for use during that day. PRZM makes the following definitions: CN_I occurs when soil moisture content is zero; CN_{II} occurs at the mean of the field capacity and wilting point; and CN_{III} occurs when soil moisture equals field capacity plus wilting point. When the PRZM-calculated soil moisture falls between these values, PRZM uses linear interpolation to arrive at a curve number. It is worth noting that because PRZM, which operates on a daily time step, drains the soil moisture to a maximum of field capacity at the end of each day, the maximum soil

moisture at the time PRZM calculates the curve number is field capacity. Thus CN_{III} is never reached in the model. A graphical presentation of the curve number and soil-moisture relationship is shown in Figure 4-29 (in comparison, SWAT (Neitsch et al., 2002) sets CN_{III} at field capacity, sets CN_I at the wilting point, and sets CN_{II} to 99 at soil saturation, allowing for a much greater span of curve numbers to be used).

Since PRZM assumes a relationship between soil moisture and curve number (see Figure 4-29), an examination of the effectiveness of this relationship may be insightful. There are many data sets that include rainfall and run-off, but surprisingly few include soil moisture measurements at or near the time of rain events. In one such test, Wauchope et al. (1999) performed runoff tests using artificial precipitation on 624-m^2 plots and measured the soil moisture prior to the simulated rain event as well as the associated run-off. Each of the rain events was approximately 2 inches and lasted 2 hours. The curve numbers for each of the events given by Wauchope et al. (1999) are potted as a function of soil moisture in Figure 4-30. The figure shows that there is no obvious relationship between curve number and soil moisture for this data set. Figure 4-30 also shows the curve numbers that would be estimated from a PRZM-type relationship. To generate the PRZM relationship in the figure, the CN_{II} value was assumed to be the median of the values calculated from the data (75.7). The field capacity and wilting point for the site were 0.043 and 0.099 (volume fraction), respectively, as given by Wauchope et al. (1999). It is clear from the figure that the variability in the curve numbers can not be explained by soil moisture variations. At least for this data set, PRZM-type soil moisture/curve number relations do not appear to improve the predictive ability of the model. Young et al. (2002) showed that the runoff data of Wauchope et al. (1999) could be represented as well or better with a constant curve number than with the PRZM curve-number/soil-moisture relationship. The runoff experiments of Wauchope et al. (1999) were conducted on relatively homogeneous small plots with rainfall events of constant duration and intensity. Yet even under these very controlled conditions, curve number variability is great. For larger spatial scales with natural rain events, the variability in curve number may be still higher. An example of curve number variability at the basin scale as a function of antecedent precipitation was shown by Kottegotada et al.(2000).

a. Incorporation of a Probabilistic Curve Number into PRZM

Because of the difficulties associated with the implementation of a causative mechanism to vary curve number (e.g., soil moisture), the PRZM 3.12 code was modified to incorporate a probabilistic interpretation of the curve number. Modifications were made to PRZM in the subroutine HYDROL. All correlations of curve number with soil moisture were removed from the code. Instead, curve numbers for any given day were determined by a random selection process. In this random selection, S is treated as having a constant value equal to S_{II} (as determined from the PRZM input), and I_a/S is assumed to have a log-normal distribution, as proposed by Hawkins et al. (1985). The mean of the $\ln(I_a/S)$ distribution is $\mu = -1.609$, and the standard distribution is 0.67, as derived by Hawkins et al. (1985) by assuming that CN_I, CN_{II} and CN_{III} represented the 10^{th}, 50^{th}, and 90^{th} percentile runoff curve numbers, respectively. There are, of course, alternative means of generating random curve numbers, by varying S for example, and

