



Department of Pesticide Regulation -
Environmental Monitoring Branch -
1001 I Street
Sacramento, California 95812

Methodology for Evaluating Pesticides for Surface Water Protection I: Initial Screening

Yuzhou Luo, Ph.D., and Xin Deng, Ph.D.

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Terminology of Chemical Properties

AERO	aerobic soil metabolism half-life, day
AERO_W	aerobic aquatic metabolism half-life, day
ANAER	anaerobic soil metabolism half-life, day
ANAER_W	anaerobic aquatic metabolism half-life, day
FD	field dissipation half-life, day
HLW	dissipation half-life in water, day
HLD	dissipation half-life in sediment (or water-sediment system), day
HYDROL	hydrolysis half-life, day
KOC	organic carbon-normalized soil adsorption coefficient, L/kg[OC]
LC ₅₀	median lethal concentration, ppb
SOL	water solubility, mg/L

1. Introduction

The Surface Water Protection Program (SWPP) is developing a more consistent and transparent method for evaluating registration packages. Historically, these evaluations have been based principally on professional judgment and experience gleaned from past assessment of the conditions and mechanisms responsible for the offsite transport of pesticides to surface water and their associated toxicological impact on aquatic life. A two-stage procedure is proposed here, including stage I evaluation with initial screening, and stage II evaluations with refined modeling (Figure 1). Initial screening is conducted solely on chemical properties (soil adsorption coefficient, water solubility, and reaction half-lives) and aquatic toxicology data of the active ingredient in evaluation. The objective of the stage I evaluation is to classify pesticides as to whether they [1] are unlikely to be a surface water quality problem, and their registrations are supported without conditions, or [2] may potentially cause surface water problems and require additional evaluation. *This document (Part I) outlined the initial screening procedure to evaluate pesticides for the protection of surface water quality.*

For pesticides requiring additional evaluations, stage II evaluation is followed with a more refined modeling approach *as presented in a companion report (Part II)*. Stage II evaluation is

performed based on risk characterization by accounting for the product-specific information (use pattern and application rate). The objective of stage II evaluation is to develop registration recommendations for pesticide products as whether [1] to support registration without conditions, [2] to support conditional registration with requests for analytical methods, or [3] not to support registration.

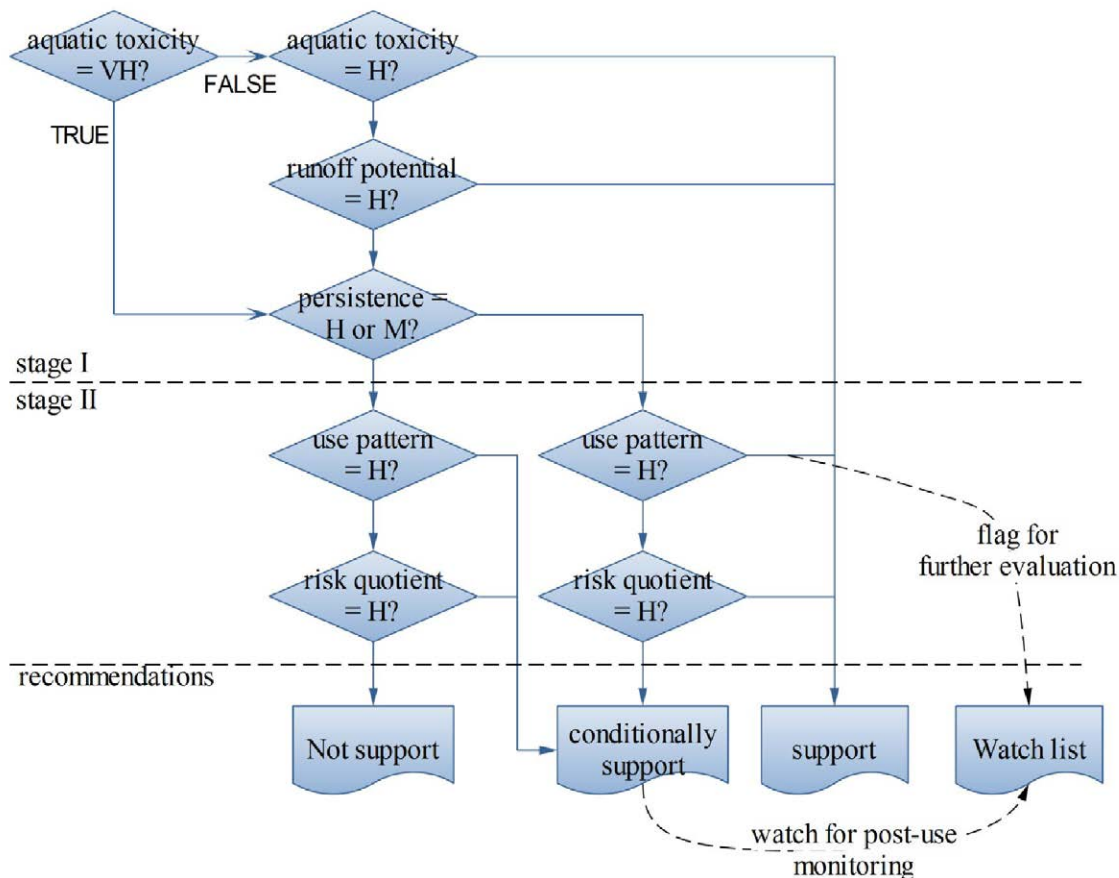


Figure 1. Decision flowchart of the two-stage procedure of pesticide evaluation for surface water protection (indicator classifications: H = “High” and M = “Intermediate”). This only shows a general procedure by highlighting indicators used in this study. Pesticide evaluation should follow the detailed procedures introduced in the reports.

The methodology addresses both water column and sediment-bound phases and considers different use patterns of a pesticide. Except for the use pattern, all other indicators (Figure 1) are defined for pesticides in both water column (aqueous phase) and sediment (adsorbed phase). Evaluation for aqueous phase is conducted for all pesticides, while evaluation for adsorbed phase is only required for pesticides with KOC > 1000. This criterion is set based on the USEPA data requirement for pesticide registration, in which acute sediment toxicity is required for pesticides with KOC > 1000 (USEPA, 2007a). In addition, a pesticide product may be associated with multiple use patterns. Pesticide evaluation could be conducted for each of the use patterns. The final registration recommendation will be based on both the evaluation results and professional judgment with additional information from the chemical properties and product label.

The objective of the methodology development is to provide a more consistent and transparent pesticide evaluation to support the pesticide registration for surface water protection. Therefore, the input data for pesticide evaluation are consistent to those available in a common registration package and used in our previous evaluation. In most cases, the registrant-submitted data has been reviewed and summarized as independent processes before delivering to SWPP. In addition, the methodology is not designed for numerically predict pesticide fate in the real environment since the actual application amount and drainage area characteristics are not available during at the stage of pesticide registration. Therefore it's inappropriate to compare the results from the methodology to the pesticide concentrations, frequency and geographic distribution detected in surface waters. Instead, we compared the derived registration recommendations to our previous evaluation based on best professional judgment for the same chemical and product.

