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

Methodology for Prioritizing Pesticides for Surface Water Monitoring in Agricultural and Urban Areas II: Refined Priority List

Yuzhou Luo, Michael Ensminger, Robert Budd, Xin Deng, April DaSilva

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1 Introduction

The Surface Water Protection Program (SWPP) is developing a methodology and computer implementation to prioritize pesticides for surface water monitoring in agricultural and urban areas of California. Phase 1 of this methodology has been developed to generate preliminary priority lists of pesticide active ingredients (AI's), mainly based on pesticide use data and aquatic life benchmarks (Luo et al., 2013). The phase-2 prioritization scheme is proposed here to refine the priority list by identifying pesticide with relatively high risks to surface water quality. In phase 2, all previously prioritized pesticides will be systematically evaluated based on their historical monitoring results, use patterns, application methods, physicochemical properties, and degradate data. The objective of phase 2 is to develop a consistent and transparent approach to further evaluate the top prioritized pesticides from phase 1, and generate "monitoring recommendations" for the actions of [1] monitoring (if the pesticide may potentially cause surface water toxicity and the analytical method is available), [2] requesting analytical methods (if the pesticide may potentially cause surface water toxicity but the analytical method is not available), or [3] not monitoring (if the pesticide is unlikely to cause surface water toxicity) in the user-defined domain of counties and months.

The following developments and improvements have been incorporated in the phase-2 prioritization:

(1) Phase-1 prioritization is refined with additional data, including physiochemical properties (runoff potential, persistence, and volatility), label information (use pattern and application method), historical monitoring data, and availability of analytical methods. The SWPP proposes annual updating on the prioritization and associated data, to reflect the changes in product registration, newly available analytical methods, and new data in Pesticide Use Report (PUR) and surface water monitoring.
(2) Options are provided for the consideration of other water quality standards and benchmarks for pesticides, including drinking water standards, human health benchmarks, and degradate toxicity.

(3) The indicators developed in phase-2 prioritization scheme for decision making are generally consistent with those for SWPP registration review (Luo and Deng, 2012a; b; Luo and Singhasemanon, 2014), thus streamline the continuous evaluation procedures from pesticide product registration to post-use monitoring.

2 Overview

Input data for phase-2 is the list of pesticides generated by the phase-1 prioritization. Those pesticides have been prioritized based on their high toxicity and high use amounts in the user-defined domain (years, counties, and months). The phase-1 results will be evaluated here for refined recommendations for surface water monitoring (Figure 1). Historical monitoring data will be first considered. If a pesticide was observed with high toxicity in surface water this pesticide will be recommended for monitoring. If sufficient use data for a pesticide are not available in the counties of interest, analysis on statewide monitoring data will be conducted. Secondly, registered use patterns and application methods are investigated for the dominant pesticide products used in the domain. Pesticides which are only associated with low-risk use patterns or low-risk application methods will be excluded from the priority list. Finally, environmental fate data are incorporated in the phase-2 study for determining runoff potential, distribution, and persistence of pesticides. The indicators and approaches used here are similar to those developed for the SWPP registration evaluation.

The priority list refined with the phase-2 prioritization scheme will be used for designing a monitoring project. The number of pesticides to be monitored in a specific project is first estimated based on the study scope, budget, and other considerations. For example, SWPP monitoring projects usually include 20-30 pesticides in each site. In this case, top 30 pesticides of the phase-2 results could be retrieved as monitoring candidates. To finalize pesticides for surface water monitoring, two additional procedures are incorporated: [1] site-specific considerations to exclude pesticides from phase-2 results, and [2] professional judgment to include additional pesticides which are not prioritized as top pesticides in the phase-2 results. Site-specific considerations include historical monitoring data for the specific sites (while monitoring data have been considered in phase 2 by aggregating for counties or for the whole state). For example, if a pesticide is prioritized in the phase 2, but no detection or water toxicity has been observed based on sufficient historical data at a monitoring site, this pesticide could be excluded for monitoring in the corresponding location. In addition, the prioritization procedures are based on county-level PUR data analysis, which may not represent the pesticide use patterns and use amounts in the drainage areas to be sampled in the counties. Similarly, professional judgment is proposed to introduce additional pesticide to be considered for surface water monitoring. In summary, final list of pesticides for monitoring would be mainly from the phase-2 results, and also include a relative small number of pesticides based on professional judgment.