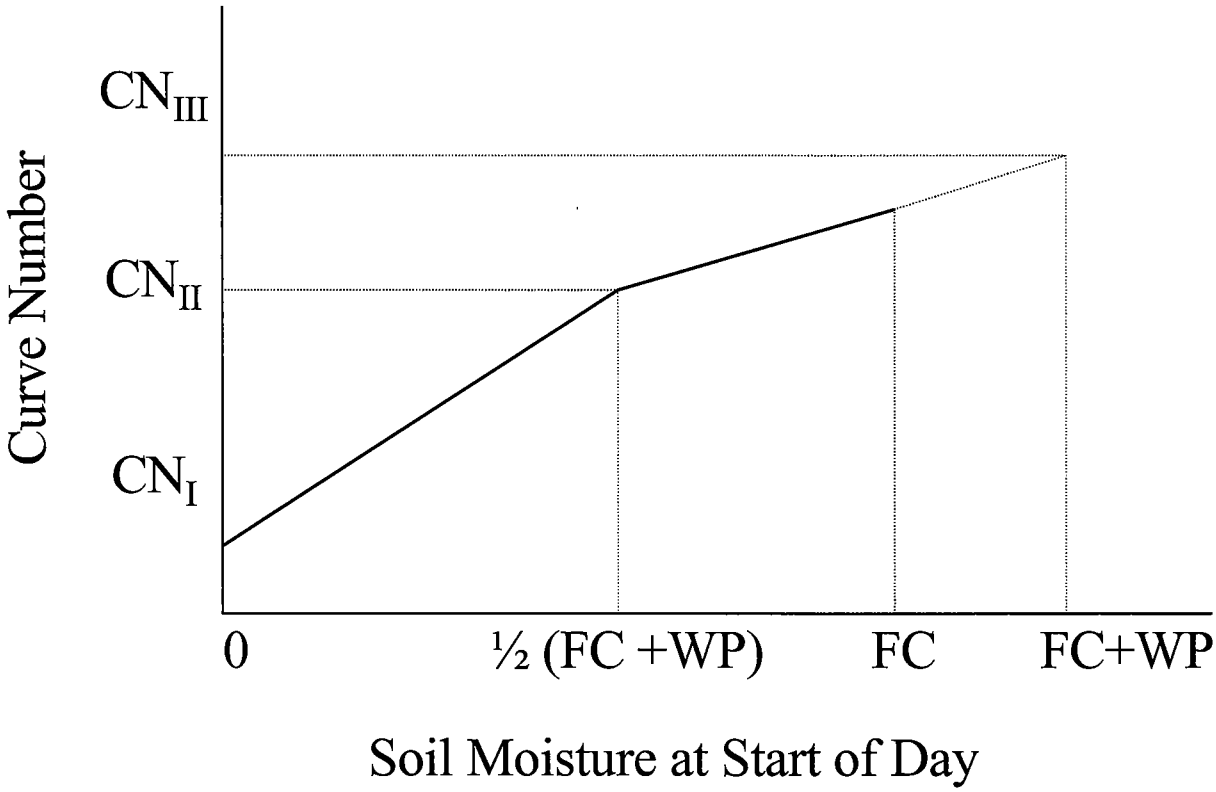


Figure 4-29. PRZM's relationship of curve number to soil moisture. FC is field capacity, and WP is wilting point. The maximum possible is at field capacity; the dotted line extending past field capacity is for referencing the relationships only.