2. Methods and Materials

2.1. Indicators for Stage I Evaluation

Three indicators are developed for pesticide active ingredient: [1] runoff potential, [2] aquatic persistence, and [3] aquatic toxicity. These indicators were derived from the registrant-submitted data, and assigned as descriptive classifications, i.e., “low”, “intermediate”, “high”, and/or “very high” (for toxicity only) classes. Based on the data availability in a regular registration package and the objectives in this project, we selected dissipation half-lives, water solubility, KOC, and aquatic toxicity value as input parameters for developing the indicators. According to the evaluation matrix presented in Table 1, the resulting indicators provide an initial screening of the environmental distribution and aquatic risks of the pesticide active ingredient. *Detailed information for the development of the three indicators is provided in the following sections.*

Table 1. Evaluation matrix for initial screening

Indicators			Results	Recommendations
Runoff potential	Persistence	Toxicity		
H	L	H or VH	The chemical may potentially cause surface water problem	Require addition evaluation
Any	Any	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

Notes: indicator ratings: “L” = low, “M” = intermediate, “H” = high, “VH” = very high

The evaluation matrix (Table 1) is applied to both dissolved and adsorbed phases of the pesticide. If the recommendations of supporting registration are made for both phases, the pesticide will be recommended for registrant with no conditions. Otherwise, additional evaluation is required for both chemical phases. Aquatic persistence does not have a direct effect on the result of stage 1 evaluation. It's listed here as an indicator since a chemical with high or intermediate persistence is more likely to cause surface water problems compared to one with

lower persistence. In addition, aquatic persistence is considered as one of the physiochemical properties of a pesticide and characterized in the stage 1 evaluation.

2.2. Runoff Potential

A screening approach developed by U.S. Department of Agriculture (USDA) (Goss, 1992) was modified for rating pesticide runoff potential. The approach was developed from over 40,000 runs of the Groundwater Loading Effects of Agricultural Management System (GLEAMS) using a wide range of soil and pesticide properties to estimate pesticide loss from soils through runoff processes. Based on a stepwise regression, physiochemical properties of field dissipation half-life (FD), KOC, and water solubility were identified as input parameters that weighted most heavily for estimating each group of pesticide loss potentials from the model runs. The groups for pesticide loss potentials are classified as: “high”, “intermediate”, and “low”. Multiple regression equations were used for each group in order to capture the highly nonlinear relationship between runoff potential and the input parameters. The USDA rating approach is currently used in the WIN-PST (Windows Pesticide Screening Tool) program (USDA, 2010).

Preliminary tests indicated that the USDA rating approach underestimated the runoff potential for pesticides with high KOC or high water solubility. For example, several pyrethroids were classified with only “intermediate” runoff potentials mainly because their field dissipation half-lives were less than 40 days. However, pyrethroids are known to bind strongly to and persist in soils and sediments, and to be toxic to many aquatic invertebrates at very low concentrations. Pyrethroids-associated sediment toxicity have been recognized in California (CEPA, 2010), and they are currently in reevaluation to address these concerns (CDPR, 2006). The other identified issue is that, the USDA rating approach excludes all pesticides with a solubility greater than 100 mg/L, such as organophosphates (dimethoate, malathion, and methidathion), from being classified as having “high” runoff potential. This is not consistent with the fact that organophosphates are frequently detected in surface waters (Pepple, 2009). Therefore, we revised the USDA rating approach for the group of “high” runoff potentials to cover the pesticides with frequent detection in surface water or high toxicity in sediment (Table 2). Testing for the revised model is provided in Section 3.1. If field dissipation half-life is not available in the registrant-submitted data, aerobic soil metabolism half-life will be used for runoff potential rating.

Table 2. Algorithm expressing pesticide runoff potential from soils

(a) Pesticide adsorbed-phase runoff potential

Criteria	Runoff potential rating
Revised criteria in this project ($FD \geq 15$ and $KOC \geq 4 \times 10^4$) or ($FD \geq 40$ and $KOC \geq 1000$) or ($FD \geq 40$ and $KOC \geq 500$ and $SOL \leq 0.5$)	High (H)
<i>Original USDA criteria</i> ($FD \geq 40$ and $KOC \geq 1000$) or ($FD \geq 40$ and $KOC \geq 500$ and $SOL \leq 0.5$)	
($FD \leq 1$) or ($FD \leq 2$ and $KOC \leq 500$) or ($FD \leq 4$ and $KOC \leq 900$ and $SOL \geq 0.5$) or ($FD \leq 40$ and $KOC \leq 500$ and $SOL \geq 0.5$) or ($FD \leq 40$ and $KOC \leq 900$ and $SOL \geq 2$)	Low (L)
Everything else	Intermediate (M)

(b) Pesticide solution-phase runoff potential

Criteria	Runoff potential rating
Revised criteria in this project ($SOL \geq 1$ and $FD > 20$ and $KOC < 1 \times 10^5$) or ($SOL \geq 10$ and $KOC \leq 2000$)	High (H)
<i>Original USDA criteria</i> ($SOL \geq 1$ and $FD > 35$ and $KOC < 1 \times 10^5$) or ($SOL \geq 10$ and $KOC \leq 700$ and $SOL < 100$)	
($KOC \geq 1 \times 10^5$) or ($KOC \geq 1000$ and $FD \leq 1$) or ($SOL < 0.5$ and $FD < 35$)	Low (L)
Everything else	Intermediate (M)

Note: modifications are made only for the criteria of “high” runoff potential, while no changes for other classes.

Pesticides vary in their runoff potential depending on their different use pattern. Some pesticides are directly applied or released into water bodies without experiencing soil runoff processes, such as applications to impervious surfaces, herbicides for rice production, pesticides for the control of mosquito and midge larvae in surface water, or those used in antifouling paint products. In this case, the runoff potential rating was skipped and “high” runoff potential was assumed for both absorbed and dissolved phases as a conservative assumption.

2.3. Aquatic Persistence

Aquatic dissipation half-lives in water (HLW) and in sediment (HLD) are used in the classification or aquatic persistence. The overall dissipation half-lives consider pesticide dissipation processes in an aquatic environment, usually including aquatic photolysis, hydrolysis,

metabolism, and volatilization. Pesticides were grouped into three categories based on their half-lives in aquatic systems: “low” persistence with a typical aquatic half-life of less than 30 days, “intermediate” persistence with a half-life of 30 to 100 days, and “high” persistence with a half-life of more than 100 day (Table 3). The breakout points were suggested by Kerle et al. (2007). For pesticide persistence in water phase, aquatic dissipation half-life (HLW) value is determined as the shortest values of hydrolysis half-life, aerobic aquatic metabolism half-life, and dissipation half-life in water phase. For persistence in sediment, USEPA suggested that dissipation half-life in sediment could be taken from the anaerobic soil or aquatic metabolism studies (USEPA, 2007a).

