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Methodology for Screening Pesticide Products with High Exposure Potentials to Marine/Estuarine Organisms

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Summary

This report presents a methodology for the Department of Pesticide Regulation's (DPR) Surface Water Protection Program (SWPP) to identify pesticide products with relatively high potentials to enter estuaries and the ocean. The method is developed to provide a standard procedure for determining the appropriate toxicity endpoint in evaluating pesticide products submitted for registration in California. Identified pesticides will be evaluated against toxicity to the most sensitive species among freshwater and marine/estuarine organisms, while other pesticides will be subject to evaluation with freshwater organisms only. The screening method is composed of two components – the use patterns of a pesticide product and the chemical properties of the pesticide active ingredient (AI):

1) Use pattern analysis identifies pesticide products with proposed use patterns that are significant in coastal areas and associated with high likelihood of releasing AIs to surface water. Pesticide products for urban uses and aquatic uses will always be included, and thus data analysis in this report mainly focuses on crop types for agricultural uses, including those receiving gravity-dominated irrigation, and extensively planted or intensively treated with pesticides in coastal areas. Based on analysis of irrigation data, GIS data and Pesticide Use Reporting (PUR) database, the following crops were identified: alfalfa/pasture, broccoli, , celery, corn, cotton, grain and hay crops (i.e., barley, oats, other hay/non alfalfa, and winter wheat), grapes, lettuce, nursery (outdoor), strawberry, and tomatoes.

2) Chemical property analysis identifies pesticide products with high potentials to be transported from remotely treated locations (such as in the Central Valley) to estuaries and the ocean, even when the products are not significantly used in coastal regions. Pesticides with high soil-runoff potential and high/intermediate aquatic persistence are considered in this analysis. Pesticides are categorized based on solubility, field dissipation half-life, soil adsorption coefficient normalized by organic carbon (Koc), and aquatic half-lives in water and sediment, by following the same criteria developed in SWPP's standard pesticide registration evaluation methodology.

1. Introduction

The USEPA Office of Pesticide Programs (OPP) requires toxicity tests for freshwater and marine/estuarine species for pesticide registration. Currently, all available toxicity values are considered in SWPP's product registration evaluation process and the lowest value is used for risk characterization. This approach becomes problematic for evaluating some pesticide products that have a low chance of releasing AIs into estuaries and the ocean under proposed uses. To address this problem, a systematic screening methodology is proposed here to standardize the criteria for determining pesticide products that are subject to evaluation with toxicity to marine/estuarine organisms.

2. Methodology Development
2.1 Overview

For the purpose of analysis, California was geographically divided into two parts – coastal and interior areas, by the USGS Hydrologic Unit Code (HUC) system. Figure 1 demonstrates the location of 4-digit HUC watersheds in California, and major streams and water bodies within each HUC watershed. HUC 1801 (Klamath-Northern California Coastal), 1805 (San Francisco Bay), 1806 (Central California Coastal), and 1807 (South California Coastal) that are situated along the coastline and drain into the Pacific Ocean were classified as coastal areas in this study, as highlighted in orange in Figure 1. This definition is consistent with the hydrologic region delineations used by the California Department of Water Resources for land and water use surveys (http://www.water.ca.gov/landwateruse/). Pesticides to be applied to coastal areas are deemed higher priority because they are more likely to enter estuaries and the ocean than those applied to the interior areas due to geographical proximity to marine/estuarine environments.

Pesticide exposures to marine/estuarine aquatic systems can be contributed by both local sources and remote sources. Local sources refer to pesticide uses within coastal areas defined in Figure 1, where pesticide use patterns are prioritized based on their potential dominance (treated areas) and risks (field conditions) of the target commodities. Remote sources refer to pesticide uses that may not be significant within the defined coastal areas but associated with potentials for long-distance transport within the stream network in California. Those pesticides could be identified by chemical properties of AIs. In summary, two types of data analysis are proposed for the screening of pesticides subject to risk assessment with toxicity to marine/estuarine organisms: use pattern analysis within coastal areas, and chemical property analysis for all pesticides.

For use pattern analysis, because of high population density in coastal areas, pesticide products proposed for urban uses, including residential, commercial and industrial, and right-of-way applications, are considered a high risk use pattern for marine/estuarine species. Aquatic pesticide products are also identified as a high risk use pattern since these products are applied directly to surface waters. For agricultural pesticide application, commodities in coastal areas and associated with a high likelihood of runoff movement into adjacent receiving water bodies (i.e., high risk use patterns) are considered a critical screening criterion. Determination of high risk use patterns and the associated crops was based on SWPP scientists' best professional judgments and modeling efforts (Luo and Deng, 2012a). Application of pesticides to the selected crops represents the most important pathways of pesticide transport from local sources to estuaries and the ocean.
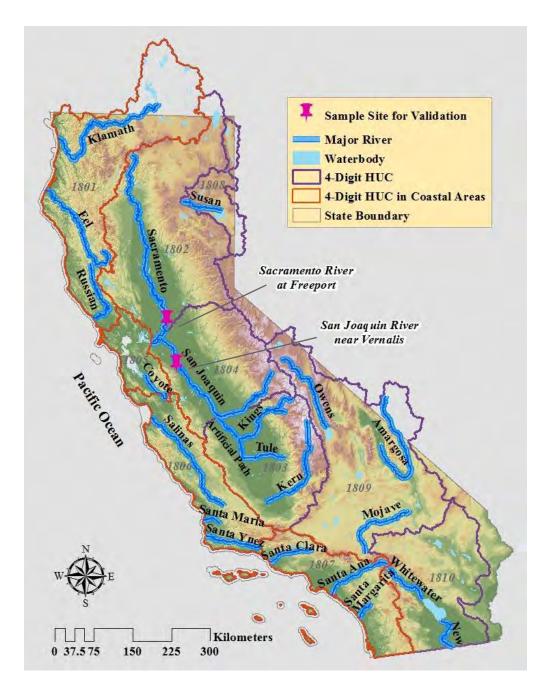
Figure 1: Location of 4-digit HUCs in California, and major streams and waterbodies in each HUC watershed, and water quality sample sites used for validation. Streamlines, waterbodies, and HUC boundaries are derived from the National Hydrology Dataset (NHD) (http://nhd.usgs.gov/data.html).

