UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF
PREVENTION, PESTICIDES, AND
TOXIC SUBSTANCES

May 8, 2007

MEMORANDUM

SUBJECT: Guidance for Tier I Estimation of Aqueous Pesticide Concentrations in Rice Paddies

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On October 29, 2002, a memorandum describing the Interim Rice Model was issued to the Division. After four years of experience in using this interim model, the Water Quality Tech Team and Division scientists found that the screening-level model estimates are conservative and correlate well with monitoring data. Based on this extensive experience and on further evaluation of the Interim Rice Model, members of the WQTT have finalized this model, which is now called the Tier I Rice Model v1.0.

The Tier I Rice Model v1.0 is based on the same basic formula and parameters as the Interim Rice Model with the exception of the organic carbon content of sediment (f_{oc}), which was lowered from 0.02 to 0.01. This update results in exposure estimates of the Tier I Rice Model v1.0 that range from 1-2 times those of the Interim Rice Model as K_{oc} values range from low to high for compounds whose sorption K_d values correlate with soil organic matter content.

Attached to this memorandum is guidance for using the Tier I Rice Model v1.0 along with a description of the development, parameterization, and evaluation of the model. As of May 8, 2007, this model and the attached guidance should be used to estimate pesticide concentrations in rice paddies. If you have any questions concerning this model, please contact the current Water Quality Tech Team co-chairs.

Attachment: Tier I Rice Model v1.0 for Estimating Pesticide Concentrations in Rice Paddies (May 8, 2007)

Tier I Rice Model v1.0 for Estimating Pesticide Concentrations in Rice Paddies

May 8, 2007

I. Introduction

This document describes a Tier I Rice Model (Version 1.0) for estimating surface water exposure from the use of pesticides in rice paddies. This screening-level model is based on the Interim Rice Model, which has been used in EFED for four years to estimate pesticide concentrations in rice paddies. The single, screening-level concentration calculated with this model represents both short and long term surface water exposure and can be used for both aquatic ecological risk assessments and drinking water exposure assessments for human health risk assessment. The formula of the Tier I Rice Model v1.0 is as follows:

$$C_w = \frac{m_{ai}'}{0.00105 + 0.00013 K_d}$$

and, if appropriate:

$$K_d = 0.01 K_{oc}$$

where:

C_w = water concentration [µg/L]
m_{ai}' = mass applied per unit area [kg/ha]
K_d = water-sediment partitioning coefficient [L/kg]
K_{oc} = organic carbon partitioning coefficient [L/kg]

II. The Conceptual Model

The Tier I Rice Model v1.0 relies on an equilibrium partitioning concept to provide conservative estimates of environmental concentrations resulting from application of pesticides to rice paddies. When a pesticide is applied to a rice paddy, the model assumes that it will instantaneously partition between a water phase and a sediment phase. The aqueous concentration that results from such partitioning is described as follows:

$$C_w = \frac{m_{ai}}{V_w + m_{sed} K_d} \qquad (1)$$

where: C_w = water concentration [mass/volume]
m_{ai} = mass of active ingredient applied to paddy [mass]
V_w = volume of water column plus pore water [volume]
m_{sed} = mass of sediment at equilibrium with water column [mass]
K_d = water-sediment partitioning coefficient [volume/mass]

Note that neither the degradation of the pesticide nor the mass transfer from the aqueous phase to the sediment is considered in this conceptualization, which greatly simplifies the model. The absence of degradation adds conservatism to the model (*i.e.*, estimated concentrations should be higher than those usually found in rice paddies). The absence of mass transfer processes can either add or reduce conservatism depending on numerous conditions such as whether the pesticide is soil or water applied and whether actual degradation occurs preferentially in the sediment or the water compartment; however, consideration of this parameter is a refinement beyond a Tier I conceptualization.