Table 3. Pesticide persistence in water and sediment (half lives in days)

Criteria	Persistence rating
HLW \geq 100	High (H) -
30 \leq HLW < 100	Intermediate (M)
HLW < 30	Low (L) -

2.4. Aquatic Toxicity

Toxicity ratings are determined by the acute toxicity value (LC₅₀, median lethal concentration) of the most sensitive species for fish and invertebrates in freshwater and saltwater (Table 4). Acute toxicity data requirements for freshwater and saltwater organisms including fish and invertebrates in water and sediment follow the definitions and conditions described in USEPA 40 CFR §158.630 and §158.660 (USEPA, 2007a) for protection of non-target aquatic organisms. Acute toxicity tests should be conducted using acceptable procedures recommended by USEPA. Acceptability of acute toxicity data should be evaluated based on the USEPA guidelines for deriving numerical national water quality criteria for aquatic organisms and their uses (USEPA, 1985). Therefore, the toxicity rating is conducted based on the toxicity values reported in the registration data package.

For sediment toxicity, only a few pesticides were tested and the corresponding toxicity ratings are not readily available. Existing data show that pyrethroids are a group of pesticides considered to be most toxic to the benthic invertebrate *Hyalella azteca* and their LC₅₀ values are generally below 10 µg/g[OC]. In this project, pesticides with sediment LC₅₀ values below/equal to 10 µg/g[OC] are classified as the highest toxic category. This critical value was scaled up in a 10 fold fashion to determine other toxicity ratings of high, intermediate, slight, and practically nontoxic categories in the sediment, respectively. The 10-fold scale is consistent with that used in rating water column toxicity (Table 4). Toxicity values for aquatic plants are not considered because these toxicity data are not required for pesticide registration by USEPA (2007a) and those are not usually included in the data package for registration evaluation. Current plant toxicity tests usually measure endpoints such as growth and reproduction that are generally associated with chronic toxicity. Moreover, the algal toxicity test guide in Environmental Toxicology Standards (ASTM, 2004) states that an algal toxicity test of short duration (72, 96 or 120 h) should not be viewed as an acute toxicity test because it examines effects upon multiple generations of an algal population.

Table 4. Descriptive acute toxicity ratings for pesticides in water column and sediment

Toxicity rating	Water column ($\mu\text{g/L}$)	Sediment ($\mu\text{g/g[OC]}$)
Very high (VH)	$\text{LC}_{50} \leq 100$	$\text{LC}_{50} \leq 10$
High (H)	$100 < \text{LC}_{50} \leq 1000$	$10 < \text{LC}_{50} \leq 100$
Intermediate (M)	$1000 < \text{LC}_{50} \leq 10000$	$100 < \text{LC}_{50} \leq 1000$
Slight (L)	$10000 < \text{LC}_{50} \leq 100000$	$1000 < \text{LC}_{50} \leq 10000$
Practically nontoxic (L)	$\text{LC}_{50} > 100000$	$\text{LC}_{50} > 10000$

Note: water column toxicity is rated by following the descriptive classifications by USEPA (Zucker, 1985).

According to USEPA (2007a), for all pesticides with $\text{KOC} > 1000$, acute sediment toxicity test is required for pesticide registration. In the demonstration of the developed approach (Section 3.2), however, sediment toxicity data is not available for some of the previously evaluated pesticides. In this case, we assumed that the sediment toxicity of a pesticide could be estimated as the product of its water toxicity and KOC value. Please note that this assumption was only utilized in the methodology testing, while in the real evaluation processes the actual sediment toxicity for the evaluated active ingredient should be used. Details of the data analysis for comparing pesticide acute toxicity in water and sediment are provided in the Appendix #1.

It's noteworthy that the toxicity values used in this study, based on acute toxicity data for fish and invertebrates, may be significantly different to those for benchmarks, drinking water and recreation water standards, aquatic plants, and chronic toxicity, which are not regularly available for pesticide registration, especially for new active ingredients. For example, diuron has a lowest LC_{50} of 1100 ppb (for mysid shrimp, Table 6), compared to the benchmark of 2.4 for nonvascular plants (USEPA, 2011a) and 2.0 for drinking water (Pepple, 2009).

3. Methodology Testing

3.1. Test for Runoff-Potential Rating

As part of the methodology testing, the indicator of runoff potential was first rated for 172 pesticides with the E-fate database compiled by Spurlock (2008). Detailed test results are presented in the Appendix #2. Pesticides with high runoff potential identified in the test results were generally consistent with those frequently detected in surface water (Pepple, 2009) or currently in reevaluation for sediment toxicity (CDPR, 2006).

3.2. Test for the Initial Screening Procedure

3.2.1. Selection of Pesticides

Two sets of pesticides were selected to test the evaluation approach. The first set of pesticides was selected from the registration evaluations by the Environmental Monitoring Branch. The following filters were used in the selection:

1. evaluations for surface water protection,

2. evaluations supplied with both chemical property data and toxicity data, and
3. evaluations posted during 2008-2010 (as of July 2010 when the study was initialized).

With all of the above filters applied, 21 pesticide active ingredients were selected and denoted with “A” to “U” in the demonstration. The registration packets and evaluation reports were used as the data source for chemical properties and toxicity data.

The second set of pesticides was suggested by scientists from the Environmental Monitoring Branch and the Registration Branch. These pesticides included bifenthrin, chlorpyrifos, diazinon, diuron, fipronil, and simazine, which are known surface water contaminants and/or are currently under re-evaluation. Chemical properties for the six pesticides were obtained from FOOTPRINT database (FOOTPRINT, 2010). Toxicity data was retrieved from multiple sources (NPIC, 2010; UCD, 2010a, 2010b, 2010c, 2010d; USEPA, 2011a). Input data for the two sets of pesticides are listed in Table 5 (chemical property data) and Table 6 (toxicity data).

3.2.2. Data Acquisition

The physicochemical properties and degradation half-lives for selected pesticides were retrieved from the registration evaluation reports or from the literature (Table 5). If multiple numerical values are available for a parameter, their geometric mean will be used in the calculation of indicators. If only a range is provided, the mean value of the upper and lower bounds will be applied.

Table 5. Summary of physicochemical property and degradation half-lives for selected pesticides

Active ingredient	SOL	KOC	HYDROL	AERO	ANERO	FD	AERO_W	ANERO_W	HLW	HLD
A	0.28	35838	30	15.8	200					
B	2.8	459	365			69			45	126.7
C	2.56	1580		101	60	77			29	163
D	2100	27	270			34			30	60
E	130	252	999	1358		1358		999		999
F	0.0225	17757	999	15			32	174		
G	0.17	11708	3				31	71		
H	22	1294	999	618	120			999	8	485
I	0.33	24300	34			90		105	4	16
J	180.6	7044	999	999		1400				
K	2040	23.5	16			23				26
L	200	576	9.9			2.2		0.56		
M	30	225				1.13	2.48	2.48		
N	2.8	328	365	365		271			91.4	777
O	78100	68.5				7				
P	15	3760		120		85			3	1053
Q	1	339.5	30			222	231	208	0.37	
R	150	1086	53.5			214			6	636
S	0.44	5247	97			0.2			0.15	0.13
T	0.492	2559	999			146			3.9	9.3
U	429	193.8	999	78	48	56			129	250
chlorpyrifos	1.05	8151	25.5			21			5	36.5
diazinon	60	643	138			18.4			4.3	10.4
diuron	35.6	1067	999			89			8.8	48
bifenthrin	0.001	236610	999			84.6			8	251
simazine	5	130	96			90			46	33
fipronil	3.78	577	999			65			54	68

Notes:

- 1) -For the first 21 pesticides, data was retrieved from registration packets and evaluation reports. For the last 6 pesticides, data was taken from FOOTPRINT database (FOOTPRINT, 2010)
- 2) -A value of 999 is set as a numerical value for the “stable” reaction processes. This is used for the convenience of programmatic data processing.