In addition to crop types, chemical properties are another critical indicator involved in the screening. Pesticides that have a high potential for off-site movement from soils and are highly persistent in aquatic environment may also have the ability to enter estuaries and the ocean even though they are applied outside of coastal areas. Screening by chemical properties is thereby a necessary supplement to the screening by commodity type to capture any chemicals posing a

sufficient risk to marine/estuarine organisms, especially with respect to those from remote sources. Figure 2 demonstrates the decision flowchart to determine agricultural pesticides that are subject to evaluation with toxicity to marine/estuarine species in addition to freshwater species.
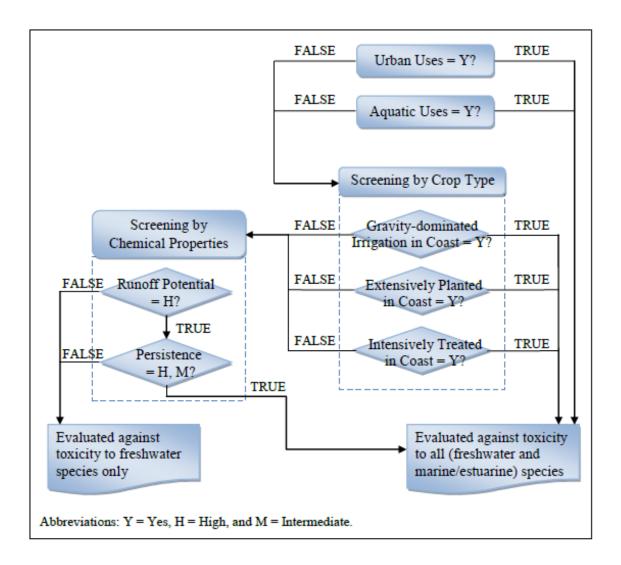

Figure 2: Decision flowchart to determine which pesticides are subject to evaluation against toxicity to marine/estuarine species in addition to freshwater species.

2.2 Screening by crop type

Development of the screening methodology starts with determination of commodities that are associated with pesticide use patterns posing a high risk to marine/estuarine organisms. Following the criteria proposed by Luo and Deng (2012a), four criteria are developed to determine high risk use patterns and the corresponding crops.

1. Crops receiving gravity-dominated (>50%) irrigation in coastal areas are selected. Gravity irrigation methods include flood irrigation, furrow irrigation, basin irrigation, and border irrigation. SWPP expects these methods to have a greater tendency to convey pesticides to waterways than other irrigation methods (e.g., sprinkler, low volume irrigation, and subsurface irrigation) (Luo and Deng, 2012a). Statistics on crop-specific irrigation methods were derived from an irrigation method survey for coastal areas that was conducted by California Department of Water Resources (CDWR, 2010). Table 6 of Appendix A summarizes the results of the latest survey, which sampled approximately 58,000 growers in California about the acreages they planted and the irrigation method they used on 20 possible crop categories in 2010 (CDWR, 2010; Orang et al., 2008). Crops that have 50% or more crop acreage receiving gravity irrigation are highlighted in Table 6. These crops are corn, cotton, and tomatoes.

2. Crops that are extensively planted in coastal areas are selected. The Cropland Data Layer (CDL) published by the US Department of Agriculture National Agricultural Statistics Service (USDA-NASS) (USDA-NASS, 2014b) was used to retrieve crop acreage in coastal areas. The CDL dataset is a raster, geo-referenced, crop-specific, land cover data layer created annually for the continental US using moderate resolution satellite imagery and extensive agricultural ground truth to provide acreage estimates for the state's major commodities (USDA-NASS, 2014a). The CDL dataset is available for California between 2007 and 2013. GIS analysis was performed to retrieve annual crop acreage estimates for 95 commodities documented by the CDL dataset in coastal areas. The share of total crop acreage in coastal areas for each commodity was summarized on a yearly basis during 2007 and 2013. Multiyear data were retrieved and examined to account for annual variation in agricultural production. The results of GIS analysis on CDL data are illustrated in Table 7 of Appendix A. Crops that were planted in 5% or more of the total crop acreage in coastal areas for at least four years during 2007 and 2013 were selected. Five crops were selected according to this criterion, as highlighted in Table 7. They are alfalfa/pasture, barley, grapes, oats, other hay/non alfalfa, and winter wheat. These crops account for 70-80% of the overall crop acreage in coastal areas. Pesticides that are applied to these extensively-planted crops have a high potential to be found in estuaries and the ocean.

3. Crops that are intensively treated with pesticides in coastal areas are selected. The PUR database was employed to derive cumulative treated area in a year in sections located within the coastal watersheds for commodities having a PUR site code between 2007 and 2012. Multiyear data were reviewed to capture the yearly variation. Table 8 of Appendix A depicts the summary statistics, including the cumulative treated areas and the corresponding rankings of the top 15 crops for each year. Crops that were ranked in top six for at least four years during 2007 and 2012 were selected, and the final list is highlighted in Table 8. These crops are broccoli, celery, grapes, lettuce (leaf and head), nursery (outdoor), and strawberry. They demand higher pesticide usage and thus tend to be more likely to produce pesticide runoff in comparison to the other crops.