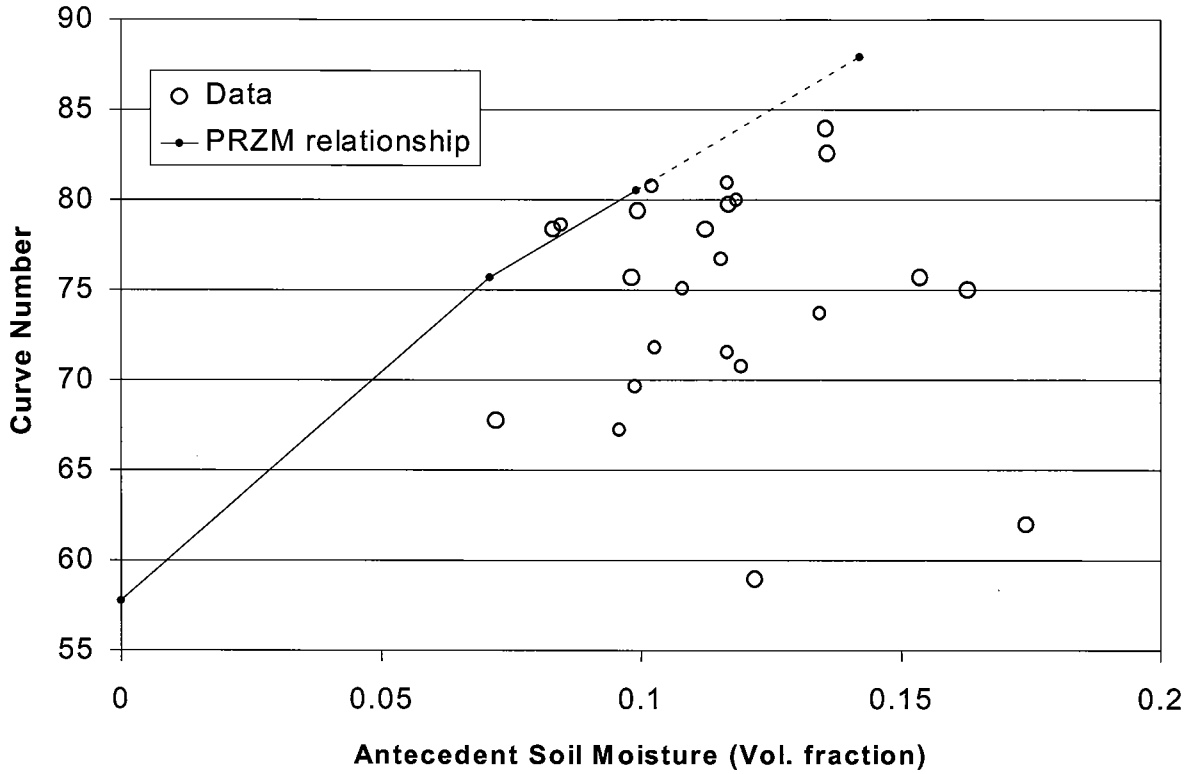


Figure 4-30. Curve numbers implied by the data of Wauchope et al. (1999) plotted as a function of soil moisture. Also shown is the curve number relationship as formulated in PRZM code. The dotted portion of the line represents a moisture content that PRZM does actually simulate (i.e., above field capacity).

these methods should also be investigated. For this initial work, however, only the random generation of I_a is explored.

In each iteration for a single-day, random selections of I_a/S are made with an IMSL (Visual Numerics, Inc.) routine (rnnof), such that the value for any day is calculated as:

$$\ln(I_a / S) = \mu_1 + R_N \sigma_1 \tag{4-64}$$

where,

R_N = a random normal number determined from an IMSL routine
σ_1 = the standard deviation in ln space = 0.67
μ_1 = the mean in ln space = -1.609

In order to minimize PRZM code changes, a PRZM-equivalent curve number (i.e., one that would give an equal amount of run-off) is determined for this randomly generated I_a and simply substituted in the code. The equivalent curve number is determined first by multiplying I_a/S (from equation 4-64) by the constant S (from input curve number). This gives the day's value for I_a. This I_a value along with the day's precipitation are substituted into the following modified version of equation 4-62 to yield the day's runoff value, Q:

$$Q = \begin{cases} 0 & \textbf{for } P \le Ia \\ \dfrac{(P - Ia)^2}{P + 4Ia} & \textbf{for } P > Ia \end{cases} \tag{4-65}$$

An equivalent value for S (designated S_e here) is then calculated from P and Q via the following rearrangement of equation 4-62:

$$S_e = 5[P + 2Q - (4Q^2 + 5PQ)^{1/2}] \tag{4-66}$$

This value is transformed into an equivalent curve number (CN_e) for the day via a rearrangement of equation 4-63, for use in the modified PRZM:

$$CN_e = \frac{1000}{10 + S_e} \tag{4-68}$$

b. Example Implementation

An arbitrarily selected 12 year rainfall/run-off data set was obtained from the USDA ARS website (http://hydrolab.arsusda.gov) for evaluation of the proposed modeling approach. The data set is from watershed "W-6", a 1.75 acre watershed in Cherokee, Oklahoma. The precipitation and runoff data were aggregated into 24 hour total depths, based on a nominal calendar day (midnight to midnight) summing period. The daily precipitation totals were saved in a text file formatted as a meteorological input data file to be read by PRZM. Starting with an initial guess, the value used for CN_{II} was adjusted and the model was rerun in an iterative fashion until the difference between measured and modeled total runoff was minimal. This CN_{II} that provided the best match between measured and modeled total runoff was 83.

