STANDARD OPERATING PROCEDURE
Methodology for Evaluating Pesticides for Surface Water Protection

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KEY WORDS

Runoff potential, aquatic persistence, aquatic toxicity, use pattern, Risk Quotient

APPROVALS

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1.0 INTRODUCTION

The methodology is based on a two-stage procedure: I. evaluation with initial screening, and II. evaluation with refined modeling (Figure 1). Detailed for the methodology development and validation have been documented in two reports (Luo and Deng, 2012a, b). Five indicators are developed for the evaluation: runoff potential, aquatic persistence, aquatic toxicity, use pattern, and Risk Quotient. These indicators are derived from chemistry and environmental fate data, aquatic toxicity data, and proposed labels submitted by the registrants, and assigned as descriptive classifications, i.e., “Low (L)”, “Intermediate (M)”, “High (H)”, or “Very High (VH)” classes.

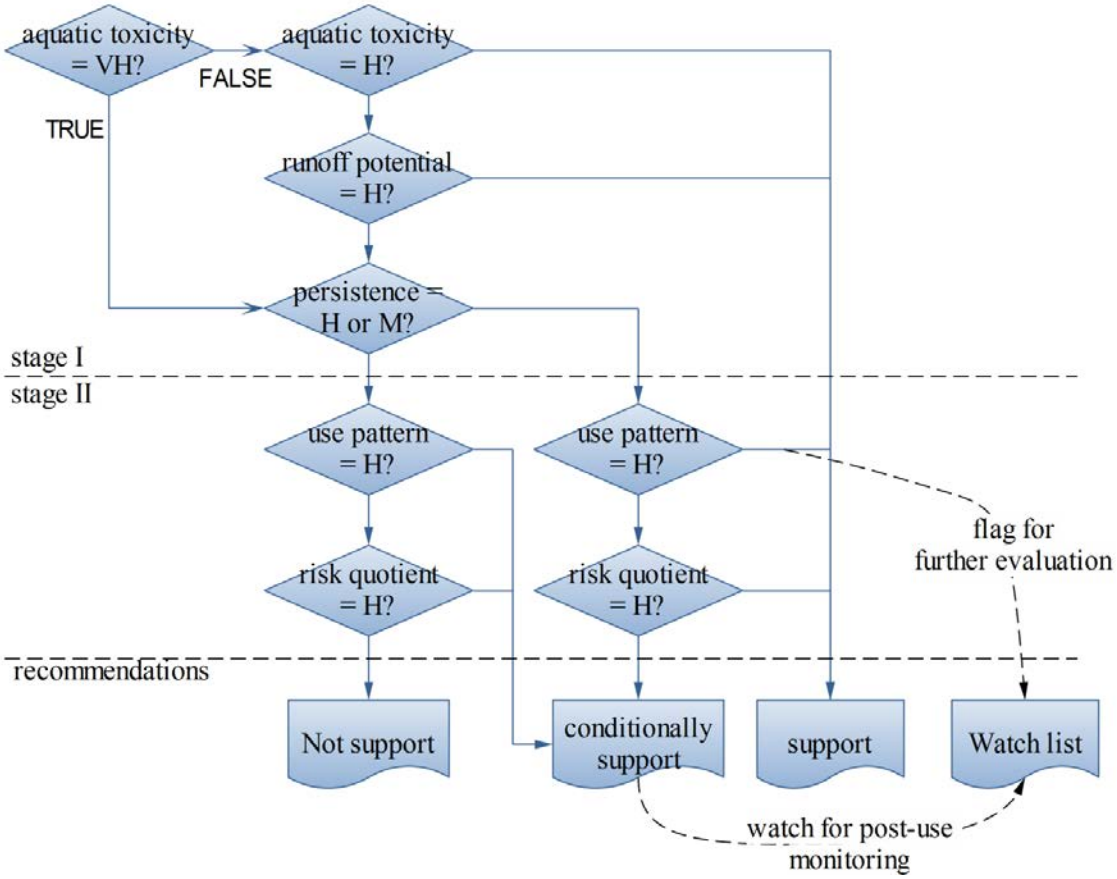

Figure 1. Decision flowchart of the two-stage procedure of pesticide evaluation for surface water protection (indicator classifications: VH = “Very High”, H = “High” and M = “Intermediate”).