Crops that are selected by any of the three criteria are placed in the final list. They are alfalfa/pasture, broccoli, celery, corn, cotton, grain and hay crops (i.e., barley, oats, other hay/non alfalfa, and winter wheat), grapes, lettuce, nursery (outdoor), strawberry, and tomatoes.

The selected crops are grouped by CDWR agricultural land use classification and summarized in Table 1. These particular crops represent pesticide use patterns that have a high risk for movement into surface water in coastal areas. Therefore, pesticides that are applied to these crops have high potentials to be detected in marine and estuarine waters and sediments.

Table 1: Crops associated with pesticide use patterns posing high risks to marine/estuarine organisms, grouped by CDWR agricultural land use classification

Selected Crop	Gravity-Dominated Irrigation in Coast	Extensively Planted in Coast	Intensively Treated in Coast
Grain and hay crops (G)			
Barley		✓	
Oats		✓	
Other Hay/Non Alfalfa		✓	
Winter wheat		✓	
Field crops (F)			
Corn	✓		
Cotton	✓		
Alfalfa/Pasture (P)		✓	
Truck, nursery and berry crops (T)			
Broccoli			✓
Celery			✓
Lettuce			✓
Nursery (Outdoor)			✓
Strawberry			✓
Tomatoes	✓		
Vineyards (V)		✓	✓

2.3 Screening by chemical properties

This section documents the procedure for developing criteria to screen pesticides that are ruled out by the crop type screening but yet have a possibility of entering estuaries and the ocean due to their environmental fate properties. Following the screening methodology developed by SWPP (Luo and Deng, 2012a, 2012b), two indicators – runoff potential from soils and aquatic persistence – were incorporated. Since pesticides are typically partitioned into solution phase and adsorbed phase in a water-sediment system, two suites of criteria were proposed to evaluate runoff potential and aquatic persistence of pesticides in the two phases. Pesticides with a Koc of 1000 or greater are subject to the adsorbed-phase evaluation in addition to the solution-phase evaluation, which is required for all pesticides per SWPP's registration evaluation model (Luo and Deng, 2012a, 2012b).

Runoff potential, defined as a function of solubility (SOL), field dissipation half-life (FD) and Koc (KOC), is one important indicator of pesticide runoff potential from fields in both solution and adsorbed phases. The criteria used to rate the levels of runoff potential are identical with those used in SWPP's pesticide registration evaluation model (Luo and Deng, 2012b) and are presented in Table 2. Pesticides that are classified into the high runoff potential category will be evaluated against the second indicator – aquatic persistence. Table 3 denotes the criteria used to

rate the levels of persistence, which are consistent with the criteria used in SWPP's registration evaluation (Luo and Deng, 2012b).

Table 2: Criteria rating pesticide runoff potential from soils

Criteria	Runoff Potential Rating
Pesticide solution-phase runoff potential	
(SOL ≥ 1 and FD > 20 and KOC < 1×10^5) or (SOL ≥ 10 and KOC ≤ 2000)	High (H)
(KOC ≥ 1×10^5) or (KOC ≥ 1000 and FD ≤ 1) or (SOL < 0.5 and FD < 35)	Low (L)
Everything else	Intermediate (M)
Pesticide adsorbed-phase runoff potential	
(FD ≥ 15 and KOC ≥ 4×10^4) or (FD ≥ 40 and KOC ≥ 1000) or (FD ≥ 40 and KOC ≥ 500 and SOL ≤ 0.5)	High (H)
(FD ≤ 1) or (FD ≤ 2 and KOC ≤ 500) or (FD ≤ 4 and KOC ≤ 900 and SOL ≥ 0.5) or (FD ≤ 40 and KOC ≤ 500 and SOL ≥ 0.5) or (FD ≤ 40 and KOC ≤ 900 and SOL ≥2)	Low (L)
Everything else	Intermediate (M)

Notes: Adopted from Table 2 of Luo and Deng (2012b). SOL = water solubility (mg/L), FD = field dissipation half-life (day), and KOC = organic carbon-normalized soil adsorption coefficient (L/kg[OC]).

Table 3: Criteria rating pesticide persistence in water and sediment

Criteria	Persistence Rating
HL ≥ 100	High (H)
30 ≤ HL < 100	Intermediate (M)
HL < 30	Low (L)

Notes: Adopted from Table 3 of Luo and Deng (2012b). HL = aquatic half-life in water (day) or in sediment.

Persistence is determined as a function of aquatic half-life in water or in sediment (HL). According to Luo and Deng (2012b), HL in water is determined as the minimum of hydrolysis half-life, aerobic aquatic metabolism half-life, and aquatic dissipation half-life in water, whereas HL in sediment is the minimum of anaerobic soil/aquatic metabolism half-life and aquatic dissipation half-life in sediment. Pesticides that are classified into both the high runoff potential category and the high/intermediate persistence category are considered to have a substantial potential to enter estuaries and the ocean even if they are not selected by the crop type screening.

In order to validate the applicability of the proposed screening criteria, a test was conducted to compare the selection results to observed detections. The E-fate database compiled by Spurlock (2008) that contains environmental fate properties of 171 common pesticides was used in the test. The same database was also used for the validation of the registration evaluation methodology, stage 1 (Luo and Deng, 2012b). According to the proposed criteria, 32 pesticides were selected, as listed in Table 4.