For toxicity data, acute toxicity values for freshwater and saltwater fish and invertebrate species were considered (Table 6). The most sensitive species (i.e., with lowest LC₅₀ or EC₅₀) was used for toxicity rating. Toxicity values for aquatic plants were not considered in the current evaluation process because data are not required for registration by USEPA and measured toxicity endpoints (i.e., growth and reproduction) for aquatic plants are usually associated with chronic toxicity.

Table 6. Aquatic acute toxicity values (µg/L) for selected pesticides

Active ingredient	Rainbow trout	Bluegill/fathead minnow	<i>Daphnia magna</i>	Mysid shrimp	Sheepshead minnow
A	30000	5940	92670	N/A	7870
B	572	320	9880	1500	960
C	435	970	940	60.4	N/A
D	>120000	>120000	2500-5000	8000	>98000
E	61000	33000	67000	34000	72000
F	2.7	13	0.57	0.02	17
G	1.3	3.2	1.5	0.98	26
H	2,200	6,300	4,200	750	3900
I	138	190	280	N/A	N/A
J	5300	3850	2630	N/A	>3400
K	>1000000	>1000000	720000	N/A	N/A
L	10300	N/A	50000	N/A	N/A
M	2,540	2,200	4270	N/A	1960
N	6600	750	1800	3200	410
O	3620	5800	19940	15000	14000
P	800	1200	770	150	N/A
Q	13800	15100	11.6	1150	12000
R	1000	1300	3200	510	N/A
S	130 (NOEL)	790	N/A	N/A	N/A
T	>820	>870	>920	490	650
U	>69000	>74000	>91000	79000	94000
chlorpyrifos	14	1.8	0.1	0.04	N/A
diazinon	90	460	0.52	4.2	N/A
diuron	4900	N/A	12000	1100	6700
bifenthrin	0.15	0.35	1.6	0.003	17.5
simazine	>10000	6400	1000	N/A	>4300
fipronil	246	83	190	0.14	N/A

Notes: For the first 21 pesticides, data was retrieved from registration packets and evaluation reports. For the last 6 pesticides, data was taken from multiple sources (NPIC, 2010; UCD, 2010a, 2010b, 2010c, 2010d; USEPA, 2000, 2007b, 2007c, 2010a, 2010b).

3.2.3. Derived Indicators

The rating criteria (Tables 2-4) are applied to the input data in Tables 5 and 6. Resulting indicators of runoff potential, persistence, and freshwater toxicity are shown in Table 7.

Table 7. Classification of runoff potential, persistence, and freshwater toxicity for the selected pesticides ^{(1),(2)}

Active ingredient	Aqueous runoff potential	Persistence in water	Freshwater toxicity	Sediment runoff potential	Persistence in sediment
A ⁽³⁾	H	M	M	H	H
B	H	M	H	M	H
C	H	L	VH	H	H
D	H	M	M	L	M
E	H	H	L	M	H
F	L	M	VH	M	H
G ⁽³⁾	H	L	VH	H	L
H	H	L	H	H	H
I ⁽³⁾	H	L	H	H	L
J	H	H	M	H	H
K	H	L	L	L	L
L	H	L	L	L	L
M	H	L	M	L	L
N	H	M	H	M	H
O	H	L	M	L	L
P	H	L	H	H	H
Q	H	L	VH	M	H
R ⁽³⁾	H	L	H	H	H
S ⁽³⁾	H	L	H	H	L
T	M	L	H	H	L
U	H	H	L	M	H
chlorpyrifos	H	L	VH	M	M
diazinon	H	L	VH	L	L
diuron	H	L	M	H	M
bifenthrin	L	L	VH	H	H
simazine	H	M	H	M	M
fipronil	H	M	VH	M	M

Notes:

- 1) - “L”=Low, “M”=Intermediate, “H”=High, and “VH”=Very High (for toxicity only, Table 4)
- 2) -Sediment toxicity values are not available for most of the selected pesticides (except for bifenthrin, chlorpyrifos, and fipronil, as provided in appendix #1), and estimated from the corresponding water toxicity and KOC value. Please refer to Section 2.4 and Appendix #1 for details. The estimated sediment toxicity is only used to demonstrate the proposed procedure of initial screening.
- 3) -For pesticides released directly into water, the runoff potential is assumed to be “high” for both absorbed and dissolved phases. See Section “2.2 Runoff Potential” for more details on this assumption, and the report part 2 for the pesticide use patterns associated with the evaluated products.

3.2.4. Initial Screening Results

Demonstrated in Table 8 are the results of initial screening for the selected pesticides, in comparison with the registration recommendations based on best professional judgment, retrieved from the evaluation reports. Sediment toxicity was not available for most of the selected pesticides, and the toxicity rating was based on the corresponding water toxicity. Therefore, the validation of the proposed method was focused on the dissolved phase. Generally, the procedure of stage I evaluation generates consistent or conservative results compared to the recommendations by best professional judgment (Table 9). Therefore, we concluded that, the proposed initial screening has the capability to identify pesticides which [1] are unlikely to cause surface water problems, or [2] may cause potential problems and require additional evaluation. All chemicals in the second set of pesticides (chlorpyrifos, diazinon, diuron, bifenthrin, simazine, and fipronil) are listed by CDPR as “pesticides with a high potential to contaminate surface water” based on detections in water column or sediment (Pepple, 2009). The results in Table 8 are generally compared to the identification, by requiring chlorpyrifos, diazinon, bifenthrin, simazine, and fipronil for additional evaluation. For diuron, it passes the stage 1 evaluation mainly because the registration evaluation is based on acute toxicity data for fish and invertebrates with a lowest LC₅₀ of 1100 ppb (Table 6), which is much lower than the benchmark (2.4) or drinking water standard (2.0) used in identifying pesticides with a high potential to contaminate surface water (Pepple, 2009).

Table 8. Recommendations from model-based evaluation vs. best professional judgment for surface water protection ⁽¹⁾

Active ingredient	Recommendations by stage I evaluation		Best professional judgment based recommendations
	Dissolved phase	Adsorbed phase (2)	
A	S	S	S
B	R	-	S
C	R	R	C (sed. toxicity test & runoff test)
D	S	-	S
E	S	-	S
F	R	R	S
G	R	R	C (marina test)
H	R	S	C (sed. toxicity test)
I	R	S	S
J	S	S	C (sed. toxicity test)
K	S	-	S
L	S	-	S
M	S	-	S
N	R	-	C (runoff test)
O	S	-	S
P	R	S	S
Q	R	-	C (runoff test)
R	R	S	N
S	R	S	S
T	S	S	S
U	S	-	S
chlorpyrifos	R	R	
diazinon	R	-	
diuron	S	S	
bifenthrin	R	R	
simazine	R	-	
fipronil	R	-	C (runoff test)

Notes:

- 1) - “S” = support registration without conditions; “N” = not support registration; “C” = support conditional registration; and “R” = require additional evaluation. “Best professional judgment based recommendation” was the original recommendations in the evaluation reports.
- 2) - Evaluations for sediment-bound pesticides were only conducted for those with KOC > 1000, for which USEPA requires sediment toxicity tests (USEPA, 2007a). For pesticides without reported sediment toxicity, we estimated sediment toxicity from the corresponding water toxicity. Therefore, the evaluation results for adsorbed pesticides won’t be used in the comparisons best professional judgment based recommendations.