The methodology evaluates pesticide in water column (dissolved phase) and bound with sediment (adsorbed phase). Except for the use pattern, all other indicators are defined for both phases. Evaluation for dissolved phase is conducted for all pesticides, while evaluation for adsorbed phase is only required for pesticides with KOC>1000.

1.1 Purpose

The purpose of this document is to standardize the pesticide evaluation for surface water protection, using the methodology developed in Luo and Deng (2012a, b).

1.2 Definitions

Chemistry data and environmental fate data:

KOC	L/kg[OC]	organic carbon (OC)-normalized soil adsorption coefficient
SOL	mg/L	water solubility
AERO	day	aerobic soil metabolism half-life
FD	day	field dissipation
HYDROL	day	hydrolysis half-life
AERO_W	day	aerobic aquatic metabolism half-life
ANAER _W	day	anaerobic aquatic metabolism half-life
HLW	day	aquatic dissipation half-life in water, or as a rate constant (k_w, day^{-1})
HLD	day	aquatic dissipation half-life in sediment or in water-sediment system, or as a rate constant (k_{sed}, day^{-1})

Toxicity data:

EC50	µg/L	median effective concentration
LC50		[1] general definition: median lethal concentration [2] as model input: aquatic toxicity value, further defined as LC50W (µg/L) for water toxicity and LC50D (µg/g[OC] or µg/kg[dry sediment]) sediment toxicity

Label information and exposure estimation:

BASE	kg/ha	a small application rate of 0.1kg/ha to normalize the aquatic exposure, used in the development of the use-exposure relationships (Luo *et al.*, 2011)
RATE	kg/ha	the maximum application rate per year or per growing season
rate	kg/ha	the maximum application rate for an individual application
INTERVAL	day	the minimal interval between two applications
M	-	the maximum number of applications per year or per growing season
EEC		estimated environmental concentration. In the methodology, EEC is estimated at the edge of fields for dissolved phase (µg/L) and adsorbed phase (µg/kg[dry sediment]).

2.0 MATERIALS

2.1 Registrant-submitted data for pesticide registration

2.2 A calculator or any computer program capable of performing basic mathematical calculations

3.0 PROCEDURES

3.1 Stage I Evaluation: Initial Screening

3.1.1 Prepare chemistry data and environmental fate data

Required data for physiochemical properties and reaction half-lives for the pesticide active ingredient (AI) are listed in Section 1.2 Definitions. Data are retrieved from the review reports of "chemistry data and environmental fate data" (http://registration/track/trackreps/trackreps.htm), in which the registrant-submitted data have been reviewed and summarized. If data summary is not available in the reports, the representative value of each variable is calculated as follows:

- If only one value is submitted, the value will be used as the representative value

- If two values are available, their mean will be used as the representative value
- If more than two values are available, their median will be used as the representative value
- If only a data range is reported, the mean value of the upper and lower bounds will be used as the representative value

HLW and HLD are usually reported only for aquatic pesticides and rice pesticides as measures for the overall dissipation process in aquatic systems. This concept is adapted for all pesticides for the evaluation purpose. If HLW and HLD are not reported, they are set to be the lowest reported half-lives in the corresponding environmental compartments (water or sediment),

HLW = min (HYDROL, AERO_W)
HLD = ANAER _W (1)

3.1.2 Prepare toxicity data

The acute aquatic toxicity in water (LC50W, µg/L) is set as the LC50 or EC50 of the most sensitive species of fish and invertebrates in freshwater and saltwater. Fish and invertebrate species commonly used for toxicity testing include *Daphnia magna*, *Hyalella azteca*, mysid shrimp, bluegill sunfish, fathead minnow, rainbow trout, and sheepshead minnow. Data are retrieved from the review reports of "fish and wildlife hazard" (http://registration/track/trackreps/trackreps.htm).

For pesticides with KOC>1000, sediment toxicity (LC50D) is set as the lowest toxicity values of reported benthic species. LC50D may be reported based on the dry sediment mass (µg/kg[dry sediment]) or normalized by OC content (µg/g[OC]). By assuming an organic carbon content of 1% in sediment, the following equation is used for the unit conversion,

1 µg/kg[dry sediment] = 0.1 µg/g[OC] (2)

3.1.3 Classify runoff potential

If the pesticide product under evaluation is proposed to be applied to aquatic sites, rice paddies, or impervious surfaces, its runoff potential is set to be "High". **Continue the evaluation in Section 3.1.4: Classify aquatic persistence**.