Figure 4-31 shows the actual (calculated) curve numbers for each event in the field data, and compares them with results from the probabilistic curve number approach (four iterations) as well as PRZM 3.12 output. As the figure demonstrates, the probabilistically generated numbers appear to capture the scatter in the field data better than the deterministic interpretation implemented in PRZM 3.12. Figure 4-32 presents the same data as a function of the soil moisture that PRZM used to vary its curve numbers. Field data were not included in Figure 4-32 because actual field-measured moisture values were not available. Plotting the field data against calculated soil moisture could distort the actual relationship.

Figure 4-33 shows a comparison between daily measured run-off and run-off predicted by PRZM 3.12 using a CN_{II} of 83. The ARC lines are also shown to give an idea of the distribution that will be accounted for by a random curve number method. The PRZM-predicted variability is much less than the variability seen in the measured values. Lower rainfalls have much greater relative variability than higher rains. Runoff from higher rains is estimated reasonably well in terms of magnitude, but variability in the measured data is still much larger than that predicted by PRZM. On the other hand, the ARC lines appear to capture the variability quite well at high rainfall volumes. However, in general the ARC lines do not appear to represent the measured run-off in terms of either absolute magnitude or variability. The implication is that run-off from small rain events in particular is not well captured by the curve number method for this data set.

Capturing small rain events with the curve number method may prove to be a difficult challenge. The form of the curve number may actually be incapable of simulating the full range of rainfall events in a continuous model, as Figure 4-33 seems to show. This analysis examined only one small watershed, and other watersheds with larger sizes and in other regions of the country may be required to make broad conclusions. A probabilistic curve number method for this watershed, however, does appear to capture the variability better than the deterministic interpretation that PRZM uses, and may provide one avenue for capturing a least part of the natural variability in rainfall runoff relationships.

6. Summary and Conclusions

Curve numbers are perhaps best treated as random variables. One way to address the variability is to associate ARC I, II, and III with the curve numbers that produce the 10^{th}, 50^{th}, and 90^{th} percentile run-off volumes for a given volume of rainfall. This conceptualization appears to be consistent with the origins of the curve number approach, although, it is not certain if this conceptualization can adequately characterize the variability in continuously modeled systems. There has been little analysis of curve number variability over the full range of potential rain events, especially at lower rainfall levels and additional research is needed to address this question. However, use of the distributions discussed could at least partially address the variability in rainfall-runoff relationships while still operating within the framework of the curve number approach. Preliminary work shows that there is more variability in rainfall run-off relationships than is currently addressed by PRZM. Clearly, further exploration needs to be persued before any definitive conclusions are reached.