Table 9. Summary of the initial screening results

Active ingredients	Recommendations by stage I evaluation (dissolved phase)	Best professional judgment based recommendations	Notes
A, D, E, J, K, L, M, O, T, and U	S	S	Consistent results
C, G, N, Q, and R	R	C (runoff test) or N	Consistent results
B, F, H, I, P, and S	R	S or C (sed. toxicity test)	Conservative results

4. - Discussion and Conclusion

1. - The proposed methodology serves as an initial screening tool for assessing runoff potential, persistence and toxicity of a pesticide active ingredient. Only physicochemical properties and aquatic toxicity are considered in the stage I procedure. The approach allows for an initial estimation of environmental distribution and aquatic risks of pesticides.
2. - For pesticides which require additional evaluation as identified by the initial screening, we proposed a second stage to incorporate additional information such as pesticide use pattern and application rate to refine the evaluation and registration recommendations.
3. - Degradates and formulated products are not included in this demonstration due to limited data availability in the registration package. But the methodology is designed for a general pesticide evaluation, and the same evaluation process can be applied to degradates and formulated products with required chemical and toxicity data, and the final recommendation should be based on combined results for all evaluated chemical species.
4. - The demonstration of the methodology in this report was mainly based on the mean or median values of physiochemical properties. A margin of safety could be introduced for the classifications of runoff potential and persistence if sufficient data is available. For example, the upper or lower 90 confidence limit of KOC, water solubility, and reaction half-lives could be applied to the classifications for more conservative evaluations.

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Appendix 1 Notes on Comparison of Pesticide Acute Toxicity on *Daphnia*, *Ceriodaphnia*, *Chironomus* and *Hyaella*

The purposes of the comparison are two folds: 1) to find out whether *Daphnia magna* and *Chironomus* or *Hyaella* LC₅₀ values are correlated and whether one can be indicative of another in toxicity rating; 2) to justify whether additional data requirement on acute toxicity of benthic invertebrates such as *Chironomus* or *Hyaella* is appropriate for the evaluation process of pesticide registration. Comparable data between species (i.e., *Daphnia* vs. *Chironomus*, *Daphnia* vs. *Hyaella*) were extracted from the OPP ecotox database (USEPA, 2011b). The toxicity values (LC₅₀) are chemical concentrations in soluble phase including water or pore-water column. Toxicity data for the comparison between *Hyaella* vs. *Ceriodaphnia* were cited from open literatures (Table 12).

Daphnia vs. *Chironomus*

Seventeen insecticides and 16 herbicides that have LC₅₀ values available for both *Daphnia magna* and *Chironomus* (*C. tentans* and *C. plumosus*) were sorted out from the OPP database (Table 1). The scattered plots (Figures 1 and 2) show poor correlations on paired LC₅₀ values between the two taxa. However, 16 out of 17 insecticides have the same toxicity ratings from both taxa (Table 1). Only 4 out of 16 herbicides are similar in toxicity rating. No correlation trend is observed in other 12 herbicides.

Daphnia vs. *Hyaella*

Only 5 pesticides with LC₅₀ values of *Daphnia* and *Hyaella* were found in the database (Table 2). There is no correlation between the LC₅₀ values of both species.

Hyaella vs. *Ceriodaphnia*

Table 3 listed *Hyaella* (water and sediment) and *Ceriodaphnia* LC₅₀ values for 5 pyrethroids, 2 OPs (chlorpyrifos and diazinon) and fipronil. In general, *Hyaella* are more sensitive to pyrethroids and fipronil but not organophosphates. However, both species are given the same toxicity rating for each chemical.

Conclusion:

- 1) - There are very limited acute toxicity data available for benthic invertebrates such as *Hyaella* and *Chironomus*.
- 2) - No correlations are observed in LC₅₀ values between *D. magna* and other benthic invertebrates.
- 3) - For insecticides that are highly toxic to *D. magna* or *C. dubia* (LC₅₀ < 1000 ppb), it is highly likely that their toxicity ratings in benthic invertebrates will fall in the same toxicity category.
- 4) - For herbicides and other pesticides with intermediate or slight toxicity to *Daphnia* or one of the invertebrates, additional toxicity data from benthic species may be helpful to re-categorize their toxicity ratings.

- 5) -By combining all data pairs in the tables, most of pesticides have sediment toxicity in the same category with their corresponding category for water toxicity.
- 6) -When data is not available, therefore, the category of sediment toxicity for a pesticide was set the same as the corresponding category for its water toxicity. This assumption was not made for numerically estimating the sediment toxicity, but used only for the descriptive classification of toxicity values for benthic invertebrates when the appropriate data is not available.