Table 4: Comparison between selection results and reported detections in Sacramento River at Freeport and San Joaquin River near Vernalis

Pesticide Selected by Proposed Criteria	Detected in Sacramento R. at Freeport OR San Joaquin R. near Vernalis
ACEPHATE	
BENSULFURON METHYL	
BUTYLATE	
CHLORPYRIFOS	✓
CHLORSULFURON	
CYANAZINE	✓
DIAZINON	✓
DICHLOBENIL	
DIMETHOATE	
DIURON	✓
EPTC	✓
ETHOFUMESATE	
ETHOPROP	
FENAMIPHOS	
FLUOMETURON	
FONOFOS	
FORAMSULFURON	
HEXAZINONE	✓
ISAZOPHOS	
LINDANE	
METALAXYL	
METHYL PARATHION	
METOLACHLOR	✓
MOLINATE	✓
NORFLURAZON	
OXADIAZON	
PARATHION	
PEBULATE	
PROPARGITE	
PROMETRYN	✓
SETHOXYDIM	
SIMAZINE	✓
TEBUTHIURON	
TERBUTRYN	
TERRAZOLE	
THIOBENCARB	✓
THIOPHANATE-METHYL	
TRIFLUMIZOLE	
TRIFLUSULFURON-METHYL	

Note: pesticides with at least 50 samples and at least 30% detection frequency as of November 2014 are checked in the table. See the text and appendix B for more information.

Detections from two US Geological Survey (USGS) monitoring sites – Sacramento River at Freeport (USGS 11447650) and San Joaquin River near Vernalis (USGS 11303500), indicated by pins in Figure 1 – were employed for the comparison. The reasons for choosing these two sites for validation are 1) HUC 1802 (Sacramento) draining into the Sacramento River, and HUC 1804 (San Joaquin) and HUC 1803 (Tulare-Buena Vista Lakes) draining into the San Joaquin River are the only three 4-digit HUC watersheds that are situated in the interior part of California but drain into the Pacific Ocean. The Sacramento River and the San Joaquin River thereby represent pathways of transportation from remote sources to estuaries and the ocean for any pesticides used in non-coastal areas; 2) the two USGS monitoring sites are located in close proximity to the river mouth, which is capable of capturing pesticides that are most likely to enter the Delta, estuaries and ultimately the ocean; and 3) long-term hydrology and water quality monitoring data are available for the sites since the 1990s providing a sample pool sufficient for reliable data analysis.

Long-term pesticide monitoring records for the two sites were retrieved from the National Water-Quality Assessment (NAWQA) program maintained by the USGS (2014). Detection frequency and sample size were summarized for a total of 78 pesticides with available monitoring data as of November 2014, and are presented in Table 10 of Appendix B. Chemicals that had a sample size of 50 or more and were detected 30% of time or over were considered sufficiently representative of the detection pool. According to this criterion, twelve pesticides, highlighted in Table 10, were identified as typical detections at the two monitoring sites. Table 4 compares the selection results with the typical detections. There was a fairly good agreement between selected pesticides and detections. Almost all typical detections were captured by the list of selected chemicals except glyphosate. Glyphosate was not captured because it was not included in the E-fate database and there was no data for its evaluation. The result of the comparison implies that the criteria proposed to rate potential runoff and persistence are viable for identifying pesticides that have high potential to enter estuaries and the ocean based on the pesticide's physico-chemical properties.

Note that validation was only conducted for the dissolved-phase evaluation. The screening criteria for adsorbed-phase evaluation could not be validated directly against measurements due to a lack of sediment monitoring data. However, they have been validated using best professional judgment for registration evaluation purpose and appear to be viable for identifying pesticides that pose high risks to sediment dwelling organisms in aquatic systems (Luo and Deng, 2012b). They are therefore considered sufficient for the sake of endpoint selection for risk assessment.

3. Demonstration

This section demonstrates the use of the proposed method to determine the risk assessment endpoint for product registration evaluation. The demonstration is illustrated in Table 5. Eight products designated for agricultural uses and evaluated for registration application in 2013 and 2014 are included in the demonstration. The products are first screened by crop type. The commodities on which the products are supposed to be applied are identified from the proposed label in the registration packet. If they are any of the crops listed in Table 1 (which are grouped in six categories – G, F, P, T, V, and M in Table 5), a "Yes" will be given for the crop type screening and a recommendation that the product is subject to evaluation against toxicity to all species will be concluded without referring to screening by chemical properties. For example,

products #3, 4, 5, 6, 7, and 8 are proposed to be used on one or more of the crops in the list and therefore identified to be of significant risks to marine/estuarine organisms and should be evaluated against the toxicity to these species in addition to freshwater species. The lowest toxicity value will be the evaluation endpoint. The endpoint recommendation is applicable to both the solution-phase and adsorbed-phase (if applicable) evaluation, respectively. For example, product #4 and 5, which require adsorbed-phase evaluation in addition to solution-phase evaluation, should be evaluated against the lowest toxicity value of all species in both phases (i.e., the lowest toxicity value of all water species and of all sediment dwelling species in freshwater and marine/estuarine aquatic systems).

Pesticide products that are to be applied to commodities other than those in the list will be given a "No" for the crop type screening and moved to the screening by chemical properties. Four chemical properties (SOL, KOC, FD, and HL in Table 5) are incorporated to rate the runoff potential and aquatic persistence of a pesticide in solution phase and adsorbed phase. Pesticides that are rated in the high runoff potential AND high/intermediate persistence category will be given a "Yes" for the chemical property screening and therefore subject to evaluation against toxicity to all species. If "No" is given to both the crop type screening and chemical property screening, the product is considered to pose a low risk to marine/estuarine species and therefore recommended for evaluation against toxicity to freshwater species only. For example, products #1 and 2are ruled out by the crop type screening and thereby moved to the chemical property screening. Product #1 is given a "Yes" for the chemical property screening and considered to pose a high risk to marine/estuarine organisms despite not being applied to crops associated with high risk use patterns, and therefore recommended for evaluation against toxicity to all species. In contrast, products #2 is given a "No" for the chemical property screening. Since this product is ruled out by both the crop type screening and the chemical property screening, SWPP considers it to pose a low risk to marine/estuarine species, and therefore recommended for evaluation against toxicity to freshwater species only. The recommendation is administered to the solution-phase and adsorbed-phase evaluation (if applicable), respectively.