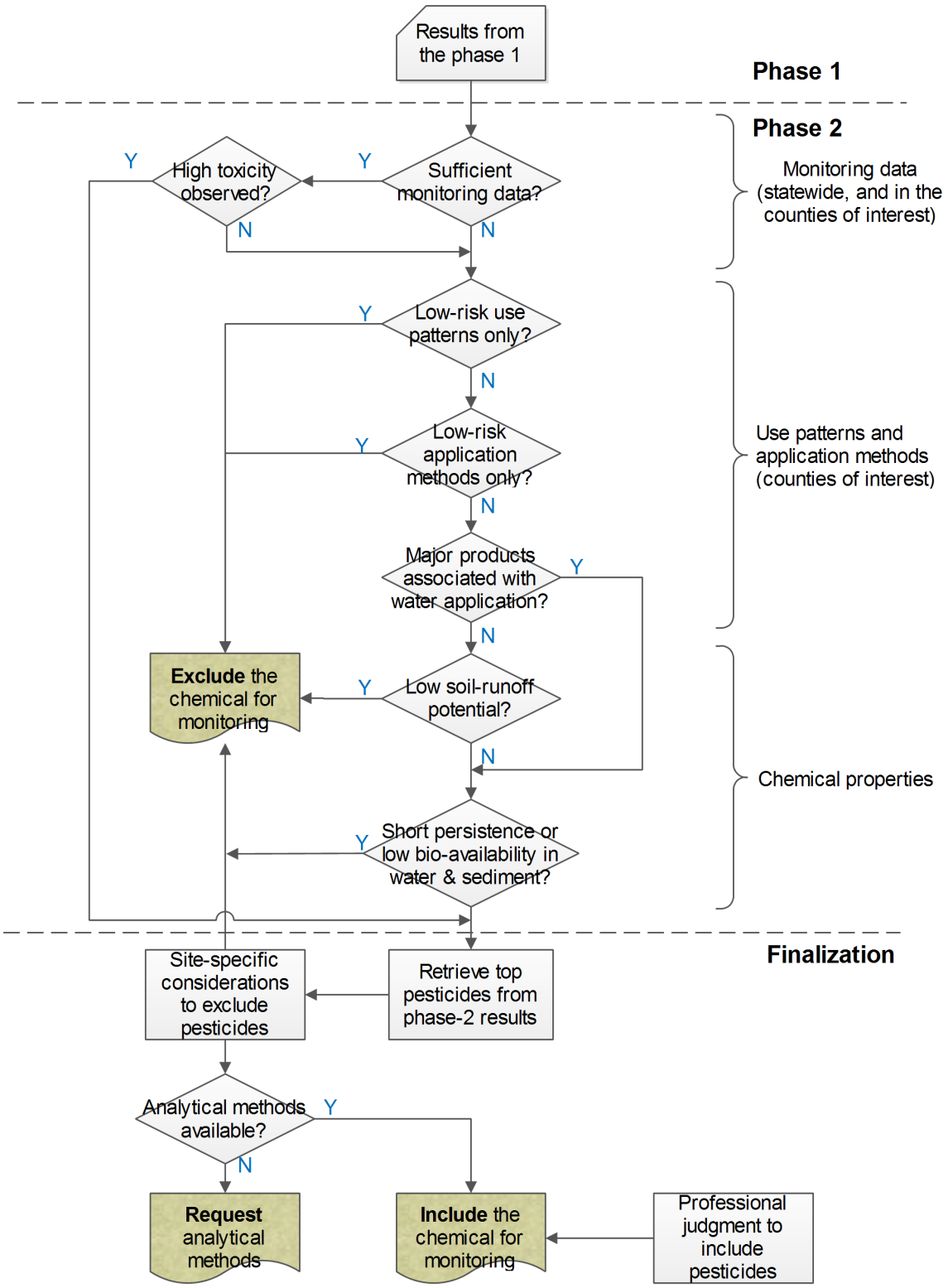

Figure 1. Decision flowchart of the phase-2 prioritization for pesticide monitoring in surface water.

3 Data

Three sets of data (monitoring data, pesticide use data, and pesticide properties and toxicity) are used (Table 1). Annual data updating is proposed for database maintenance.

Table 1. Databases used in this study
(a) Database descriptions

Database	**Description**
SWPP Surface Water Database (SURF) (CDPR, 2014b)	Version: April 2014
USGS National Water Information System (NWIS) (USGS, 2014)	Data retrieved for water years of 2001 to 2013 (i.e., October 2000 to September 2013)
California Environmental Data Exchange Network (CEDEN) (CEDEN, 2014)	Data retrieved for the period of 1/1/2000 to 6/25/2013
Pesticide Use Report (PUR) (CDPR, 2014a)	Aggregated data used in this study, by product, county, application site, and application date
IUPAC Pesticide Properties Database (PPDB) (FOOTPRINT, 2014)	Data for 1839 pesticides, updated on April 14, 2014
USEPA drinking water standards (USEPA, 2014)	Maximum contaminant level goal (MCLG) used in this study
USEPA human health benchmarks (HHBP) (USEPA, 2013)	Acute or one day HHBP, and chronic or life time HHBP used in this study

(b) Variables and datasets used in this study

Database	**Variable/dataset**	**Notes**
SURF	"County"	County of the sampling site
	"Samp_date"	Sampling date
	"Chemical"	Chemical name
	"Conc_ppb" and "Loq_ppb"	Concentration and limit of quantitation, respectively. Non-detection is reported as zero concentration
	"Media"	Environmental media as surface water (sw) or bottom material (bm).
NWIS	"county_cd"	County of the sampling site (http://help.waterdata.usgs.gov/code/county_query)
	"sample_dt"	Sampling date
	"para_code", and "parameter_nm"	Chemical code, name, and unit of monitoring results
	"result_va", "parameter_unit",	Concentration and unit, respectively. Units of "ng/L" and "µg/L" are used for surface water samples, and "µg/kg" for bottom material
	"medium_cd"	"WS" for surface water, SB for bottom material (http://help.waterdata.usgs.gov/code/medium_cd_

		query)
CEDEN	"county"	County of the sampling site
	"SampleDate"	Sampling date
	"Analyte"	Chemical name
	"Result", and "Unit"	Concentration and unit, respectively
	"MatrixName"	"samplewater" or "sediment"
PUR	Table: PUR	Product use amounts, sites and counties of application. See phase-1 report for details in PUR query (Luo et al., 2013)
	Table: PROD_CHEM	Mass fraction of the active ingredient (AI) in a product
	Table: PROD_SITE	Registered use patterns indicated by SITE_CODE
	Table: PROD_APPL_METHOD	Registered application method for a product. For example, soil applied ("A0"), fumigate ("B0"), fog ("C0"), etc.
PPDB	"Active"	Chemical name
	"Solubility-water"	Solubility in water (SOL, mg/L) at 20°C
	"logP"	Octanol-water partition coefficient (KOW) at pH7, 20°C, common (base 10) log transformed
	"Vapour pressure"	Vapor pressure (VP, mPa) at 25°C
	"Henrys constant"	Henry's law constant (HENRY, Pa×m^3/mol) at 25°C
	"Soil DT50 field"	Terrestrial field dissipation half-life (FD, day)
	"Koc" or "Kfoc"	Linear organic carbon (OC)-normalized linear adsorption coefficient (KOC, L/kg[OC]). If KOC is not reported, OC-normalized Freundlich adsorption coefficient (KfOC) will be retrieved
	"Aqueous hydrolysis DT50"	Hydrolysis half-life (HYDRO, day)
	"Water phase DT50"	Aquatic degradation half-life for water phase only (HLW, day)
	"Whole water-sed system DT50"	Aquatic dissipation half-life for the whole water system (HLWD, day)
	"Metabolite"	Chemical names for up to 4 major degradates
	Ecotoxicology data	Acute toxicity data for fish, invertebrates, and algae have been retrieved to generate "benchmark equivalent" as described in the phase-1 report (Luo et al., 2013) for active ingredients and their degradates