Otherwise, pesticide runoff potential is classified based on SOL, FD, and KOC by the criteria in Table 1.

Table 1. Classification of Runoff Potential from Soils

	Criteria	**Classification**
Dissolved phase	(SOL ≥ 1 and FD > 20 and KOC < 1×10^5) or (SOL ≥ 10 and KOC ≤ 2000)	High (H) runoff potential
	Otherwise	Low (L) runoff potential
Adsorbed phase	(FD ≥ 15 and KOC ≥ 4×10^4) or (FD ≥ 40 and KOC ≥ 1000) or (SOL ≤ 0.5 and FD ≥ 40 and KOC ≥ 500)	High (H) runoff potential
	Otherwise	Low (L) runoff potential

3.1.4 Classify aquatic persistence

Pesticide persistence in aquatic system is classified based on HLW and HLD by the criteria in Table 2.

Table 2. Classification of Aquatic Persistence

	Criteria	**Classification**
Dissolved phase	HLW ≥ 100	High (H) persistence
	30 ≤ HLW < 100	Intermediate (M) persistence
	HLW < 30	Low (L) persistence
Adsorbed phase	HLD ≥ 100	High (H) persistence
	30 ≤ HLD < 100	Intermediate (M) persistence
	HLD < 30	Low (L) persistence

3.1.5 Classify aquatic toxicity

Pesticide toxicity in aquatic system is classified based on LC50W and LC50D by the criteria in Table 3.

Table 3. Classification of Aquatic Toxicity

	Criteria	**Classification**
Dissolved phase	LC50W ≤ 100	Very High (VH) toxicity
	100 < LC50W ≤ 1000	High (H) toxicity
	Otherwise	Intermediate or low toxicity
Adsorbed phase	LC50D (µg/g[OC]) ≤ 10 or LC50D (µg/kg[dry sediment])) ≤ 100	Very High (VH) toxicity
	10 < LC50D (µg/g[OC]) ≤ 100 or 100 < LC50D (µg/kg[dry sediment])) ≤ 1000	High (H) toxicity
	Otherwise	Intermediate or low toxicity

3.1.6 Make recommendations based on the stage I evaluation

Registration recommendations are made according to the evaluation matrix in Table 4. For pesticide with KOC>1000, the evaluation matrix is applied to both dissolved and adsorbed phases. If additional evaluation is required for either phase, the pesticide will be evaluated in the stage II procedures.

Table 4. Evaluation Matrix for the Stage I Evaluation

Indicators			**Description**	**Recommendations**
Runoff Potential	**Aquatic Persistence**	**Aquatic Toxicity**		
Any	Any	VH	The chemical may potentially cause surface water problem	Require additional evaluation. **Continue the evaluation in Section 3.2 Stage II evaluation**
H	L	H or VH		
H	M or H	H or VH	The chemical may pose too high of a potential surface water risk	
Everything else			The chemical is unlikely to cause surface water problems	Support registration with no conditions, and **the evaluation process stops here**

Notes: indicator classifications: “L” = Low, “M” = Intermediate, “H” = High, and “VH” = Very High.

3.2 Stage II Evaluation: Refined Modeling

3.2.1 Prepare data for use pattern and label rates

The following information is obtained from the proposed label:

- Pesticide use patterns
- (for use patterns with high exposure potential to surface water listed in Table 5) Application rates as [a] maximum application rate (kg[AI]/ha) per year or per growing season, and/or, [b] Maximum application rate for each application, maximum number of applications, and minimal interval between two applications.

  Unit conversions for application rates:

  1 pound [AI]/acre = 1.12 kg [AI]/ha
  1 fluid ounce [AI]/acre = 0.07 kg [AI]/ha (3)

- (for rice pesticides only) Water holding period

  The model input of pesticide application rate (RATE, kg[AI]/ha) is defined as the maximum pesticide mass available in the field and subject to surface runoff. RATE value is set according to the label rates selected for the evaluation:

  [1] If the maximum application rate per year or per growing season is used, RATE is set as the maximum application rate.

  [2] If label rates for multiple applications are used, RATE is calculated as (Luo *et al.*, 2011),

$$RATE = rate \cdot \sum_{i=1}^{M-1} \exp[-\frac{\ln 2}{FD}(M-i) \cdot INTERVAL] \quad (4)$$

3.2.2 Classify pesticide use pattern

Table 5 classifies use patterns according to their exposure potentials to surface water. It also summarizes the methods for calculating the Risk Quotient (RQ).