Because it is more customary to describe a rice paddy in terms of depth rather than in terms of volume and mass, the following equations are defined:

$$m_{sed} = d_{sed} A \rho_b \tag{2}$$

$$V_w = d_w A + d_{sed} \theta_{sed} A \tag{3}$$

where: d_{sed} = sediment depth [length]
d_w = water column depth [length]
A = area of the rice paddy [area]
θ_{sed} = porosity of sediment [–]
ρ_b = bulk density of sediment [mass/volume]

Further, the input mass per unit area is defined as:

$$m_{ai}' = \frac{m_{ai}}{A} \tag{4}$$

where: m_{ai}' = mass applied per unit area [mass/area]

Substitution of equations (2), (3), and (4) into (1) produces the conceptual model with commonly understood parameters:

$$C_w = \frac{m_{ai}'}{d_w + d_{sed}\left(\theta_{sed} + \rho_b K_d\right)} \tag{5}$$

III. Parameterization

The physical parameter values that describe the rice paddy for the Tier I Rice Model v1.0 represent a reasonably conservative system and are summarized in Table 1. The selection of these values was based to a large extent on typical properties of rice paddies. In some cases where such information was not available (*e.g.*, sediment depth), the parameter values were calibrated from field data. The rationale for choosing these values is described in Sections III A, B, and C of this document.

Table 1. Physical Values of the Tier I Rice Model v1.0.

Parameter	**Symbol**	**Value**	**Reference**
Water column depth	d_w	0.10 m	USDA (1998, 2002)
Sediment depth	d_{sed}	0.01 m	Calibration described in Section III C of this document.
Organic content of sediment	f_{oc}	0.01	Justification provided in Section III B of this document.
Sediment bulk density	ρ_b	1300 kg/m^3	Brady (1984), Hillel (1982)
Grain density	ρ_g	2650 kg/m^3	Density of quartz, typical assumption; Brady(1984), Hillel (1982)
Sediment porosity	θ_{sed}	0.509	$\theta_{sed} = 1 - (\rho_b/\rho_g)$

A. Water Depth, Bulk Density, Porosity

The water column depth (d_w) of 10 cm is a typical average rice paddy water depth at the time of flood release (USDA, 1998; 2002). Bulk density is assumed to be roughly the same as agricultural soils (Brady, 1984; Hillel, 1982). Grain density is assumed to be that of quartz (2.65 g/ml), and thus the porosity of the sediment is 0.509 (see relationship in Table 1).

B. Organic Carbon Content

The organic carbon content (f_{oc}) represents the mean of the organic carbon content in sediments taken from 15 rice fields (see Table 2). These sediments are described in 17 studies submitted in support of the registration of rice pesticides, and are assumed to be typical for rice paddies. Thirteen of the rice fields are located in the southeastern U.S. and two are located in California. The mean organic carbon content of the sediment in these 15 rice fields is 0.01.

The Interim Rice Model assumes an organic carbon content of 0.02. Interim Rice Model exposure estimates are compared with those of the Tier I Rice Model v1.0 for applications of 1 kg/ha of compounds of differing K_{oc} to show how the exposure estimates are affected by the different modeled organic carbon contents (Appendix II). The Tier I Rice Model v1.0 exposure estimates are approximately twice those of the Interim Rice Model for compounds that have a K_{oc}>100,000. As compounds of decreasing K_{oc} are modeled, partitioning to sediment becomes a less important dissipation process and Tier I Rice Model v1.0 exposure estimates approach those of the Interim Rice Model.

C. Water Calibration of Sediment Depth

The sediment interaction depth (d_{sed}) was estimated by calibration using direct paddy measurements from 15 sites in 17 studies. The results of these studies are summarized in Table 2. The maximum observed concentration was that of the overlying water at any time after application. The application rate was the total amount of pesticide applied during the study. Multiple pesticide applications were typically made within one season in these studies. During a multiple application study, no attempt was made to associate concentration measurements with any particular application. Thus, there are cases where the highest concentration was observed prior to the final application. This situation is consistent with the Tier 1 model concept in which the timing of a measurement is not a consideration. Also consistent with the Tier 1 concept is the lack of differentiation among various application methods such as applications prior to flooding.

Table 2. Summary of Studies Used for Calibration of Sediment Interaction Depth.

Site	Chemical	K_{oc} (L/kg)	OC %	~Depth (cm)	Application (kg/ha)	Observed Maximum (ppb)	Reference/ MRID
TX	Iprodione	426	0.5	2	1.12	489	43718301
MS	Iprodione	426	0.5	2	1.12	550	43718301
MS	Quinclorac	36	1.26	unknown	0.84	13	41063565
AR	Propaconazole	648	1.8	10	0.378	61	42560501
AR	Propaconazole	648	0.63	10	1.512	214	42560501
TX	Propaconazole	648	1.15	7.6	0.378	48	42560502
TX	Propaconazole	648	1.15	7.6	1.512	138	42560502
MS	Bentazon	35	0.75	7	2.24	2073	43431901
LA	Bentazon	35	0.53	7	2.24	1545	43431901
MS	Lambda cyhalothrin	300000	0.47	9	0.18	3	44367403
AR	Trifloxystrobin	3500	1.1	13	0.38	69	45080803
AR	Molinate	186	0.64	unknown	10.1	4200	40391706
TX	Molinate	186	0.29	unknown	10.1	270	40391707
CA	Molinate	186	1.57	10	11.2	581	41421803
TX	Molinate	186	0.29	unknown	3.36	240	44970003
MS	Molinate	186	0.35	10	3.36	3	44970002
CA	Molinate	186	5.8	15	3.36	1800	Soderquist *et al.*, 1977