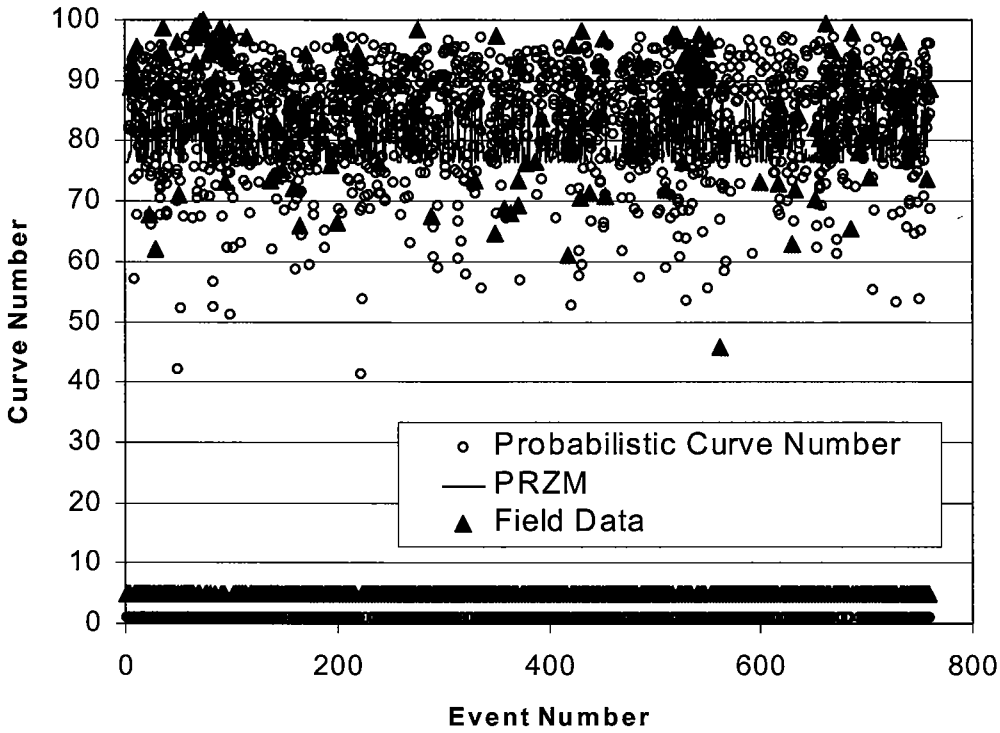


Figure 4-31. A comparison of curve numbers derived from field data with those generated by the probabilistic curve number and those generated by PRZM. The probabilistic curve numbers only show 4 iterations in order to reduce clutter on the figure (and thus the presented distribution is not well developed but does give an idea of the probabilistically modeled scatter). The probabilistic curve number values and the field data values at the bottom of the graph represent events in which I_a was too high to produce runoff and thus curve number is undefined for these points.