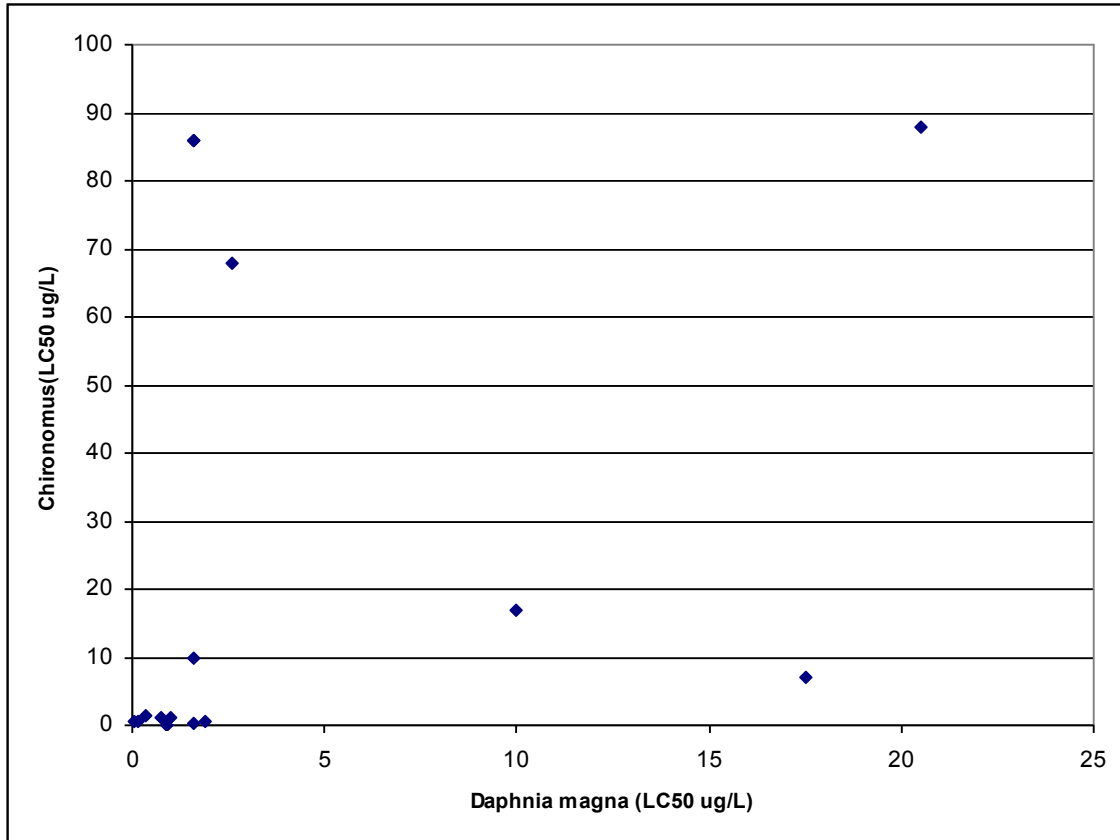


Figure 2. Scattered plot of acute toxicity between *Daphnia magna* and *Chironomus* for 15 insecticides. Note: kepone and oxamyl in Table 10 were not included because their LC₅₀ values were out of the scale of the figure scale

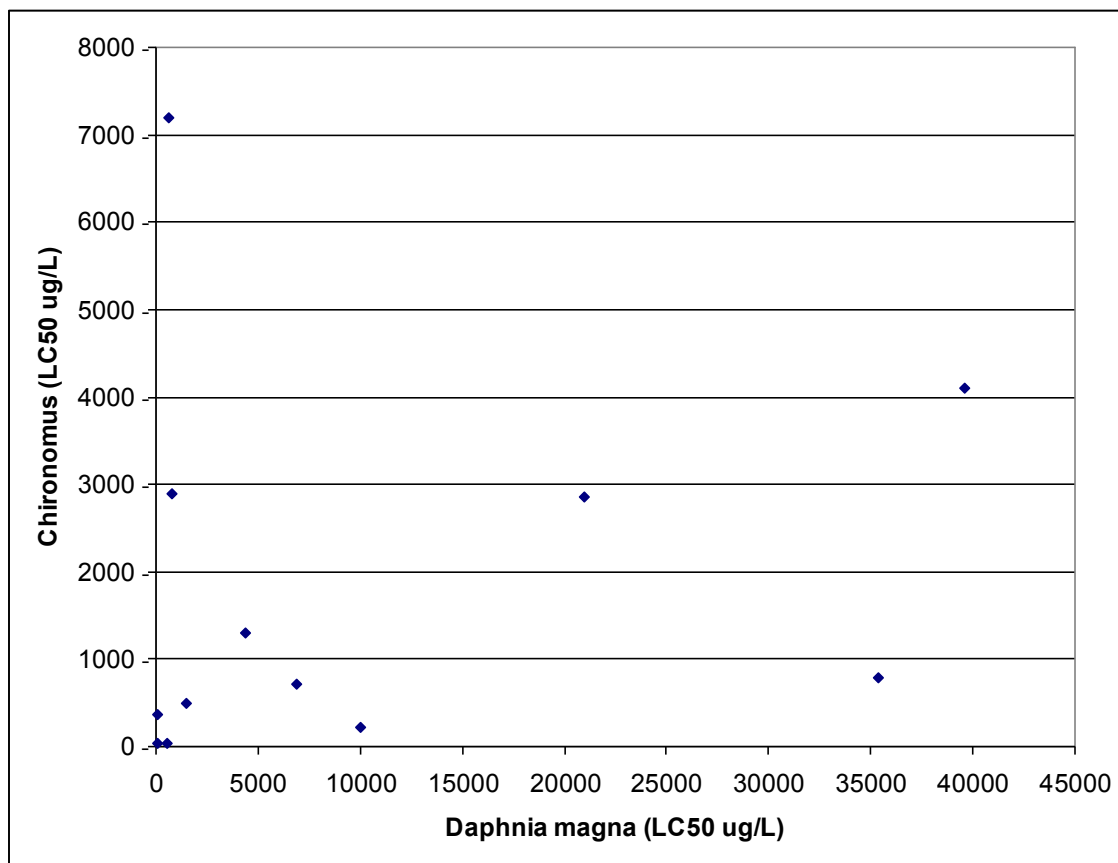


Figure 3. Scattered plot of acute toxicity between *Daphnia magna* and *Chironomus* for 12 herbicides. Note: ethephon, benomyl, chlorthal dimethyl, and glyphosate in Table 10 were not included because their LC₅₀ values were out of the scale of the figure scale -

Table 10. Acute toxicity ratings of insecticides and herbicides on *Daphnia magna* and *Chironomus*. Chemical concentrations were measured from water or pore-water column (USEPA, 2011b)

Chemical	Use pattern	Acute toxicity (LC ₅₀ µg/L)		Toxicity rating
		<i>D. magna</i>	<i>Chironomus</i>	<i>D. magna/Chironomus</i>
Bifenthrin	insecticide	1.6	0.33	VH/VH
Chlorpyrifos	insecticide	0.9	0.017	VH/VH
Cyfluthrin	insecticide	0.141	0.44	VH/VH
Cypermethrin	insecticide	0.75	1.2	VH/VH
Diflubenzuron	insecticide	2.6	68	VH/VH
Profenofos	insecticide	1.6	86	VH/VH
Fenitrothion	insecticide	17.5	7	VH/VH
Fenvalerate	insecticide	0.05	0.43	VH/VH
Pydrin	insecticide	1.6	10	VH/VH
Kepone	insecticide	260	320	H/H
Methomyl	insecticide	20.5	88	VH/VH
Mirex	insecticide	1	1	VH/VH
Oxamyl	insecticide	3050	180	M/H
Permethrin	insecticide	1.88	0.56	VH/VH
Profenofos	insecticide	1.6	86	VH/VH
Terbufos	insecticide	0.35	1.4	VH/VH
Toxaphene	insecticide	10	17	VH/VH
Atrazine	herbicide	6900	720	M/H
Ethephon	herbicide	31700	165000	M/N
Oxyfluorfen	herbicide	1500	498.5	M/H
Thiobencarb	herbicide	101.2	364	H/H
2,4-D	herbicide	600	7200	H/M
Alachlor	herbicide	21000	2850	L/M
Benomyl	herbicide	317.5	100000	H/N
Chlorthal dimethyl	herbicide	100000	100000	N/N
Fluchloralin	herbicide	560	31.1	H/VH
Fluometuron	herbicide	10000	220	M/H
Fluridone	herbicide	4400	1300	M/M
Glyphosate	herbicide	780000	43000	N/M
Linuron	herbicide	767	2900	H/M
Metolachlor	herbicide	39600	4100	L/M
Propachlor	herbicide	35400	790	L/H
Tribufos	herbicide	58.4	40	VH/VH

Note: VH=very highly toxic; H=highly toxic; M=intermediately toxic; L=slightly toxic; N=non-toxic.