4 Methods

Table 2. Indicators used. Highlighted are key indicators as shown in the flowchart (Figure 1) and others are supporting data. Chemical properties are defined in Table 1

Indictor	**Inputs and prerequisite**	**Criteria, references, and justifications**

Sufficient monitoring data	Monitoring databases	True if >100 samples for statewide analysis, or >min(100, 20*[number of counties of interest]) for county-based analysis
High observed water toxicity	Sufficient monitoring data	True if the 99.9th percentile of the monitoring data > the lowest benchmark
Dominant products	PUR	Defined as those top used products of the AI if their total use amount >80% of the total AI use in the counties and years of interest
Low-risk use patterns	Dominant products	True if all of the dominant products in the counties and years of interest are registered for low-risk use patterns according to the PROD_SITE table in the PUR database
Low-risk application methods	Dominant products	True if **none** of the dominant products in the counties and years of interest are associated with the following high-risk methods: spray (code "D0"), chemigation ("F0"), water applications ("O0"), broadcast ("Q0"), or turf treatment ("R0") (Table 4 in the Appendix 1)
Volatility from soil and plant	VP	High volatility if VP >1×10^{-4} mmHg, otherwise low (Kerle et al., 2007; AERU, 2014)
Transferability for particle-bound runoff	FD, KOC, SOL	High, low and intermediate potentials as defined in the SWPP registration evaluation (Luo and Deng, 2012a), and summarized in Table 3.
Transferability for solution-phase runoff		
Low soil-runoff potential	Volatility and transferability as defined above	True if: [high volatility] OR ([low transferability for particle-bound AND solution-phase runoff])
Mobility in water	KOC	Low mobility if KOC>4000, otherwise moderate-to-high (AERU, 2014)
Volatility from water	HENRY	High volatility if HENRY>100 Pa×m^3/mol (AERU, 2014)
Water-phase persistence	HYDRO, HLW	Short persistence if [HYDRO<30] OR [HLW<1] (Luo and Deng, 2012a; AERU, 2014; Luo and Singhasemanon, 2014)
Short persistence in water	Mobility, volatility, and persistence as defined above	True if: [moderate-to-high mobility] AND ([high volatility from water] OR [short water-phase half-life])
Aquatic-system persistence	Aquatic system dissipation (HLWD)	Short persistence if HLWD<30 (Luo and Deng, 2012a; AERU, 2014)
Bio-accumulation	Log[KOW]	Low bio-accumulation if log[KOW]<2.7 (AERU, 2014)
Low bio-	Mobility,	True if:

availability in water-sediment system	persistence, bio-accumulation, as defined above	[low mobility] AND [short aquatic-system persistence] AND [low bio-accumulation]

4.1 Observed water toxicity

Observed water toxicity is defined by the exceedance of monitoring data relative to the lowest aquatic life benchmark. Specially, the 99.9th percentile of available data (detected and non-detected) in each monitoring database was calculated, then compared to the lowest benchmark value of the corresponding AI. If the resultant percentile is higher than the benchmark, the AI is considered to be associated with "**observed toxicity in water**". This approach is consistent with SWPP registration evaluation (Luo and Deng, 2012b). The critical percentile is suggested by USEPA and California Department of Fish and Game (CDFG) (Siepmann and Finlayson, 2000; USEPA, 2005) in the development of water quality criteria for chlorpyrifos and diazinon, where the 1-in-3-year peak concentrations (1-1/3*365=99.9%) were calculated based on monitoring data.

Data analysis will only be conducted on pesticides with sufficient monitoring data (more than 100 samples, detected and non-detected). Otherwise, monitoring data are not considered in phase 2.

4.2 Dominant pesticide products for a given AI

For a specific AI and user-defined conditions (counties, months, and years), its dominant products are defined as the top used products which together explain more than 80% of the total use of the AI. Dominant products are identified to simplify the subsequent data analysis on registered use patterns and application methods, especially for AI's associated with a large number of active products. It's assumed that, compared to the dominant products, other minor products have negligible effects on the monitoring prioritization of the specific AI. Taking agricultural uses of chlorpyrifos in Imperial County during 2012 as an example: use data in the specified county and year are grouped by product and sorted by total use of each product in a descending order. There are 21 chlorpyrifos products with total use of 83,192 lbs. The top 3 (by use) products together account for 79% of total chlorpyrifos, while the top 4 for 84%. Therefore, the top 4 products are considered as dominant products (PUR product numbers of "58202", "63154", "54109", and "25121").

4.3 Potential risk based on registered use patterns

For agricultural pesticide applications, use patterns are specified by the variable "SITE_CODE" in the PUR database. For urban and right-of-way applications, however, "SITE_CODE" only provides very general information such as "structural pest control" (SITE_CODE=10), "landscape maintenance" (30), and "rights of way" (40). In this case, registered use patterns are retrieved from PROD_SITE table for further analysis.

There are about 2,500 unique SITE_CODE in the PUR database. Some of them are associated with low potentials to cause surface water toxicity, and thus defined as low-risk use patterns.

Those uses include applications to ornamental plants, soil applications, containers and storage areas, animals and animal products, and food/feed processing. For the dominant pesticide products identified in section 4.2 for an AI, if their registered SITE_CODE are only with low risk, the AI is assigned with an indicator of "**low-risk use pattern**".

4.4 Potential risk based on registered application methods

The registered application methods of the dominant products are retrieved from PUR table PROD_APPL_METHOD. Available application methods are listed in Table 4 in Appendix 1, where spray (code "D0"), chemigation ("F0"), water applications ("O0"), broadcast ("Q0"), or turf treatment ("R0") are considered high-risk methods. For the dominant pesticide products identified in section 4.2 for an AI, if none of the application methods is associated with high risk potential to surface water, the AI is assigned with an indicator of "**low-risk application method**".