Table 5. Classification of Use Patterns and Corresponding Methods for Calculating the Risk Quotients

Use Pattern	**Classification of Exposure Potential**	**USEPA Modeling Scenarios used for the RQ Calculation**
Alfalfa and pasture	High	Alfalfa
Cotton	High	Cotton
Grains	High	Wheat
Sugar beet	High	Sugar beet
Other field crops (corn, dry beans, safflower, etc.)	High	Cotton or Sugar beet
Oranges	High	Citrus
Grapes	High	Grapes
Tomato	High	Tomato
Almond, pistachio, walnut, peach, plume	High	Almond
Rice pesticides	High	Rice
Other aquatic applications	High	Not associated with any modeling scenario, the RQ is set to be High
Residential turf	High	Residential turf
Rights-of-way	High	Rights-of-way
Other urban applications	High	Not associated with any modeling scenario, the RQ is set to be High
Winter rain season application	High	Almond
Pre-emergent herbicides	High	Turf
Other use patterns not listed above	Low	The RQ is not required for pesticides with low exposure potentials

Notes: The rice scenario is a USEPA Tier 1 modeling scenario based on the national average conditions. Other scenarios are USEPA Tier 2 modeling scenarios for California.

3.2.3 Classify the Risk Quotient

The method for the classification of RQ is associated with the pesticide use patterns:

[1] For use patterns associated with US EPA Tier 1 or Tier 2 modeling scenarios (Table 5), the RQ is defined as the EEC at the edge of fields divided by the acute toxicity value,

$$RQ = \frac{EEC}{LC50} \quad (5)$$

If the RQ value is larger than 0.5, the product under evaluation is classified to have a "High (H)" RQ. Otherwise, the product was classified with a "Low (L)" RQ. LC50 values are taken from the stage I evaluation, while EEC will be calculated by following the procedures in **Section 3.2.4** for rice pesticides, and **Section 3.2.5** for other pesticides, respectively.

[2] For use patterns not covered by USEPA modeling scenarios, e.g., applications to aquatic sites and to impervious surfaces (Table 5), the RQ is set to be "High". **Continue the evaluation in Section 3.2.7: Make recommendations based on Stage II evaluation**.

[3] For use patterns with "Low" exposure potential to surface water, the RQ is not required for evaluation. **Continue the evaluation in Section 3.2.7: Make recommendations based on Stage II evaluation.**

3.2.4 Calculate the EEC by the modified USEPA Tier I Rice Model

The dissolved concentration of pesticide in the paddy water immediately after application ($EEC_w(0)$, µg/L) is calculated based on the US EPA Tier 1 Rice Model (USEPA, 2007),

$$EEC_w(0) = \frac{RATE}{1.05\times10^{-3} + 1.3\times10^{-6}\cdot KOC} \quad (6)$$

The concentration at the end of the water-holding period (t, day) is calculated according to the first-order decay,

$$EEC_w(t) = EEC_w(0) \cdot \exp(-kt) \quad (7)$$

where k (day^{-1}) is an overall dissipation rate constant of the pesticide in rice paddy, which can be estimated based on the dissipation rate constants in water (k_w, day^{-1}) and in sediment (k_{sed}, day^{-1})

$$k = \frac{d_w k_w + d_{sed}(\theta_{sed} + KOC \cdot f_{oc}\rho_b)k_{sed}}{d_w + d_{sed}(\theta_{sed} + KOC \cdot f_{oc}\rho_b)} \quad (8)$$

The rate constants can be calculated from the corresponding half-lives,

$$k_w = \frac{\ln 2}{HLW}; k_{sed} = \frac{\ln 2}{HLD} \quad (9)$$

Other variables in Eq. (8) should be set to the default values according to the USEPA Tier 1 Rice Model (Table 6).

Table 6. Physical Values of the USEPA Tier 1 Rice Model (USEPA, 2007)

Variable	Description	Default Value
d_w	Water column depth	0.10 m
θ_{sed}	Sediment porosity	0.509
f_{oc}	Organic content of sediment	0.01
ρ_b	Sediment bulk density	1300 kg/m^3

For pesticide adsorbed on suspended solids and bed sediment, the concentration (EEC_d, µg/kg[dry sediment]) is calculated by assuming instantaneous equilibrium,

$$EEC_d(t) = EEC_w(t) \cdot KOC \cdot f_{oc} \quad (10)$$

Calculate RQ by Eq. (5) **and continue the evaluation in Section 3.2.7: Make recommendations based on Stage II evaluation**.