Among the eight products involved in the demonstration for solution-phase evaluation, only one is suggested for evaluation against toxicity to freshwater species only, while the remainder should be evaluated against the lowest toxicity value of all species, which is consistent with the current procedure used for endpoint selection in registration evaluation. For the two products that require adsorbed-phase evaluation, they are suggested for evaluation against the lowest toxicity value of all species, which is again consistent with the current procedure.

Table 5: Demonstration of endpoint determination for registration evaluation by using the proposed methodology

#	AI and Product Info.	Screening by Crop Type					Screening by Chemical Properties					Screening Output			Recommendation (Evaluation with toxicity to)	
		G	F	P	T	V	SOL	KOC	FD	HLw	HLd	Crop	Chem. Prop. Water	Sed	Solution-phase	Adsorbed-phase
1	Clothianidin (insecticide, rice)						327	345	282	999 [a]	26.7	N	Y	-	ALL species	-
2	Cyantraniliprole (insecticide, seed treatment)						12.3	128	49.7	2.9	14	N	N	-	Freshwater species ONLY	-
3	Cyantraniliprole (insecticide)		✓				12.3	128	49.7	2.9	14	Y	N	-	ALL species	-
4	Etofenprox (mosquito adulticide)		✓	✓			0.02	17757	4.8	1.7	15	Y	N	N	ALL species	ALL species
5	Fenazaquin (insecticide)				✓		0.22	28950	44	19.5	266.5	Y	N	Y	ALL species	ALL species
6	Penflufen (fungicide, seed treatment)	✓	✓	✓			10.9	342	62	157	86	Y	Y	-	ALL species	-
7	Picoxystrobin (fungicide)	✓	✓				3.1	965	63.9	36.7	85.5	Y	Y	-	ALL species	-
8	Sulfoxaflor (insecticide)	✓	✓		✓		965	54	1.6	43	188.5	Y	Y	-	ALL species	-

[a]: a value of 999 for half-lives indicates being stable.

Notes: adsorbed-phase evaluation for endpoint selection is only performed for pesticides with a Koc of 1000 or over.

Abbreviations: Screening by crop type – G = grain and hay crops (i.e., barley, oats, other hay/non alfalfa, winter wheat), F = field crops (i.e., corn and cotton), P = alfalfa/pasture, T = truck, nursery and berry crops (i.e., broccoli, celery, lettuce, nursery (outdoor), strawberry, and tomatoes), and V = vineyards. Screening by chemical properties – SOL = water solubility (mg/L), KOC = organic carbon-normalized soil adsorption coefficient (L/kg[OC]), FD = field dissipation half-life (day), HLw = aquatic half-life in water (day), and HLd = aquatic half-life in sediment (day). Screening Output – Chem. Prop. = chemical properties, Water = solution-phase, Sed = adsorbed-phase, Y = Yes, and N = No.

4. Conclusion

Pesticide products associated with the following use patterns or chemical properties will be evaluated for toxicity to marine/estuarine species in addition to freshwater species:

1. Use patterns
   1.1. All urban uses.
   1.2. Aquatic uses.
   1.3. Agricultural uses for the following crops: alfalfa/pasture, broccoli, celery, corn, cotton, grain and hay crops (i.e., barley, oats, other hay/non alfalfa, and winter wheat), grapes, lettuce, nursery (outdoor), strawberry, and tomatoes.
2. Chemical properties: active ingredients with high soil-runoff potential AND high/intermediate aquatic persistence, as defined by the criteria in Table 2 and 3.

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Appendix A: Supporting tables for screening by crop type

Table 6: Crop selection based on irrigation method in coastal areas. Highlighted are crops dominated by gravity-based irrigation (>50%).

Crop	Irrigation Method			
	Gravity (%)	Sprinkler (%)	Low Volume (%)	Other (%)
Corn	**74.7**	7.0	18.0	0.3
Cotton	**100.0**	0.0	0.0	0.0
Beans (dry)	10.1	72.3	17.7	0.0
Grains	31.1	42.4	4.4	22.1
Safflower	23.1	76.9	0.0	0.0
Sugar beets	4.7	93.5	1.9	0.0
Other Field Crops	37.1	32.2	20.7	9.9
Alfalfa	45.7	51.1	0.9	2.3
Pasture	44.2	53.1	0.0	2.7
Cucurbit	38.3	32.9	28.7	0.0
Onions & Garlic	1.7	70.3	28.0	0.0
Potatoes	0.1	86.1	13.8	0.0
Tomatoes (fresh)	0.1	0.1	99.6	0.1
Tomatoes (process)	**64.6**	2.3	33.2	0.0
Other Truck Crops	20.6	37.2	42.0	0.2
Almonds & Pistachios	2.3	27.8	69.9	0.0
Other Deciduous	5.4	45.3	48.4	0.9
Subtropical Trees	3.4	20.4	70.1	6.1
Turfgrass & Landscape	0.0	80.9	16.8	2.3
Vineyard	0.3	6.1	89.1	4.5

Source: irrigation methods survey for coastal areas conducted by California Department of Water Resources (CDWR, 2010).

Table 7: Crop selection based on shares of total crop acreage in coastal areas between 2007 and 2013. Highlighted are the most important crops extensively planted in coastal areas (>5% of the total crop acreage in coastal areas for 4 years or more).