The model sediment depth was calibrated by comparing maximum observed concentrations to model outputs based on a range of depths (0.5 cm to 3 cm). These results are shown in Table 3. The values at the bottom of the table summarize the number of simulated concentrations that are less than the observed concentration. A depth of 1 cm appears appropriate as the model simulates only three concentrations that are below the observed value, and two of these values underpredict the observed concentration by only 1%.

Table 3. Calibration of the Sediment Depth (Concentrations Expressed as ppb).

Study Chemical	**Observed Concentration**	**Model Concentration d_{sed} = 0.5 cm**	**Model Concentration d_{sed} = 1.0 cm**	**Model Concentration d_{sed} = 2.0 cm**	**Model Concentration d_{sed} = 3.0 cm**
Iprodione	489	860	698	507	**398**
Iprodione	550	860	698	**507**	**398**
Quinclorac	13	801	765	703	650
Propaconazole	61	261	200	136	103
Propaconazole	214	1045	799	543	411
Propaconazole	48	261	200	136	103
Propaconazole	138	1045	799	543	441
Bentazon	2073	2137	**2043**	**1878**	**1738**
Bentazon	1545	2137	2043	1878	1738
Lambda cyhalothrin	3	**0.92**	**0.46**	**0.23**	**0.15**
Trifloxystrobin	69	115	**68**	**37**	**26**
Molinate	4200	8801	7805	6364	5372
Molinate	270	8801	7805	6364	5372
Molinate	581	9779	8672	7071	5969
Molinate	240	2934	2602	2121	1791
Molinate	3[1]	2934	2602	2121	1791
Molinate	1800	2934	2602	2121	**1791**
Number of modeled concentrations less than the observed		**1**	**3**	**4**	**6**

[1] This concentration was observed 14 days after application.

IV. Formula of the Tier I Rice Model v1.0

Substituting the values in Table 1 into equation (5) and using common units for K_d (L/kg), m_{ai}' (kg/ha), and C_w (µg/L), the Tier I rice conceptual model is simplified to the Tier I Rice Model v1.0 (see Appendix I for derivation):

$$C_w = \frac{m_{ai}'}{0.00105 + 0.00013K_d} \tag{6}$$

where, in this case:

C_w = water concentration [µg/L]
m_{ai}' = mass applied per unit area [kg/ha]
K_d = water-sediment partitioning coefficient [L/kg]

Model input values for the water-sediment partitioning coefficient (K_d) should represent a mean K_d of relevant soil (or sediment). A mean K_{oc} value should be used to generate model input values for K_d in cases where sorption K_d values correlate with soil organic matter content. In these cases, K_d model input values should be calculated from the mean K_{oc} using a fraction of organic carbon (f_{oc}) of 0.01 (Table 2). K_d can thus be estimated by the following equations:

$$K_d = f_{oc}K_{oc} \tag{7}$$

$$K_d = 0.01K_{oc} \tag{8}$$

Alternatively, mean K_{oc} values can be directly entered into equation (9):

$$C_w = \frac{m_{ai}'}{0.00105 + 0.0000013K_{oc}} \tag{9}$$

V. Assumptions

Most of the assumptions used in this model help ensure that the outputs are protective of most environments associated with rice agriculture. The model assumptions include the following:

1. Movement of pesticide on suspended sediment is not considered.
2. Degradation does not occur.
3. Volatilization and other dissipation processes are not considered.
4. Partitioning to sediment is instantaneous.
5. Water is available for human or wildlife exposure instantaneously.
6. Water column depth is 10 cm.
7. Sediment depth is 1 cm.
8. All pore space is saturated with water.
9. Organic carbon fraction is 0.01.
10. Bulk density is 1300 kg/m^3.