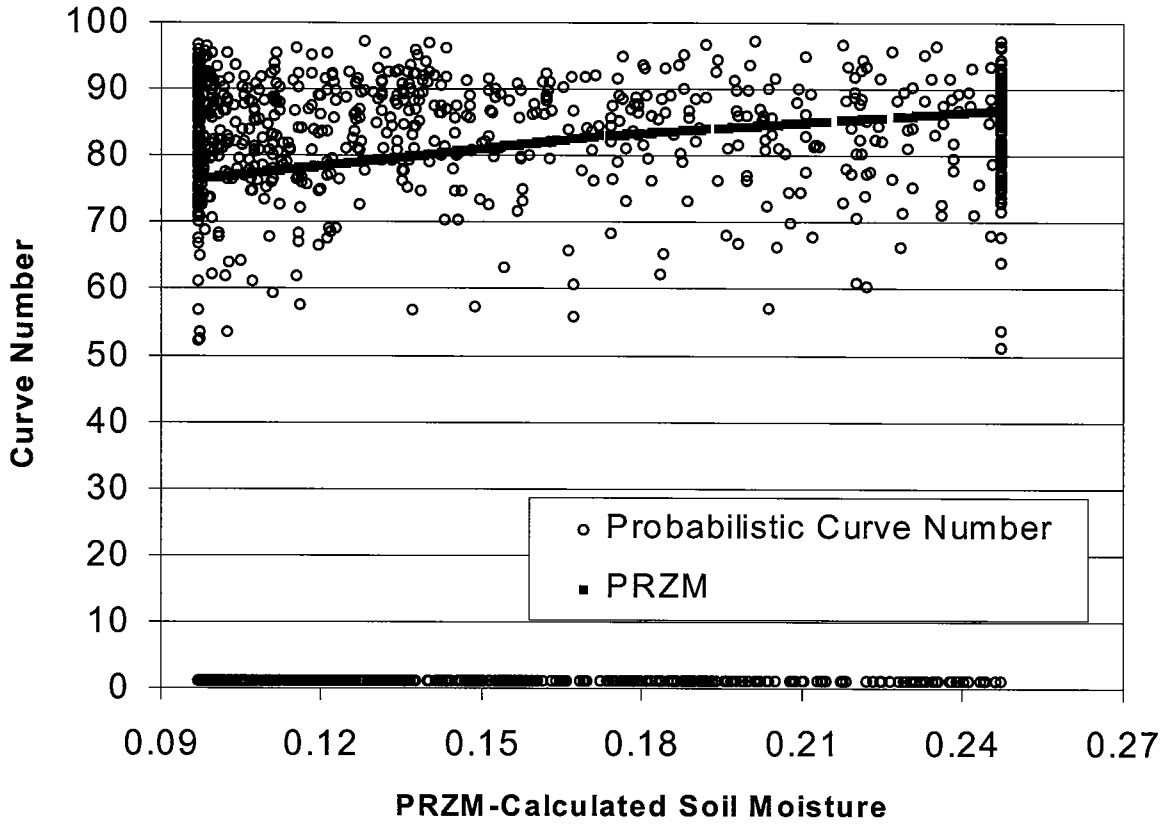


Figure 4-32. Curve numbers generated probabilistically and by PRZM shown as a function of soil moisture. (Probabilistic values have no intrinsic correlation to soil moisture). The probabilistic curve number values at the bottom of the graph represent events in which I_a was too high to produce runoff and thus curve number is undefined for these points.

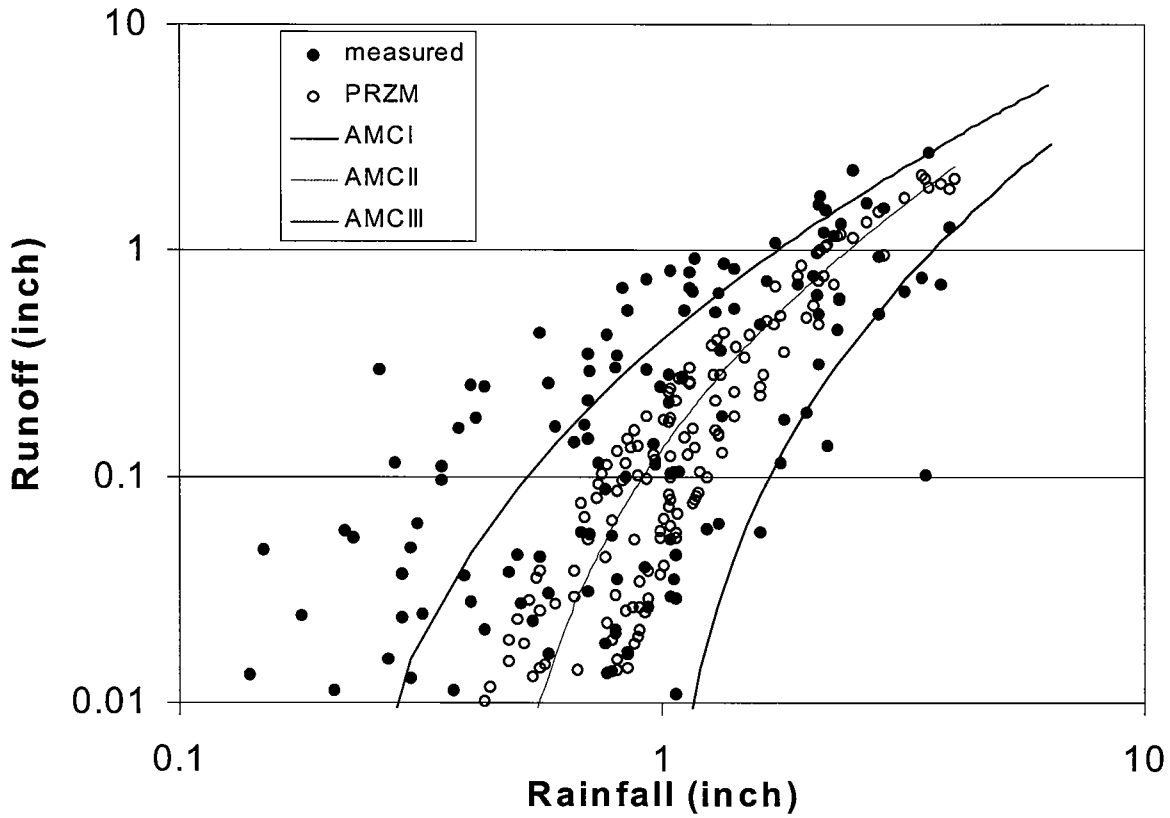


Figure 4-33. A depiction of the runoff/rainfall relationship of the measured field data and PRZM 3.12 simulated values. The ARC lines represent the distribution (10, 50, and 90%) that would occur for the probabilistic curve number model.