Table 11. Acute toxicity ratings of pesticides on *Daphnia magna* and *Hyalella azteca*. Chemical concentrations were measured from water or pore-water column (USEPA, 2011b)

Pesticide	Use pattern	Acute toxicity (LC ₅₀ µg/L)		Toxicity rating
		<i>D. magna</i>	<i>H. azteca</i>	
Pentachlorophenol	Preservative	452	230	H/H
Boscalid	Fungicide	2630	97000	M/L
Thiacloprid	Insecticide	1050	37	M/VH
Thiacloprid metabolite	Insecticide	96100	31180	L/L
Chlorantraniliprole	Insecticide	16.6	389	VH/H

Note: VH=very highly toxic; H=highly toxic; M=intermediately toxic; L=slightly toxic; N=non-toxic.

Table 12. Acute toxicity ratings of insecticides on *Ceriodaphnia dubia* and *Hyalella azteca* in water and in sediment

Pesticide	Acute toxicity (LC ₅₀ µg/L)			Toxicity rating	References
	<i>H. azteca</i>	<i>H. azteca</i>	<i>C. dubia</i>		
	Water (µg/L)	Sediment (µg/g [OC])	Water (µg/L)		
bifenthrin	0.0093	0.0129	0.142	VH	[1][2][3]
cyfluthrin	0.0023	0.0137	0.344	VH	[1][3][4]
L-cyhalothrin	N/A	0.0056	0.2	VH	[1][3]
permethrin	0.021	0.2	0.25	VH	[1][2][3]
cypermethrin	0.00125	0.015	0.683	VH	[3][5]
chlorpyrifos	0.086	0.399	0.053	VH	[1][6][7]
diazinon	6.51	N/A	0.32	VH	[7][8]
fipronil	N/A	0.306	17.7	VH	[9][10]

Note: VH=very highly toxic; H=highly toxic; M=intermediately toxic; L=slightly toxic; N=non-toxic.

References: [1] (Amweg *et al.*, 2005); [2] (Anderson *et al.*, 2006); [3] (Wheelock *et al.*, 2004); [4] (Weston and Jackson, 2009); [5] (Maund *et al.*, 2002); [6] (Phipps *et al.*, 1995); [7] (Bailey *et al.*, 1997); [8] (Ankley and Collyard, 1995); [9] (Ma, 2006); [10] (Konwick *et al.*, 2005)

Appendix 2 Testing Results for Runoff-Potential Rating

Notes:

[1] Runoff potential test results for the 172 pesticides in the E fate database (Spurlock, 2008). Only “High” runoff potentials are identified as “H”, while other groups of “Intermediate” and “Low” runoff potentials are indicated by blank cells.

[2] The chemical properties in the E fate database (Spurlock, 2008) may have different values from those registrant-submitted data as shown in Table 5 and Appendix 2, and thus may result in different runoff-potential classifications.

Chem-code	Chemical name	SOL	KOC	FD	Runoff potential	
					sediment	aqueous
573	1,3-DICHLOROPROPENE	2250	66	51.6		H
1685	ACEPHATE	818000	2	1.685		H
5762	ACETAMIPRID	3600	244.8929	13.55		H
5338	ACIBENZOLAR-S-METHYL	7.7	978.5714	4.15		
3	ACROLEIN	238000	89.7619	6		H
678	ALACHLOR	240	127.5	13.15		H
575	ALDICARB	5870	49.8	16.7		H
18	AMETRYNE	112.2	236.25	73		H
2016	AMITRAZ	0.093	576.1364	0.5		
256	ANILAZINE	8.02	2071.667	11		
45	ATRAZINE	32.5	86.45	85.9		H
5025	AZAFENIDIN	16	247.9221	66.5		H
314	AZINPHOS METHYL	27.95	776.5	8.115		H
4037	AZOXYSTROBIN	6.35	527.7778	31.9		H
53	BENEFIN	0.0998	9310.417	123.8606	H	
1552	BENOMYL	2	1212.167	82	H	H
2263	BENSULFURON METHYL	216	288.1818	26.85		H
70	BENSULIDE	5.6	3900	15.2		
5657	BIFENAZATE	3.76	1778	4		
2300	BIFENTHRIN	0.000014	264276	109.5	H	
83	BROMACIL	700	14.05882	146		H
834	BROMOXYNIL OCTANOATE	0.08	190	4.31		
3947	BUPROFEZIN	0.2635	3298.113	45.6	H	
565	BUTYLATE	44	422.2222	12.3		H
104	CAPTAN	3.3	151	4.05		
105	CARBARYL	113	138.6667	9.485		H
106	CARBOFURAN	351	50.11872	30.35		H
5130	CARFENTRAZONE-ETHYL	22	17.58454	4.75		H
2184	CHLORAMBEN	700	21	14		H
677	CHLOROTHALONIL	1.2	1111.111	60	H	H
253	CHLORPYRIFOS	1.39	9373.249	46	H	H
2143	CHLORSULFURON	31800	35.47273	22.15		H
179	CHLORTHAL-DIMETHYL	0.5	2565	21.4		

Chem-code	Chemical name	SOL	KOC	FD	Runoff potential	
					sediment	aqueous
3566	CLETHODIM	384	60.5	3.09		H
2249	CLOFENTEZINE	0.0025	45300	25	H	
3537	CLOMAZONE	1100	159.8772	16.9		H
5792	CLOTHIANIDIN	259	123.3333	561.5		H
1640	CYANAZINE	155	236.7547	37.5		H
516	CYCLOATE	95	272	10.71		H
2223	CYFLUTHRIN	0.0023	124000	22	H	
4002	CYMOXANIL	780	106.575	4.8		H
2171	CYPERMETHRIN	0.004	310000	27	H	
233	DAZOMET	3630	260	0.188		H
3010	DELTAMETHRIN	0.0002	533750	54.5	H	
1748	DESMEDIPHAM	0.901	691.3684	26.65		
198	DIAZINON	60	1856.111	9.07		H
112	DICHOLOBENIL	2.1	171	55		H
5060	DICHLORPROP-P	108000	15.55556	4.8		H
2034	DICLOFOP-METHYL	1.9	14025	41	H	H
81	DICLORAN	6.4	747.5	93.8		H
346	DICOFOL	0.83	6994.643	65.55	H	
468	DIENOCHLOR	0.025	510571.4	3.9		
1995	DIETHATYL-ETHYL	120	202.0287	20		H
1930	DIFENZOQUAT METHYL SULFATE	817000	64637.36	83	H	H
1992	DIFLUBENZURON	0.08	7584.615	40.7	H	
216	DIMETHOATE	39800	10	7.8		H
231	DIURON	36.4	540.2321	114.5	H	
259	ENDOSULFAN	0.32	12000	89.75	H	
264	EPTC	345	144.5707	2.07		H
2321	ESFENVALERATE	0.00131	436515.8	31.05	H	
2166	ETHALFLURALIN	0.293	5344.444	51	H	
1900	ETHOFUMESATE	50	145.9821	122.25		H
404	ETHOPROP	843	183.4995	23.3		H
5849	ETOXAZOLE	0.0704	20550	3.5		
5878	FAMOXADONE	0.0815	3636.957	12.3		
1857	FENAMIPHOS	329	224.2619	9.95		H
1980	FENARIMOL	13.8	723.75	280.5	H	
3905	FENBUCONAZOLE	2.15	2925.714	302	H	H
4032	FENHEXAMID	23.7	905.625	5.33		H
2311	FENOXAPROP ETHYL	0.8	9490	8.1		
2283	FENOXYCARB	5.66	1752.778	28.3		H
2234	FENPROPATHRIN	0.0363	42500	16.35	H	
3995	FIPRONIL	1.9	668.75	131	H	
5886	FLONICAMID	5200	12.3	3.1		H
2186	FLUAZIFOP-BUTYL	1.1	1812.857	7.095		
5027	FLUDIOXONIL	1.83	1340.833	191	H	H
5802	FLUMIOXAZIN	1.79	244.5455	15.05		
166	FLUOMETURON	111	87.16667	103		H
5768	FLUROXYPYR	6500	291.8016	19		H