11. Grain density is 2650 kg/m^3.

VI. Model Evaluation for Drinking Water Exposure

Tier I model estimates are screening estimates and, as such, are expected to exceed peak values found in the environment in most cases. This expectation is due to the protective assumptions of the model listed in Section V of this document, such as exclusion of degradation as well as dilution with uncontaminated water outside the paddy. In order to evaluate the Tier I Rice Model v1.0 for drinking water exposure estimation, modeled estimates, which are calibrated to indicate exposure within rice paddies, were compared to measured concentrations of pesticides in rice-growing environments well downstream of the actual rice paddies. The results of these comparisons are summarized in Table 4 and discussed in Sections VI A, B, C, and D of this document.

Table 4. Summary of Comparisons of Within-Paddy Simulations with Downstream Observations.

Site	**Chemical**	**K_{oc} (L/kg)**	**Application Rate (kg/ha)**	**Observed Maximum (ppb)**	**Model Estimate (ppb)**	**MRID or Reference**
LA 1	Fipronil	727	0.056	8.41	28.1	LDAF, 2000
LA 2	Fipronil	727	0.056	2.12	28.1	45349901
CA	Methyl parathion	523	0.89	0.11	512	44632501
CA	Thiobencarb	909	4.5	12.3	2010	44632501
CA	Molinate	186	10	25.7	7810	44632501

A. Louisiana Downstream Measurements 1 (LA 1)

The Louisiana Department of Agriculture and Forestry collected data from 23 monitoring sites where surface water bodies received rice paddy discharge water in Acadia, Calcasieu, Cameron, Jefferson-Davis, and Vermilion Parishes (LDAF, 2000). The maximum detected fipronil concentration from March 6, 2000 to May 15, 2000 was 8.41 µg/L. Although the actual use history of fipronil is unknown in this area, the labeled maximum application rate of 0.05 lbs a.i./acre was assumed in order to compare rice model results. The rice model gives an estimate that is 3.5 times greater than the maximum detected value.

B. Louisiana Downstream Measurements 2 (LA 2)

Fipronil surface water monitoring data were submitted for the Mermentau River and Lake Arthur (MRID 45349901). The Mermentau River drains a large portion of the rice acreage in southern Louisiana from the mouths of Bayou Plaquemine and Bayou Nezpique. There are 250,000 acres of rice in this area, 70% of which was treated with fipronil in 1999. The monitoring program was designed to provide a snapshot of concentrations on May 11, 1999, just after a 0.45-inch rainfall event, at 0 to 1 feet and 4 to 6 feet depth. The maximum detected concentrations were sampled from the mouth of the Bayou Plaquemine, where fipronil was detected at a maximum concentration of 2.118 µg/L and total residues of fipronil and three of its degradates were detected at a maximum concentration of 3.509 µg/L. The rice model gives an estimate that is approximately one order of magnitude greater than the maximum detected value for fipronil.

C. California Indirect Measurements (CA)

The California Department of Pesticide Regulation collected data from six monitoring sites in the Sacramento Valley that were sampled from March 31, 1997 to May 29, 1997 as part of a cooperative water quality monitoring program (MRID 44632501). Residues of molinate, thiobencarb, and methyl parathion were monitored in water bodies near rice agriculture that may not have necessarily contained concentrations representative of those found in rice paddy water or released paddy discharge water. Maximum concentrations of 0.11 µg/L of methyl parathion, 12.3 µg/L of thiobencarb, and 25.7 µg/L of molinate were detected in the Colusa Basin Drain monitoring site near State Highway 20 on the 13th, 20th, and 22nd of May, 1997, respectively. The rice model gives estimates that are two to three orders of magnitude larger than the respective maximum detected values of these pesticides.

D. Evaluation Summary

Evaluation of the Tier I Rice Model v1.0 indicates that modeled within-paddy estimates are conservative, exceeding peak measured concentrations of pesticides in water bodies well downstream of rice paddies by less than one order of magnitude to multiple orders of magnitude. The range of modeled estimate exceedances over measured concentrations is most likely in response to chemical, environmental, and study-specific factors.

VII. Model Characterization

Estimates from the Tier I model generally do not represent typical concentrations found in human drinking water, as they represent paddy discharge water. However, these concentrations may be a reasonable estimate of acute concentrations for use in ecological assessment where exposure occurs at or near the rice paddy. In both cases, human drinking water and ecological exposure, the chronic concentrations as well as offsite concentrations are expected to be conservative. A higher tier rice model should be used to estimate chronic exposure to compounds that degrade rapidly into degradates that are not of risk concern.