CDL Value	Crop Name	2013	2012	2011	2010	2009	2008	2007
69	Grapes	**35.16%**	**37.23%**	**5.07%**	**6.37%**	**3.21%**	**5.15%**	**7.43%**
36	Alfalfa	**16.83%**	**19.20%**	**30.12%**	**23.39%**	**18.10%**	**28.13%**	**26.64%**
24	Winter Wheat	**8.52%**	**8.50%**	**9.01%**	**15.56%**	**11.12%**	**14.82%**	**12.12%**
37	Other Hay/Non Alfalfa	**7.75%**	**9.04%**	**13.39%**	**9.22%**	**39.53%**	NA	0.13%
21	Barley	**7.25%**	**7.35%**	**7.22%**	**7.96%**	**5.92%**	**8.87%**	**7.33%**
71	Other Tree Crops	**5.77%**	0.00%	0.01%	0.02%	0.00%	0.04%	0.02%
28	Oats	3.66%	3.92%	**5.13%**	**6.34%**	4.88%	**8.71%**	**8.82%**
23	Spring Wheat	2.81%	2.22%	**6.69%**	2.15%	3.73%	2.89%	4.37%
221	Strawberries	2.40%	4.42%	3.24%	**5.53%**	3.35%	**5.34%**	1.60%
54	Tomatoes	1.70%	2.02%	3.00%	1.49%	0.51%	1.43%	2.11%
44	Other Crops	1.26%	0.21%	0.03%	0.03%	0.03%	0.15%	NA
43	Potatoes	1.09%	1.16%	1.72%	1.48%	1.85%	1.02%	0.00%
27	Rye	0.66%	0.49%	1.36%	1.26%	1.02%	1.32%	0.77%
57	Herbs	0.56%	0.23%	0.47%	0.21%	0.07%	0.10%	1.59%
75	Almonds	0.36%	0.25%	0.66%	2.64%	0.80%	2.25%	3.34%
206	Carrots	0.36%	0.35%	1.24%	0.69%	0.13%	0.00%	0.49%
42	Dry Beans	0.34%	0.35%	2.50%	1.32%	0.46%	0.94%	3.80%
205	Triticale	0.32%	0.24%	0.17%	0.41%	0.32%	0.32%	0.80%
2	Cotton	0.27%	0.12%	1.00%	0.24%	0.32%	0.99%	0.96%
3	Rice	0.27%	0.02%	0.06%	0.29%	0.06%	0.30%	0.30%
49	Onions	0.27%	0.40%	0.45%	0.02%	0.08%	0.00%	0.44%
1	Corn	0.25%	0.35%	0.79%	2.08%	0.94%	2.16%	4.21%
47	Misc Vegs & Fruits	0.25%	0.26%	1.54%	1.70%	0.35%	1.91%	0.87%
33	Safflower	0.20%	0.26%	0.36%	0.95%	0.11%	0.80%	0.77%
58	Clover/Wildflowers	0.19%	0.25%	0.36%	0.46%	0.59%	0.82%	0.44%
76	Walnuts	0.18%	0.04%	0.36%	1.82%	0.46%	2.50%	3.83%
12	Sweet Corn	0.14%	0.04%	0.06%	0.05%	NA	0.00%	0.05%

Table 7 (continued)

53	Peas	0.13%	0.14%	0.23%	0.37%	0.16%	0.06%	0.29%
204	Pistachios	0.11%	0.04%	0.30%	1.42%	0.08%	0.23%	0.97%
14	Mint	0.09%	0.18%	0.24%	0.58%	NA	0.43%	NA
226	Dbl Crop Oats/Corn	0.09%	0.09%	0.21%	0.65%	NA	0.54%	0.04%
225	Dbl Crop WinWht/Corn	0.08%	0.13%	0.15%	0.14%	NA	0.85%	0.05%
4	Sorghum	0.07%	0.01%	0.06%	0.02%	0.09%	0.01%	0.09%
6	Sunflower	0.07%	0.04%	0.08%	0.02%	0.03%	0.02%	0.00%
216	Peppers	0.06%	0.01%	0.01%	0.01%	0.01%	0.27%	0.52%
72	Citrus	0.05%	0.03%	0.28%	0.47%	0.38%	0.57%	0.55%
214	Broccoli	0.05%	0.00%	0.09%	0.01%	NA	NA	0.36%
66	Cherries	0.04%	0.01%	0.01%	0.14%	0.04%	1.37%	0.09%
217	Pomegranates	0.04%	0.01%	0.04%	0.02%	0.04%	0.17%	0.04%
236	Dbl Crop WinWht/Sorghum	0.04%	0.05%	0.02%	0.06%	NA	0.00%	NA
22	Durum Wheat	0.03%	0.02%	0.01%	0.02%	0.05%	0.02%	0.03%
46	Sweet Potatoes	0.03%	0.00%	0.00%	0.01%	0.00%	0.03%	0.00%
212	Oranges	0.03%	0.00%	0.08%	0.23%	0.02%	0.17%	0.81%
238	Dbl Crop WinWht/Cotton	0.03%	0.00%	0.00%	NA	NA	NA	NA
55	Caneberries	0.02%	0.04%	0.01%	NA	NA	NA	NA
209	Cantaloupes	0.02%	0.03%	0.03%	0.28%	0.26%	0.08%	0.57%
211	Olives	0.02%	0.00%	0.02%	0.03%	0.20%	0.05%	0.72%
222	Squash	0.02%	0.03%	0.01%	0.08%	0.00%	0.00%	0.09%
227	Lettuce	0.02%	0.17%	1.38%	1.04%	NA	1.61%	NA
48	Watermelons	0.01%	0.00%	0.05%	0.01%	0.05%	0.04%	0.05%
59	Sod/Grass Seed	0.01%	0.00%	0.16%	0.15%	0.01%	0.24%	0.22%
207	Asparagus	0.01%	0.00%	0.03%	0.02%	0.00%	0.00%	0.02%
208	Garlic	0.01%	0.01%	0.02%	0.01%	0.04%	0.00%	0.00%
213	Honeydew Melons	0.01%	0.00%	0.00%	NA	NA	0.00%	0.11%
224	Vetch	0.01%	0.00%	0.02%	0.00%	0.01%	0.00%	0.01%
242	Blueberries	0.01%	0.00%	0.00%	0.03%	NA	0.00%	NA
13	Pop or Orn Corn	0.00%	NA	0.00%	NA	0.00%	0.00%	0.00%
25	Other Small Grains	0.00%	0.00%	NA	NA	NA	0.00%	NA