Chem-code	Chemical name	SOL	KOC	FD	Runoff potential	
					sediment	aqueous
254	FONOFOS	16.9	1051.296	22.35		H
5851	FORAMSULFURON	3290	65	12.15		H
1871	HEXAZINONE	33000	45.2392	138.5		H
2303	HEXYTHIAZOX	0.12	2754.248	295.5	H	
2203	HYDRAMETHYLNON	0.2	200595.2	44	H	
5911	IMAZAPIC	479000	55.55556	148		H
2340	IMAZETHAPYR	711	58.61538	110		H
3849	IMIDACLOPRID	514	288.9835	58.9		H
5331	INDOXACARB	0.2	4928.571	20.1		
2282	ISAZOPHOS	168	107.2727	33.9		H
5451	KRESOXIM-METHYL	2	499.6364	6.6		
2297	LAMBDA CYHALOTHRIN	0.005	297500	23.35	H	
359	LINDANE	7	1636.508	172	H	H
361	LINURON	77.2	417.165	65.9		H
367	MALATHION	125	165	9		H
211	MANCOZEB	13.1	6000	98.95	H	H
5898	MESOSULFURON-METHYL	483	40	78		H
2132	METALAXYL	7100	167.381	65.25		H
379	METALDEHYDE	188	33.9359	180		H
1689	METHIDATHION	240	310	5		H
375	METHIOCARB	27	617.4877	12		H
383	METHOMYL	57900	40	29.785		H
5698	METHOXYFENOZIDE	3.3	394.1667	145		H
385	METHYL BROMIDE	17500	126.4996	3.8		H
394	METHYL PARATHION	70.3	522.9167	2		H
1996	METOLACHLOR	492.5	210.8333	113		H
1692	METRIBUZIN	1031.5	50	88.75		H
2222	METSULFURON-METHYL	2790	61.09091	10		H
480	MEVINPHOS	600000	78.4	4.1875		H
449	MOLINATE	970	216.6667	14.54		H
418	NALED	200	221.4286	1.53		H
1728	NAPROPAMIDE	74	667.8608	10		H
3829	NICOSULFURON	1036.5	27.87879	34.6		H
439	NITRAPYRIN	72.1	355.3571	33.2		H
2019	NORFLURAZON	33.7	460	180		H
5754	NOVALURON	0.053	2296.382	125	H	
1868	ORYZALIN	2.6	886.6667	121	H	
2017	OXADIAZON	1	2311.667	130	H	H
1910	OXAMYL	280000	31.57895	31.82		H
1973	OXYFLUORFEN	0.116	6601.389	175	H	
410	OXYTHIOQUINOX	1	22583.33	1.55		
459	PARATHION	12.5	1420	17.25		H
464	PCNB	0.1	5975	224.5	H	
590	PEBULATE	100	512.3529	6.055		H
1929	PENDIMETHALIN	0.275	15000	42	H	
5889	PENOX SULAM	408	43.55	11.8		H
2008	PERMETHRIN	0.07	277000	38.35	H	

Chem-code	Chemical name	SOL	KOC	FD	Runoff potential	
					sediment	aqueous
675	PHENMEDIPHAM	1.8	7500	63.15	H	H
478	PHORATE	29	538.3523	1.76		H
335	PHOSMET	25	6288.71	8.24		
593	PICLORAM	430	29	108		H
486	PIPERONYL BUTOXIDE	14.3	1536.438	13.1		H
2236	PRODIAMINE	0.183	8190	83.8	H	
2042	PROFENOFOS	28.4	2414.286	14.295		
499	PROMETON	393.5	100	246.5		H
502	PROMETRYN	32.9	240.3333	71.1		H
503	PROPANIL	152	468	1.38		H
445	PROPARGITE	1.93	7283.333	87	H	H
2276	PROPICONAZOLE	100	600	115	H	
694	PROPYZAMIDE	12.9	825	53.5		H
5232	PYMETROZINE	290	49.63889	169		H
5759	PYRACLOSTROBIN	19	8444.444	71	H	H
3939	PYRIDATE	1.49	40.96997	18.85		
4019	PYRIPROXYFEN	0.367	14436.36	26.05		
3835	RIMSULFURON	5560	55	7.95		H
190	S,S,S-TRIBUTYL PHOSPHOROTRITHIOATE	2.3	9466.667	31.5		H
2177	SETHOXYDIM	10295	50.13095	70.4		H
603	SIDURON	22.3	223.9556	50.75		H
531	SIMAZINE	6.15	151.7011	83.5		H
2149	SULFOMETURON METHYL	244	91.86655	15		H
2195	TAU-FLUVALINATE	0.0122	447204.7	62	H	
3850	TEBUCONAZOLE	32	936.1806	224	H	
3957	TEBUFENOZIDE	0.83	665.8824	36.05		
1810	TEBUTHIURON	2600	79.75	690.5		H
532	TERBACIL	710	56.66667	208		H
1691	TERBUTRYN	22	2375	127	H	H
580	TERRAZOLE	105	93.33333	8.6		H
5598	THIAMETHOXAM	4100	48.47059	92		H
3984	THIAZOPYR	2.33	219.6667	69.9		H
1933	THIOBENCARB	27.5	594.7368	27.8		H
2202	THIODICARB	23.5	206.1538	5		H
1696	THIOPHANATE-METHYL	24.6	300	4.2		H
2329	TRALOMETHRIN	0.08	504092.3	2.29		
2133	TRIADIMEFON	64	387	35.1		H
88	TRICHLORFON	120000	13.91636	2.2		H
5321	TRIFLOXYSTROBIN	0.61	3580	9.425		
2260	TRIFLUMIZOLE	18.1	710.625	6.4		H
597	TRIFLURALIN	0.3	3532.465	114.5	H	
3875	TRIFLUSULFURON-METHYL	260	55.65217	2.895		H
2345	TRINEXAPAC-ETHYL	15650	534.1667	1.335		H
2129	VINCLOZOLIN	3.41	292.0741	181		H
5769	ZOXAMIDE	0.681	1240	12.3		