3.2.5 Calculate the EEC by the Use-Exposure Relationship

For the pesticides with use patterns associated with the Use-Exposure Relationship (Table 5), the edge-of-field EEC is estimated as,

$$EEC = \frac{RATE}{BASE} EEC_{BASE} \quad (11)$$

where EEC and EEC_{BASE} (with unit µg/L for pesticide in dissolved phase, and µg/kg[dry sediment] for adsorbed phase) are the EECs at the edge of field in response to the maximum (RATE) and base (BASE) application rates, respectively.

For the USEPA Tier 2 modeling scenarios for pervious surfaces, or for the pervious portion of the residential and rights-of-way surfaces, the EEC_{BASE} is a function of AERO and KOC (Luo *et al.*, 2011),

$$\ln(EEC_{BASE}) = f(AERO, KOC) = \begin{cases} b_1 + b_2 \ln(AERO) + b_3 \ln[\max(KOC, KOC^*)], \text{ for dissolved phase} \\ b_1 + b_2 \ln(AERO) + b_3 \ln[\min(KOC, KOC^*)], \text{ for adsorbed phase} \end{cases} \quad (12)$$

with b's for regression coefficients and KOC* (L/kg[OC]) as a breakpoint KOC value determined for each modeling scenario. Table 7 summarizes the derived coefficients from USEPA Tier 2 modeling scenarios for California, which are associated with high exposure potentials as identified in Table 5.

Table 7. Regression Coefficients for the Use-exposure Relationships from USEPA Tier 2 Modeling Scenarios for California

(a) Dissolved Pesticides

Scenarios	**Coefficients**			R^2	**ln(KOC*)**
	b_1	b_2	b_3		
Alfalfa	5.2156	0.1907	-0.8288	0.9494	3.5
Almond	4.8131	0.1869	-0.7467	0.9335	4.5
Citrus	6.6724	0.1597	-0.7952	0.9161	5.0
Cotton	6.3173	0.1467	-0.7662	0.9102	5.5
Grapes	6.5127	0.1694	-0.8081	0.9286	4.5
Sugar beet	4.9105	0.2412	-0.8377	0.9193	3.0
Tomato	5.9979	0.1785	-0.7844	0.8970	4.0
Turf	3.3647	0.2821	-0.8248	0.9546	0.5
Wheat	6.0764	0.1853	-0.7954	0.9487	5.0
Residential [1]	3.3054	0.2457	-0.8182	0.9554	0.5
Rights-of-way [1]	6.0914	0.2416	-0.7856	0.9330	5.0

(b) Sediment-Bound pesticides

Scenarios	**Coefficients**			R^2	**ln(KOC*)**
	b_1	b_2	b_3		
Alfalfa	1.7756	0.3140	0.4936	0.6896	9.5
Almond	0.1179	0.2116	0.6937	0.7955	10.0
Citrus	3.4796	0.2098	0.6346	0.8189	10.5
Cotton	0.9213	0.1890	0.7221	0.8466	11.0
Grapes	3.0443	0.2376	0.5991	0.7780	10.0
Sugar beet	2.7386	0.3254	0.5118	0.6409	8.5
Tomato	3.2070	0.1912	0.6062	0.7770	10.0
Turf	2.7715	0.2832	0.4486	0.6106	6.5
Wheat	1.0782	0.3233	0.5848	0.7210	10.5
Residential [1]	0.7986	0.2911	0.6262	0.7693	6.5
Rights-of-way [1]	3.0013	0.2283	0.5177	0.8035	10.5

Note: [1] coefficients are reported for the pervious portion of residential or rights-of-way surfaces.

3.2.6 Estimate the EECBASE for mixed landscape with pervious and impervious surfaces

For the residential and rights-of-way modeling scenarios which consist of paired pervious and impervious surfaces, the EECs are calculated based on the EEC from the previous surface ($EEC_{BASE,p}$) and that from the impervious surfaces ($EEC_{BASE,imp}$),

For dissolved phase,

$$EEC_{BASE} = (1 - f_{imp})EEC_{BASE,p} + f_{imp}EEC_{BASE,imp} \quad (13)$$

For adsorbed phase,

$$EEC_{BASE} = EEC_{BASE,p}$$

where the coverage faction of the impervious surface (f_{imp}) was set as 5.68% for residential area, and 1.00% for rights-of-way area (USEPA, 2008). $EEC_{BASE,p}$ is calculated by Equation (12) and coefficients in Table 7, and $EEC_{BASE,imp}$ is conservatively estimated as,

$$\ln EEC_{BASE,imp} = 0.625 \cdot \min(\ln AERO, 2) + 3.25 \quad (14)$$

3.2.7 Make recommendations based on the Stage II evaluation

Registration recommendations are made according to the evaluation matrix in Table 8.