Table 7 (continued)

26	Dbl Crop WinWht/Soybeans	0.00%	NA	NA	NA	NA	NA	NA
29	Millet	0.00%	NA	0.00%	NA	NA	NA	NA
31	Canola	0.00%	0.00%	0.00%	NA	NA	NA	0.00%
38	Camelina	0.00%	0.00%	NA	NA	NA	NA	NA
41	Sugarbeets	0.00%	0.00%	0.00%	NA	0.00%	0.00%	0.20%
50	Cucumbers	0.00%	0.00%	0.06%	NA	NA	NA	NA
52	Lentils	0.00%	0.00%	NA	NA	NA	NA	NA
67	Peaches	0.00%	0.00%	0.01%	0.02%	0.11%	0.01%	0.03%
68	Apples	0.00%	0.00%	0.01%	0.07%	0.03%	0.08%	0.00%
74	Pecans	0.00%	0.00%	0.00%	0.00%	0.00%	0.01%	NA
77	Pears	0.00%	0.00%	0.17%	NA	NA	NA	NA
92	Aquaculture	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
218	Nectarines	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.02%
219	Greens	0.00%	0.00%	0.00%	NA	0.33%	1.31%	0.14%
220	Plums	0.00%	0.01%	0.04%	0.02%	0.03%	0.00%	0.06%
223	Apricots	0.00%	0.00%	0.01%	0.08%	0.01%	0.39%	0.14%
229	Pumpkins	0.00%	0.04%	0.00%	0.02%	0.01%	0.00%	NA
230	Dbl Crop Lettuce/Durum Wht	0.00%	0.00%	0.00%	0.00%	NA	0.00%	NA
234	Dbl Crop Durum Wht/Sorghum	0.00%	NA	NA	NA	NA	0.00%	NA
235	Dbl Crop Barley/Sorghum	0.00%	0.01%	0.00%	0.00%	NA	NA	NA
237	Dbl Crop Barley/Corn	0.00%	0.00%	0.00%	0.00%	NA	0.00%	NA
243	Cabbage	0.00%	0.00%	0.12%	NA	NA	0.02%	NA
244	Cauliflower	0.00%	0.00%	0.00%	NA	NA	NA	NA
248	Eggplants	0.00%	0.00%	0.00%	NA	NA	NA	NA
231	Dbl Crop Lettuce/Cantaloupe	NA	0.00%	0.00%	NA	NA	NA	NA
232	Dbl Crop Lettuce/Cotton	NA	NA	0.00%	NA	NA	NA	NA
245	Celery	NA	0.00%	0.00%	NA	NA	0.08%	NA
246	Radishes	NA	0.00%	0.04%	NA	NA	0.02%	NA
5	Soybeans	NA	NA	0.00%	0.00%	NA	NA	NA
35	Mustard	NA	NA	0.00%	NA	NA	NA	NA
247	Turnips	NA	NA	0.00%	NA	NA	NA	NA

Table 7 (continued)

63	Forest	NA	NA	NA	0.00%	0.00%	NA	0.01%
87	Wetlands	NA	NA	NA	0.01%	0.01%	NA	0.00%
210	Prunes	NA	NA	NA	0.27%	0.04%	0.35%	0.53%
250	Cranberries	NA	NA	NA	0.00%	NA	NA	NA
45	Sugarcane	NA	NA	NA	NA	0.00%	0.00%	0.00%
70	Christmas Trees	NA	NA	NA	NA	NA	NA	0.00%
-	Total	100%	100%	100%	100%	100%	100%	100%

Source: Cropland Data Layer (CDL) published by the US Department of Agriculture National Agricultural Statistics Service (USDA-NASS) (USDA-NASS, 2014a, 2014b).

Table 8: Crop selection based on rankings of cumulative treated acreage in coastal areas between 2007 and 2012. Highlighted are the top six crops for 4 years or more between 2007 and 2012 (Lettuce, leaf and lettuce, head are combined into one crop – lettuce).

PUR Site Code	PUR Site Name	Cumulative Treated Acreage in a Year						Rank in Cumulative Treated Acreage					
		2012	2011	2010	2009	2008	2007	2012	2011	2010	2009	2008	2007
29143	GRAPES, WINE	4339764	4440406	4168796	3479039	3454758	3853043	1	1	1	1	1	1
1016	STRAWBERRY	2560529	2300090	2312199	1921542	1776608	1600974	2	2	2	2	2	2
13031	LETTUCE, LEAF	1493743	1394305	1392055	1256320	1452471	1515686	3	3	3	4	3	4
13045	LETTUCE, HEAD	1279900	1238373	1331587	1327728	1437464	1522211	4	4	4	3	4	3
13005	BROCCOLI	609366	533904	583495	520775	583780	607211	5	5	5	5	5	5
29113	CELERY, GENERAL	488610	472979	482328	401637	472752	429519	6	6	6	6	6	7
152,154, 156	OUTDOOR NURSERY	374816	326122	338811	267675	299784	463617	7	7	7	8	7	6
11005	TOMATO	154116	184734	249856	263026	232145	299600	15	11	8	9	9	8
13024	SPINACH	368030	287677	243598	199984	191729	163181	8	8	9	10	10	13
13018	ARTICHOKE (GLOBE)	223694	251910	236399	291046	265584	286058	9	9	10	7	8	9
2004	LEMON	161489	180486	200992	189406	191430	173615	14	12	11	11	11	10
28000	AVOCADO	190121	217851	186689	156463	130550	170319	10	10	12	14	16	11
11003	PEPPERS (FRUITING VEGETABLE)	187826	169928	179294	153170	151802	169694	11	13	13	15	12	12
151,153, 155	GREENHOUSE	117400	114803	140384	109623	121740	110787	18	18	14	18	18	17
13008	CAULIFLOWER	161568	139311	139380	123994	139294	153361	13	15	15	17	14	14
29111	CARROTS, GENERAL	108730	109276	107452	93090	137436	105327	19	20	16	20	15	19
14011	ONION	168803	155415	100152	164376	123033	137019	12	14	17	12	17	15