4.5 Runoff potential from soils

Pesticide runoff potential is related to two processes [1] volatilization from soil and plant, and [2] transport with water and sediment runoff. Generally, "**low soil-runoff potential**" can be determined with high volatility OR low transferability.

Descriptive classification for volatility from soil and plant is based on vapor pressure (VP) (Kerle et al., 2007; AERU, 2014): high volatility for chemicals with $VP>1\times10^{-4}$ mmHg. Please note that unit conversion is required from PPDB data (mPa) to the mmHg in the criteria.

Pesticide transferability from soils is determined based on the method in the SWPP registration evaluation (Table 3) (Luo and Deng, 2012a). The criteria for particle-bound transferability is also used in PPDB as "particle bound transport indicator" (AERU, 2014).

Table 3. Algorithm expressing pesticide runoff potential from soils. Chemical properties are defined in Table 1

Transferability rating	**Criteria**	
	solution-phase runoff	**Particle-bound runoff**
Low	($KOC \geq 1\times10^5$) or ($KOC \geq 1000$ and $FD \leq 1$) or ($SOL < 0.5$ and $FD < 35$)	($FD \leq 1$) 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 $SOL \geq 2$)
Moderate-to-high	Otherwise	Otherwise

4.6 Persistence and bio-accumulation in water and sediment

Based on the data availability of chemical properties (Table 1), pesticides in water-sediment system are evaluated for solution phase or particle-bound phase according to their mobility. Based on the descriptive classification in PPDB (AERU, 2014), chemicals with KOC>4000 are

non-mobile and mainly distributed in particle-bound phase. Otherwise, significant portion of the pesticide is in solution phase and subject to volatilization, hydrolysis, photolysis, and other fate processes represented by the water-phase DT50 (HLW, Table 1). Therefore,

[1] if KOC≤4000, the fate and effect of the pesticide will be determined by HENRY (Henry's law constant), HYDRO (hydrolysis), and HLW (water-phase only dissipation). High volatility from water is with HENRY>100 Pa×m^3/mol (AERU, 2014). Short dissipation half-life is indicated by HYDRO<30 OR HLW<1 (Luo and Deng, 2012a; AERU, 2014; Luo and Singhasemanon, 2014). For pesticides with KOC≤4000, "**short persistence in water-sediment system**" is set with high volatility OR short half-life in water.

[2] if KOC>4000, the pesticide is mainly particle-bound but no environmental fate data is available for this phase. In this study, the fate and effect of particle-bound pesticide is determined by KOW-indicated bio-accumulation and whole-system dissipation (HLWD). Low bio-accumulation is suggested by log[KOW]<2.7 (AERU, 2014), and short dissipation in the water-sediment system by HLWD<30 (Luo and Deng, 2012a; AERU, 2014). For pesticides with KOC>4000, "**short persistence in water-sediment system**" is set with low bio-accumulation AND short half-life in water-sediment system.

The critical values for half-lives are determined based on the following considerations: [a] FOOTPRINT database uses the same values for chemical property rating: "non-persistent" for hydrolysis less than 30 days and "fast" dissipation for photolysis or water-phase DT50 less than 1 day (AERU, 2014), and [b] HYDRO<30 is also used in the SWPP registration evaluation as the criterion for low aquatic persistence of a pesticide (Luo and Deng, 2012a).

5 Model testing

5.1 Application to the SWPP monitoring projects

The methodology was tested for the ongoing SWPP monitoring studies

[1] Urban use, Sacramento and Placer counties (county code=31, 34), DPR study 269 (Ensminger, 2013)
[2] Urban use, Orange County (30), DPR study 270 (Budd, 2013)
[3] Agricultural use, Imperial County (13), DPR study 290 (Deng, 2014)

Prioritization results are provided in Appendix 2, with pesticides highlighted if they are currently monitoring by the corresponding projects. All tests are based on annual PUR data for years 2010-2012. The priority list shows the top 50 chemicals (by final score) with the same data format as the phase-1 results. The phase-2 results are displayed in the last column of "Phase2": "FALSE" indicates that it's recommended that the corresponding chemical be excluded from surface water monitoring, and "TRUE" means that the chemical has high potentials to cause surface water toxicity and should be included in monitoring studies. Detailed explanations for the excluded pesticides by the phase-2 analysis are summarized below each priority list. Currently monitored pesticides are generally captured by the phase-2 priority list, especially by the top-20 pesticides. In addition, all excluded pesticides are not monitored by SWPP studies, except for

chlorothalonil. This chemical was included in the monitoring protocols for both urban (Orange County) and agricultural (Imperial County) areas (Budd, 2013; Deng, 2014). Previous monitoring results showed that there were 433 samples of chlorothalonil during 1993 to 2011 in SURF database (version Apr2014), all were non-detected.

5.2 Comparison to the previously identified pesticides for surface water contamination

In 2009, CDPR identified pesticides that have a high potential to contaminate surface water (Pepple, 2009), mainly based on the pesticide detection in surface water or sediment from the SURF database (CDPR, 2014b) and toxicity data from multiple sources (USEPA aquatic life benchmarks, USEPA Ecotoxicity database, and California Central Valley Regional Water Quality Control Board's Compilation of Water Quality Goals). In total 84 pesticides were identified, in which fenpropathrin was labeled as "initially omitted" and MCPA and MCPA dimethylamine salt are combined in the prioritization process. Finally, 82 pesticides (Table 8) are used in the comparison. Other two sets of data involved in the comparison include:
[1] phase-2 prioritization results for total pesticide uses (agricultural, urban, and right-of-way) in California during 2010-2012, and [2] pesticides currently monitored in surface water by CDPR, based on the three active monitoring projects of CDPR studies #269 (Ensminger, 2013), #270 (Budd, 2013), and #290 (Deng, 2014). Detailed results of the comparison are provided in Appendix 3.