Table 8. Evaluation Matrix for the Stage II Evaluation

Use Pattern	**Risk Quotient**	**Aquatic Persistence**	**Recommendations**
H	H	H or M	not to support registration
L	Any	H or M	support conditional registration, and place the pesticide into the watch-list
H	L	H or M	
H	H	L	
L	Any	L	support registration with no conditions, and place the pesticide into the watch-list
H	L	L	support registration with no condition

Notes: indicator classifications: “L” = low, “M” = intermediate, and “H” = high

4.0 CALCULATIONS

A Windows-based computer program was developed to implement the above standard operating procedure for pesticide registration evaluation. The interface, source code, and documentation are presented in a separate report (Luo and Deng, 2012c).

5.0 REFERENCES

Luo, Y. and X. Deng (2012a). Methodology for evaluating pesticides for surface water protection, I: initial screening (http://cdpr.ca.gov/docs/emon/surfwtr/review.htm). California Department of Pesticide Regulation. Sacramento, CA.

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6.0 APPENDIX

6.1 Report template

An example report of registration evaluation for surface water quality based on the results from the new methodology is attached.

California Department of Pesticide Regulation
Environmental Monitoring Branch

EVALUATION REPORT - PESTICIDE Date:
Surface Water-

Tracking ID No.	:	
Product Name	:	
Study No.	:	
Applicant	:	
EPA Reg. No.	:	
Document No.	:	
Active Ingredient	:	
Use	:	Herbicide
Registration Action	:	Section 3
Area of Review	:	Environmental Monitoring, Surface Water
Registration Specialist	:	

[X] Data/Information Support Registration

[ ] Data/Information Support Conditional Registration

[ ] Data/Information Do Not Support Registration

[ ] No Registration Action Required

Summary

submitted an application to register , a new herbicide for controlling various weeds in spring and winter wheat.

Registrant submitted data were evaluated for potential surface water impacts using model input parameters as listed in Tables 1-2. Modeling results (Table 3) from Phase 1 evaluation support registration with no conditions, based on HIGH runoff potential, LOW persistence, and LOW toxicity for the chemical (Luo 2011a). Therefore, additional evaluation with Phase 2 refined modeling is not needed (Luo 2011b).

Model Input Parameters

Table 1. Model input- Chemistry data

Test	Value	Unit	Source	Notes
KOC	31.12	L/kg[OC]	R	Range = 7.92-54.32
Water solubility (SOL)	62.6	ppm	R	
Hydrolytic half-life	Stable	day	R	
Aerobic soil metabolism	16.55	day	R	Range = 7.5-25.6
Anaerobic soil metabolism	32	day	R2	
Field dissipation FD	17	day	R, R2	Range = 5-29
Aerobic aquatic metabolism	17.15	day	R	Median of DPR-calculated half-lives ($t_{1/2}$)
Anaerobic aquatic metabolism	20	day	R2	

Data Sources R- registrant supplied.
R2 - registrant supplied.

Table 2. Model input- Aquatic toxicity values

Test	Value	Units	Source
Rainbow trout (96 hr LC50)	>87,000	µg/L	R3
Daphnia magna (48 hrs EC50)	>100,000	µg/L	R3
Fathead minnow (96 hr LC50)	>94,400	µg/L	R3

Data source: R3- registrant supplied.

Modeling Results

[1] KOC<1000: only dissolved phases ware evaluated.
[2] Registration is supported based on the initial screening, and the calculation of risk quotient is not needed

Table 3. Modeling results for indicators and decisions

Indicator	Dissolve phase	Adsorbed phase [1]
Runoff potential	High	-
Aquatic persistence	Low	-
Toxicity	Low	-
Use pattern	High exposure potential	
Risk quotient	-	-
Model-based decisions	**Support**	-
Registration commendation		

Conclusion and Recommendation

Surface Water Protection Program staff recommend registration of
with no conditions.

Original Signed by

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Senior Environmental Scientist

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