Source: California Pesticide Use Reporting (PUR) database 2007-2012.

Appendix B: Supporting table for validation of screening by chemical properties

Table 9: Pesticide detection in Sacramento River at Freeport and San Joaquin River near Vernalis as of November 2014. Highlighted are the typical detections (sample size >50 AND detection frequency >30% at either site).

Chemical Reported by USGS Gauges	Sacramento River at Freeport		San Joaquin River near Vernails	
	Detection Frequency	Sample Size	Detection Frequency	Sample Size
2-(4-tert-Butylphenoxy)-cyclohexanol	NA	0	18.18%	22
2,4-D	NA	0	6.00%	50
2,4-D plus 2	NA	0	15.79%	19
2,6-Diethylaniline	NA	0	0.46%	436
2-Hydroxy-4-isopropylamino-6-ethylamino-s-triazine	NA	0	2.56%	39
3,4-Dichloroaniline	6.78%	118	13.87%	173
3,5-Dichloroaniline	0.95%	105	0.62%	160
Alachlor	NA	0	5.50%	436
Alachlor sulfonic acid	NA	0	4.17%	24
alpha-HCH	NA	0	0.68%	293
Aminomethylphosphonic acid	100.00%	6	97.96%	98
Atrazine	1.96%	204	24.04%	445
Azoxystrobin	66.67%	3	62.50%	8
Benfluralin	NA	0	0.23%	436
Bensulfuron-methyl	NA	0	2.56%	39
Boscalid	33.33%	3	87.50%	8
Bromacil	NA	0	1.45%	69
Butylate	NA	0	5.12%	293
Carbofuran	NA	0	5.80%	69
Chlorpyrifos	4.90%	204	**38.96%**	**444**
cis-Permethrin	NA	0	0.23%	436
cis-Propiconazole	NA	0	0.62%	160
Clomazone	100.00%	3	NA	0
Cyanazine	2.07%	193	**32.48%**	**431**
Cyprodinil	NA	0	12.50%	8
DCPA	6.37%	204	24.31%	436
Desulfinylfipronil	1.49%	134	2.76%	181
Diazinon	15.20%	204	**55.84%**	**437**
Dichlorprop	NA	0	1.43%	70
Dieldrin	NA	0	0.46%	437
Difenoconazole	NA	0	12.50%	8
Diuron	20.69%	29	**63.64%**	**77**
EPTC	2.07%	193	**39.86%**	**439**
Ethalfluralin	NA	0	5.46%	293
Ethion monoxon	0.86%	116	NA	0
Ethoprop	NA	0	2.78%	431

Table 9 (continued)

Fonofos	NA	0	2.52%	436
Glufosinate	NA	0	1.02%	98
Glyphosate	50.00%	6	**77.55%**	**98**
Hexazinone	**63.03%**	**119**	**66.67%**	**168**
Imazalil	NA	0	12.50%	8
Lindane	NA	0	1.02%	294
Linuron	NA	0	0.55%	362
Malathion	3.92%	204	4.13%	436
MCPA	NA	0	1.43%	70
Metalaxyl	0.86%	116	5.88%	204
Methidathion	3.45%	116	2.42%	165
Methyl parathion	NA	0	0.46%	435
Metolachlor	**38.65%**	**207**	**65.77%**	**444**
Metolachlor oxanilic acid	NA	0	70.83%	24
Metolachlor sulfonic acid	NA	0	100.00%	24
Metribuzin	1.96%	204	5.28%	436
Molinate	**37.82%**	**193**	6.26%	431
Myclobutanil	0.86%	116	13.94%	165
N-(3-4-Dichlorophenyl)-N'-methylurea	NA	0	100.00%	8
Napropamide	NA	0	24.23%	293
Norflurazon	NA	0	2.90%	69
Oryzalin	NA	0	1.45%	69
Oxyfluorfen	0.95%	105	13.12%	160
Pebulate	1.14%	88	8.87%	293
Pendimethalin	2.45%	204	22.48%	436
p-p'-DDE	NA	0	1.02%	293
Prometon	1.96%	204	0.23%	436
Prometryn	NA	0	**53.33%**	**165**
Propanil	12.95%	193	NA	0
Propargite	NA	0	2.35%	425
Propiconazole	33.33%	3	12.50%	8
Propoxur	NA	0	4.35%	69
Propyzamide	0.49%	204	0.23%	436
Pyraclostrobin	NA	0	12.50%	8
Siduron	NA	0	5.13%	39
Simazine	**44.12%**	**204**	**89.19%**	**444**
Tebuthiuron	0.49%	204	1.61%	436
Terbufos	NA	0	0.23%	436
Thiobencarb	**34.69%**	**196**	2.09%	431
Triallate	NA	0	0.34%	293
Triclopyr	11.54%	26	1.43%	70
Trifluralin	0.98%	204	22.94%	436

Source: National Water-Quality Assessment (NAWQA) program maintained by the USGS (2014).