According to the prioritization results, 30 out of the 82 pesticides are associated with total scores less than 8 due to low use (indicated by use score ≤ 3) and/or low toxicity (toxicity score =1). In addition, most of those pesticides are not usually included in surface water monitoring. Only 2 of them are currently monitored by SWPP (dicamba and prometon, both in urban areas). Historically, the two pesticides were detected in Northern California urban areas (Ensminger and Kelley, 2011b; a), but the concentrations were significantly lower than the corresponding aquatic life benchmarks.

The remaining 52 (=82-30) pesticides are all identified by the phase-1 prioritization with final score ≥ 8. There are 46 pesticides (labeled as "TRUE" in Table 8) recommended for monitoring based on phase-2 analysis (the other 6 are excluded mainly because of their short persistence in water, and labeled as "FALSE" in Table 8). Actually, 29 out of the 46 phase-2 identified pesticides have been included in current CDPR monitoring. In summary, for the 32 pesticides (except for fipronil degradates) currently monitored by SWPP (highlighted in *Table 8*), 29 pesticides (91%) are captured by the results of phase-2 prioritization.

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Appendix 1 Application methods

Table 4. Application methods in the APPL_METHOD table of PUR

APPLMETH_CD	APPLMETH_DSC
A0	SOIL APPLIED(INJECT,SHANK,CHISEL, OR WORK INTO SOI
B0	FUMIGATE (APPLY AS VAPOR OR VOLATILE LIQUID OTHER
C0	FOG
D0	SPRAY
E0	BAIT (BAITS, PASTES)
F0	CHEMIGATE (CHEMIGATION ALLOWED OR WITH RESTRICTION
G0	CHEMIGATION NOT ALLOWED
H0	PAINT (WOOD PRESERVATIVES, COATINGS)
I0	COATING (I.E. SEED COATINGS)
J0	DUST
K0	WASH, SOAK, DIP
L0	TOPICAL APPLICATION (RUB ON, WIPE ON)
M0	SMOKE
N0	INJECT (OTHER THAN SOIL)
O0	WATER APPLICATIONS
P0	ATTACH (E.G. COLLARS, EAR TAGS)
Q0	BROADCAST
R0	TURF TREATMENT/TURF DRENCH
S0	SEEDLING STAGE
T0	ANT-WASP/RODENT MOUNDS
U0	FILTRATION SYSTEM
V0	TRAP/DEVICE
W0	WICK APPLICATION

Appendix 2 Phase-2 results for the settings of SWPP monitoring studies

Note: The phase-2 results are displayed in the last column of "Phase2": "FALSE" indicates that it's recommended that the corresponding chemical be excluded from surface water monitoring, and "TRUE" means that the chemical has high potentials to cause surface water toxicity and should be included in monitoring studies.

Table 5. Phase-2 results (top 20) for urban and right-of-way uses in Sacramento County and Placer County, 2010-2012. Highlighted are pesticides monitored in the study 269 (Ensminger, 2013).

Chem_code	CHEMNAME	use	usescore	benchmark	toxscore	finalscore	Phase2
2008	PERMETHRIN	10861.6	5	0.01	7	35	TRUE
2300	BIFENTHRIN	20378.2	5	0.075	6	30	TRUE
2223	CYFLUTHRIN	7468.4	4	0.0125	6	24	TRUE
3995	FIPRONIL	4393.9	4	0.11	5	20	TRUE
677	CHLOROTHALONIL	5562.9	4	1.8	4	16	FALSE
1929	PENDIMETHALIN	5074.5	4	5.2	4	16	TRUE
2236	PRODIAMINE	4324	4	3	4	16	TRUE
2171	CYPERMETHRIN	2028	3	0.195	5	15	TRUE
105	CARBARYL	1487.8	3	0.85	5	15	TRUE
229	DIQUAT DIBROMIDE	1125.1	3	0.75	5	15	FALSE
1973	OXYFLUORFEN	898.6	3	0.29	5	15	TRUE
2149	SULFOMETURON-METHYL	888.4	3	0.48	5	15	TRUE
367	MALATHION	881.4	3	0.3	5	15	TRUE
5802	FLUMIOXAZIN	753.7	3	0.852	5	15	FALSE
2297	LAMBDA-CYHALOTHRIN	465	2	0.0035	7	14	TRUE
1868	ORYZALIN	3919.9	4	15.4	3	12	TRUE
2170	TRICLOPYR, BUTOXYETHYL ESTER	3913.1	4	70	3	12	TRUE
3849	IMIDACLOPRID	3821.7	4	35	3	12	TRUE
2308	DITHIOPYR	3597.2	4	20	3	12	TRUE
3919	HALOSULFURON-METHYL	2364.2	3	5.3	4	12	FALSE
231	DIURON	1331.3	3	2.4	4	12	TRUE
3938	CHLORFENAPYR	707.3	3	2.915	4	12	TRUE
3	ACROLEIN	602.8	3	7	4	12	FALSE
3010	DELTAMETHRIN	406.1	2	0.055	6	12	TRUE
2143	CHLORSULFURON	210.7	2	0.055	6	12	TRUE
211	MANCOZEB	1661.7	3	47	3	9	FALSE
636	2,4-D	781.6	3	13.1	3	9	TRUE
1810	TEBUTHIURON	647.2	3	50	3	9	TRUE
597	TRIFLURALIN	496.9	2	7.52	4	8	TRUE
5964	CHLORANTRANILIPROLE	210.8	2	4.9	4	8	TRUE
5923	SULFENTRAZONE	156.8	2	1.8	4	8	TRUE
5759	PYRACLOSTROBIN	73.7	2	1.5	4	8	TRUE
1992	DIFLUBENZURON	18.3	1	0.0014	7	7	FALSE