If Tier I estimates calculated by this screening method do not exceed the level of concern in a risk assessment, there is high confidence that there will be little or no risk above the level of concern from exposure through water resources. However, because of the uncertainties associated with a screening method, when a level of concern is exceeded it cannot be determined whether the exceedance will in fact occur or whether this method has overestimated the exposure.

Sample input and output tables for use in ecological and/or drinking water exposure assessments are provided in Appendix III.

VIII. References

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Appendix I:
Units Analysis

The Tier I Rice Model with commonly understood parameters (equation (5)) is:

$$C_w = \frac{m_{ai}'}{d_w + d_{sed}\left(\theta_{sed} + \rho_b K_d\right)}$$

Substituting the parameter values for sediment depth (d_{sed}=0.01 m), water depth (d_w=0.10 m), sediment bulk density (ρ_b=1300 kg/m^3), and porosity (θ_{sed}=0.509), we can develop the following expression with unit conversions in place:

$$C_w\left[\frac{\mu g}{L}\right] = \frac{m_{ai}'\left[\frac{kg}{ha}\right]10^{-4}\left[\frac{ha}{m^2}\right]10^{9}\left[\frac{\mu g}{kg}\right]}{0.10\,m + 0.01\,m\left(0.509 + 1300\left[\frac{kg}{m^3}\right]K_d\left[\frac{L}{kg}\right]10^{-3}\left[\frac{m^3}{L}\right]\right)}10^{-3}\left[\frac{m^3}{L}\right] \qquad (10)$$

Simplifying equation (10) forms the Tier I Rice Model expression (with units shown):

$$C_w\left[\frac{\mu g}{L}\right] = \frac{m_{ai}'\left[\frac{kg}{ha}\right]}{1.05[10^{-3}]\left[\frac{L\cdot kg}{ha\cdot \mu g}\right] + 1.3[10^{-4}]\left[\frac{kg^2}{ha\cdot \mu g}\right]K_d\left[\frac{L}{kg}\right]} \qquad (11)$$

The Tier I Rice Model v1.0 (equation (6)) is equation (11) written with implied units:

$$C_w = \frac{m_{ai}'}{0.00105 + 0.00013 K_d} \qquad (6)$$

where:

C_w = water concentration [µg/L]
m_{ai}' = mass applied per unit area [kg/ha]
K_d = water-sediment partitioning coefficient [L/kg]

Appendix II:
Model Comparison

Table II. Comparison of Interim Rice Model Exposure Estimates with Those of the Tier I Rice Model v1.0.

Compound	K_{oc}	Interim Rice Model Output (ppb)	Tier I Rice Model v1.0 Output (ppb)	Ratio of Model Outputs (—)
Bentazon	35	876	913	1.04
Molinate	186	652	774	1.19
Propaconazole	648	366	528	1.44
Trifloxystrobin	3500	98.5	179	1.81
Lambda cyhalothrin	300000	1.28	2.56	2.00

Appendix III:
Sample Input and Output Tables

Sample Input Table:

Table III.1. Tier I Rice Model v1.0 input parameters for [chemical name]. Source data are in Table [X].

Input Parameter	**Value**	**Justification**	**Source**
Application Rate (kg a.i./ha)	0.0622	0.0555 lbs a.i./A x 1.121 kg·A/ha·lbs = 0.0622 kg a.i./ha	Proposed label
Soil-to-Water Partition Coefficient (K_d) (L/kg)	4.00	Mean K_{oc} (400 L/kg$_{oc}$) x 1% organic carbon content = 4.00 L/kg	[MRID #(s)]

Sample Ecological Exposure Assessment Output Table:

Table III.2. Tier I surface water estimated exposure concentrations (EEC) of [chemical name] from use on rice.

Source	**App. Rate (lbs a.i./A)**	**Peak & Chronic EEC (µg/L)**
Paddy Water/Tail Water	0.0555	39.6

Sample Drinking Water Exposure Assessment Output Table:

Table III.3. Tier I drinking water exposure estimates for [chemical name] use on rice.[1]

Source	**Peak Exposure (µg/L)**	**Annual Mean Exposure (µg/L)**
Surface Water	39.6	<39.6
Ground Water	[SCI-GROW value]	<[SCI-GROW value]

[1] Surface water concentrations calculated by the Tier I Rice Model v1.0 and ground water concentrations calculated by SCI-GROW do not distinguish between peak and chronic concentrations.