2289	ISOXABEN	1165.9	3	550	2	6	TRUE
1696	THIOPHANATE-METHYL	801.3	3	930	2	6	FALSE
2326	MCPA	604.2	3	170	2	6	TRUE
5331	INDOXACARB	585.4	3	110	2	6	TRUE
2276	PROPICONAZOLE	541.6	2	21	3	6	TRUE
531	SIMAZINE	477.4	2	36	3	6	TRUE
2081	IPRODIONE	372.3	2	50	3	6	FALSE
464	PCNB	271.3	2	50	3	6	FALSE
4037	AZOXYSTROBIN	199.9	2	49	3	6	TRUE
2244	HYDROPRENE	140.6	2	65	3	6	FALSE
5333	MCPP-P, DIMETHYLAMINE SALT	91	2	14	3	6	TRUE
253	CHLORPYRIFOS	57.2	1	0.05	6	6	TRUE
2321	ESFENVALERATE	47.7	1	0.025	6	6	TRUE
259	ENDOSULFAN	17.5	1	0.05	6	6	TRUE
1963	FENVALERATE	2	1	0.015	6	6	TRUE
2329	TRALOMETHRIN	0.3	1	0.0195	6	6	TRUE
187	DDVP	0.2	1	0.035	6	6	TRUE

Notes for the phase-2 prioritization results:

The following pesticides have been excluded based on the phase-2 analysis:

==========

PUR Chem_code: 677
Chemical name: CHLOROTHALONIL
Short persistence in water, based on hydrolysis or other degradation processes

==========

PUR Chem_code: 229
Chemical name: DIQUAT DIBROMIDE
Low bio-availability in water-sediment system

==========

PUR Chem_code: 5802
Chemical name: FLUMIOXAZIN
Short persistence in water, based on hydrolysis or other degradation processes

==========

PUR Chem_code: 3919
Chemical name: HALOSULFURON-METHYL
Short persistence in water, based on hydrolysis or other degradation processes

==========

PUR Chem_code: 3
Chemical name: ACROLEIN
All dominant products are registered with low-risk use patterns or low-risk application methods
Low soil runoff potentials, based on vapor pressure

==========

PUR Chem_code: 211
Chemical name: MANCOZEB
Short persistence in water, based on hydrolysis or other degradation processes

==========
PUR Chem_code: 1992
Chemical name: DIFLUBENZURON
All dominant products are registered with low-risk use patterns or low-risk application methods

==========
PUR Chem_code: 1696
Chemical name: THIOPHANATE-METHYL
Low bio-availability in water-sediment system

==========
PUR Chem_code: 2081
Chemical name: IPRODIONE
Short persistence in water, based on hydrolysis or other degradation processes

==========
PUR Chem_code: 464
Chemical name: PCNB
All dominant products are registered with low-risk use patterns or low-risk application methods

==========
PUR Chem_code: 2244
Chemical name: HYDROPRENE
Low soil runoff potentials, based on vapor pressure

Table 6. Phase-2 results (top 50) for urban and right-of-way uses in the Orange County, 2010-2012. Highlighted are pesticides monitored in the study 270 (Budd, 2013).

Chem_code	CHEMNAME	use	usescore	benchmark	toxscore	finalscore	Phase2
2008	PERMETHRIN	21569.5	5	0.01	7	35	TRUE
2300	BIFENTHRIN	16005.6	5	0.075	6	30	TRUE
2297	LAMBDA-CYHALOTHRIN	2406.7	4	0.0035	7	28	TRUE
2223	CYFLUTHRIN	3905.2	4	0.0125	6	24	TRUE
677	CHLOROTHALONIL	15945.7	5	1.8	4	20	FALSE
3995	FIPRONIL	5097.2	4	0.11	5	20	TRUE
231	DIURON	8729.4	4	2.4	4	16	TRUE
229	DIQUAT DIBROMIDE	1434.2	3	0.75	5	15	FALSE
2171	CYPERMETHRIN	990.7	3	0.195	5	15	TRUE
1973	OXYFLUORFEN	896.8	3	0.29	5	15	TRUE
2149	SULFOMETURON-METHYL	752.8	3	0.48	5	15	TRUE
367	MALATHION	740.3	3	0.3	5	15	TRUE
211	MANCOZEB	5713.5	4	47	3	12	FALSE
2170	TRICLOPYR, BUTOXYETHYL ESTER	4334.8	4	70	3	12	TRUE
1868	ORYZALIN	2933.6	4	15.4	3	12	TRUE
636	2,4-D	2383.6	4	13.1	3	12	TRUE
112	DICHLOBENIL	1865.8	4	30	3	12	FALSE
83	BROMACIL	1739.5	3	6.8	4	12	TRUE
2236	PRODIAMINE	1677.8	3	3	4	12	TRUE
1929	PENDIMETHALIN	1652.5	3	5.2	4	12	TRUE
3938	CHLORFENAPYR	874	3	2.915	4	12	TRUE
3010	DELTAMETHRIN	663.8	2	0.055	6	12	TRUE

253	CHLORPYRIFOS	281.1	2	0.05	6	12	TRUE
2143	CHLORSULFURON	178.4	2	0.055	6	12	TRUE
5802	FLUMIOXAZIN	242.9	2	0.852	5	10	FALSE
3849	IMIDACLOPRID	1783.2	3	35	3	9	TRUE
2081	IPRODIONE	1677.7	3	50	3	9	FALSE
2276	PROPICONAZOLE	1024.8	3	21	3	9	TRUE
2308	DITHIOPYR	735	3	20	3	9	TRUE
1696	THIOPHANATE-METHYL	3812.4	4	930	2	8	FALSE
2017	OXADIAZON	628.1	2	5.2	4	8	TRUE
1871	HEXAZINONE	576.2	2	7	4	8	TRUE
5759	PYRACLOSTROBIN	146.8	2	1.5	4	8	TRUE
597	TRIFLURALIN	98.3	2	7.52	4	8	TRUE
1992	DIFLUBENZURON	0.1	1	0.0014	7	7	TRUE
1749	2,2-DIBROMO-3-NITRILOPROPIONAMIDE	895.3	3	450	2	6	FALSE
2326	MCPA	868.8	3	170	2	6	TRUE
2289	ISOXABEN	848.3	3	550	2	6	TRUE
2244	HYDROPRENE	360.6	2	65	3	6	FALSE
1810	TEBUTHIURON	265.8	2	50	3	6	TRUE
4037	AZOXYSTROBIN	219.6	2	49	3	6	TRUE
5027	FLUDIOXONIL	153.4	2	70	3	6	TRUE
5333	MCPP-P, DIMETHYLAMINE SALT	150.7	2	14	3	6	TRUE
200	DICAMBA	141.7	2	61	3	6	TRUE
464	PCNB	132.9	2	50	3	6	TRUE
2321	ESFENVALERATE	57.3	1	0.025	6	6	TRUE
187	DDVP	4.8	1	0.035	6	6	TRUE
2329	TRALOMETHRIN	0.5	1	0.0195	6	6	TRUE
1855	GLYPHOSATE, ISOPROPYLAMINE SALT	58344.6	5	42450	1	5	TRUE
5820	GLYPHOSATE, POTASSIUM SALT	17256.7	5	35000	1	5	TRUE

Notes for the phase-2 prioritization results:

The following pesticides have been excluded based on the phase-2 analysis:

==========

PUR Chem_code: 677
Chemical name: CHLOROTHALONIL
Short persistence in water, based on hydrolysis or other degradation processes

==========

PUR Chem_code: 229
Chemical name: DIQUAT DIBROMIDE
Low bio-availability in water-sediment system

==========

PUR Chem_code: 211
Chemical name: MANCOZEB
Short persistence in water, based on hydrolysis or other degradation processes

==========

PUR Chem_code: 112
Chemical name: DICHLOBENIL
All dominant products are registered with low-risk use patterns or low-risk application methods

==========
PUR Chem_code: 5802
Chemical name: FLUMIOXAZIN
Short persistence in water, based on hydrolysis or other degradation processes

==========
PUR Chem_code: 2081
Chemical name: IPRODIONE
Short persistence in water, based on hydrolysis or other degradation processes

==========
PUR Chem_code: 1696
Chemical name: THIOPHANATE-METHYL
Low bio-availability in water-sediment system

==========
PUR Chem_code: 1749
Chemical name: 2,2-DIBROMO-3-NITRILOPROPIONAMIDE
All dominant products are registered with low-risk use patterns or low-risk application methods

==========
PUR Chem_code: 2244
Chemical name: HYDROPRENE
Low soil runoff potentials, based on vapor pressure

Table 7. Phase-2 results (top 50) for agricultural uses in the Imperial County, 2010-2012. Highlighted are pesticides monitored in the study 290 (Deng, 2014) for sites in the county.

Chem_code	CHEMNAME	use	usescore	benchmark	toxscore	finalscore	Phase2
253	CHLORPYRIFOS	67818.4	4	0.05	6	24	TRUE
2008	PERMETHRIN	9014.6	3	0.01	7	21	TRUE
1929	PENDIMETHALIN	187833.7	5	5.2	4	20	TRUE
597	TRIFLURALIN	119388.7	5	7.52	4	20	TRUE
367	MALATHION	29090.7	4	0.3	5	20	TRUE
383	METHOMYL	43456.3	4	2.5	4	16	TRUE
45	ATRAZINE	19503.7	3	1	5	15	TRUE
2297	LAMBDA-CYHALOTHRIN	4366.7	2	0.0035	7	14	TRUE
636	2,4-D	35473.1	4	13.1	3	12	TRUE
216	DIMETHOATE	30473	4	21.5	3	12	TRUE
834	BROMOXYNIL OCTANOATE	21336.4	4	26.5	3	12	FALSE
677	CHLOROTHALONIL	18028.3	3	1.8	4	12	FALSE
361	LINURON	7728.5	3	2.5	4	12	TRUE
2321	ESFENVALERATE	3534.4	2	0.025	6	12	TRUE
2300	BIFENTHRIN	2496.8	2	0.075	6	12	TRUE
2223	CYFLUTHRIN	1795.6	2	0.0125	6	12	TRUE
70	BENSULIDE	104016.4	5	290	2	10	TRUE
229	DIQUAT DIBROMIDE	7224.6	2	0.75	5	10	FALSE

2171	CYPERMETHRIN	6198.8	2	0.195	5	10	TRUE
1973	OXYFLUORFEN	6175.5	2	0.29	5	10	TRUE
1601	PARAQUAT DICHLORIDE	2762.2	2	0.396	5	10	TRUE
198	DIAZINON	2399	2	0.11	5	10	TRUE
211	MANCOZEB	16846.9	3	47	3	9	FALSE
3849	IMIDACLOPRID	15317.6	3	35	3	9	TRUE
445	PROPARGITE	10218.8	3	37	3	9	TRUE
53	BENEFIN	8142.2	3	34.85	3	9	TRUE
369	MANEB	7885.4	3	13.4	3	9	FALSE
190	S,S,S-TRIBUTYL PHOSPHOROTRITHIOATE	2894.5	2	3.4	4	8	TRUE
5964	CHLORANTRANILIPROLE	1992.3	2	4.9	4	8	TRUE
5759	PYRACLOSTROBIN	1919.7	2	1.5	4	8	TRUE
1992	DIFLUBENZURON	2	1	0.0014	7	7	TRUE
2081	IPRODIONE	5431.3	2	50	3	6	FALSE
5791	FENAMIDONE	4070.9	2	95	3	6	TRUE
418	NALED	3997.3	2	25	3	6	FALSE
5946	SPINETORAM	3694.2	2	77.9	3	6	TRUE
3983	SPINOSAD	2248.3	2	90	3	6	TRUE
5036	BROMOXYNIL HEPTANOATE	1641.4	2	14.5	3	6	FALSE
111	FORMETANATE HYDROCHLORIDE	1639	2	45	3	6	TRUE
259	ENDOSULFAN	41.8	1	0.05	6	6	TRUE
480	MEVINPHOS	18.8	1	0.08	6	6	TRUE
2629	KAOLIN	94862.3	5	1250000	1	5	TRUE
478	PHORATE	1538.4	1	0.3	5	5	TRUE
502	PROMETRYN	1059	1	1	5	5	TRUE
5802	FLUMIOXAZIN	282.5	1	0.852	5	5	FALSE
2234	FENPROPATHRIN	141.4	1	0.265	5	5	TRUE
5865	PYRAFLUFEN-ETHYL	3.4	1	0.23	5	5	FALSE
335	PHOSMET	1.9	1	1	5	5	FALSE
394	METHYL PARATHION	0.7	1	0.49	5	5	TRUE
264	EPTC	63067.9	4	1400	1	4	FALSE
179	CHLORTHAL-DIMETHYL	50418.2	4	11000	1	4	TRUE

Notes for the phase-2 prioritization results:

The following pesticides have been excluded based on the phase-2 analysis:

==========

PUR Chem_code: 834
Chemical name: BROMOXYNIL OCTANOATE
Short persistence in water, based on hydrolysis or other degradation processes

==========

PUR Chem_code: 677
Chemical name: CHLOROTHALONIL
Short persistence in water, based on hydrolysis or other degradation processes

==========

PUR Chem_code: 229

Chemical name: DIQUAT DIBROMIDE
Low bio-availability in water-sediment system

==========
PUR Chem_code: 211
Chemical name: MANCOZEB
Short persistence in water, based on hydrolysis or other degradation processes

==========
PUR Chem_code: 369
Chemical name: MANEB
Short persistence in water, based on hydrolysis or other degradation processes

==========
PUR Chem_code: 2081
Chemical name: IPRODIONE
Short persistence in water, based on hydrolysis or other degradation processes

==========
PUR Chem_code: 418
Chemical name: NALED
Low soil runoff potentials, based on vapor pressure

==========
PUR Chem_code: 5036
Chemical name: BROMOXYNIL HEPTANOATE
Low soil runoff potentials, based on field dissipation, KOC, and solubility

==========
PUR Chem_code: 5802
Chemical name: FLUMIOXAZIN
Short persistence in water, based on hydrolysis or other degradation processes

==========
PUR Chem_code: 5865
Chemical name: PYRAFLUFEN-ETHYL
Short persistence in water, based on hydrolysis or other degradation processes

==========
PUR Chem_code: 335
Chemical name: PHOSMET
Short persistence in water, based on hydrolysis or other degradation processes

==========
PUR Chem_code: 264
Chemical name: EPTC
Low soil runoff potentials, based on vapor pressure

Appendix 3 Comparison to the previously identified pesticides for surface water contamination

Table 8. Phase-2 results (based on statewide uses during 2010-2012 for agriculture, urban and rights-of-way) in comparison with the previous identified pesticides for surface water contamination (Pepple, 2009), with highlights for pesticides currently monitored by SWPP (Budd, 2013; Ensminger, 2013; Deng, 2014)

Chem_code	Identified pesticides (Pepple, 2009)	Phase-2 results for top pesticides (with final score>8)	Notes
636	2,4-D	TRUE	
678	alachlor	FALSE	
575	aldicarb	FALSE	Low-risk use patterns
45	atrazine	TRUE	
314	azinphos-methyl		low use
53	benefin		low use
1944	bentazon, sodium salt		low use
2300	bifenthrin	TRUE	
83	bromacil	TRUE	
834	bromoxynil octanoate	FALSE	
565	butylate		low use
105	carbaryl	TRUE	
106	carbofuran		low use
253	chlorpyrifos	TRUE	
179	chlorthal-dimethyl		low toxicity
516	cycloate		low use
2223	cyfluthrin	TRUE	
2171	cypermethrin	TRUE	
187	DDVP		low use
3010	deltamethrin	TRUE	
198	diazinon	TRUE	
200	dicamba		low use
346	dicofol		low use
216	dimethoate	TRUE	
230	disulfoton	TRUE	
231	diuron	TRUE	
259	endosulfan	TRUE	
264	EPTC		low use
2321	esfenvalerate	TRUE	
2166	ethalfluralin	TRUE	
404	ethoprop		low use
1857	fenamiphos	TRUE	

2283	fenoxycarb		low use
3995	fipronil	TRUE	
2997	glyphosate		low toxicity
1871	hexazinone	TRUE	
2203	hydramethylnon		low use
3849	imidacloprid	TRUE	
2297	lambda cyhalothrin	TRUE	
361	linuron	TRUE	
367	malathion	TRUE	
2326	MCPA	TRUE	
2132	metalaxyl		low use
1689	methidathion	FALSE	
375	methiocarb		low use
383	methomyl	TRUE	
392	methyl isothiocyanate		no reported use
394	methyl parathion	TRUE	
1996	metolachlor	TRUE	
1692	metribuzin	TRUE	
449	molinate		low use
1728	napropamide		low use
2019	norflurazon	TRUE	
1868	oryzalin	TRUE	
2017	oxadiazon	TRUE	
1910	oxamyl	FALSE	
1973	oxyfluorfen	TRUE	
1601	paraquat dichloride	TRUE	
1929	pendimethalin	TRUE	
2008	permethrin	TRUE	
478	phorate	TRUE	
335	phosmet	FALSE	
2236	prodiamine	TRUE	
499	prometon		low use
502	prometryn	TRUE	
503	propanil	TRUE	
445	propargite	TRUE	
2276	propiconazole	TRUE	
62	propoxur		low use
694	propyzamide		low use
510	pyrethrins		no reported use
4019	pyriproxyfen		low use
190	S.S.S-tributyl phosphorotrithioate	TRUE	
603	siduron		low use
531	simazine	TRUE	

1810	tebuthiuron		low use
3004	terbuthylazine		low use
305	tetrachlorvinphos		low use
1933	thiobencarb	TRUE	
49	triallate		low use
2131	triclopyr	TRUE	
597	trifluralin	TRUE	