Methodology for Prioritizing Pesticides for Surface Water Monitoring in Agricultural and Urban Areas

CDPR Surface Water Protection Program
Prioritization Workgroup

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Outline

- Background and previous studies
- (*complex*) Methodology
  - Phase 1: 2 variables of pesticide use and toxicity
  - Phase 2: 16 additional variables
- (*simple*) Graphical user interface and demonstrations
  - Agriculture uses
  - Urban uses
  - Watershed-scale prioritization

Background

- Questions to be answered
  - Hundreds of pesticides are being used in CA, but we only monitor some of them
  - Where, when, and what to sample?
- Development philosophy
  - Developed based on mathematic representations of the previous monitoring experiences by CDPR Surface Water Protection Program (SWPP)
  - Developed to justify and improve SWPP monitoring projects

Previous studies

- *"Assessment of acute aquatic toxicity of current-use pesticides in California, with monitoring recommendations"* (Starner, 2007)
- Monitoring priority of top 23 pesticides: 5 high, 11 medium, and 7 low/very low

- Pesticide use
- Toxicity data

Chemical	Toxicity	Use	Monitoring Priority
Malathion	very high	high	high
Diazinon	high	high	high
Carbaryl	very high	moderate	high
Thiram	high	moderate	high
Trifluralin	moderate	very high	high

Previous studies

- *"Procedure for identifying pesticides with a high potential to contaminate surface water"* (Pepple, 2009)
- Draft list (71 pesticides) for surface water regulation

- Pesticide use
- Toxicity data
- Standards for drinking water and human health
- Monitoring results

Previous studies

- Registration evaluations for surface water protection

dpr

Department of Pesticide Regulation

Environmental Monitoring Branch

Internal web site

Home | Publications | Databases | Programs & Special Projects | Resources

Publications / Registration Reviews

Guidance Memorandum Environmental Monitoring Registration Evaluation Memorandum Routing Process.

2014				
Review & ID Number	**Author**	**Product Name**	**Active Ingredient**	**Area of Review**
RR 14-38 (263469)	Deng, X.	Various Pyrethroids	Pyrethroids	Environmental Fate-Surface Water Pyrethroids Reevaluation
RR 14-37 (260203, 260213)	Y. Xie, Deng, X.	Cupron Anti-fungal Fibers	Cuprox Oxide (1.95%, 2.60%)	Environmental Fate-Surface Water
RR 14-35 (255340)	Sighasemanon, N., Kelley, K.	Lexicon Intrinsic Brand Fungicide	Fluxapyroxad 14.33%, Pyraclostrobin 28.58%	Environmental Fate-Surface Water
RR 14-34 (251334)	Sighasemanon, N., Kelley, K.	Clipper Aquatic Herbicide	Flumioxazin	Environmental Fate-Surface

- Pesticide use
- Toxicity data
- Standards for drinking water and human health
- Monitoring results
- Chemical properties
- Label information

Study design

- Phase 1
  - Based on pesticide uses and aquatic toxicity data
  - To generate “priority scores”
- Phase 2
  - Based on monitoring results, chemical properties, product information
  - To make “monitoring recommendations”
- Watershed-scale prioritization (implementation of phases 1 and 2 with finer spatial resolution)

- Pesticide use
- Toxicity data
- Standards for drinking water and human health
- Monitoring results
- Chemical properties
- Label information

Phase 1, Initial priority list

- Results for statewide agricultural uses 2010-2012

chem_code	CHEMNAME	use	usescore	benchmark	toxscore	finalscore	toxflag
253	CHLORPYRIFOS	1225664.4	5	0.05	6	30	
1601	PARAQUAT DICHLORIDE	856215.1	5	0.396	5	25	
2008	PERMETHRIN	109891.1	3	0.01	7	21	
2297	LAMBDA-CYHALOTHRIN	46526.9	3	0.0035	7	21	
1929	PENDIMETHALIN	1828873.6	5	5.2	4	20	
677	CHLOROTHALONIL	994390.2	5	1.8	4	20	
629	ZIRAM	890609.6	5	9.7	4	20	
1973	OXYFLUORFEN	580854.7	4	0.29	5	20	
367	MALATHION	463661.7	4	0.3	5	20	
2300	BIFENTHRIN	115280.9	3	0.075	6	18	
597	TRIFLURALIN	475117.7	4	7.52	4	16	
231	DIURON	323798.9	4	2.4	4	16	
5133	S-METOLACHLOR	271979.6	4	8	4	16	
383	METHOMYL	241613.7	4	2.5	4	16	
503	PROPANIL	2128463.9	5	16	3	15	

Phase 1: Toxicity scores

- [priority score]=[toxicity score]*[use score]
- Toxicity score =1 (lower toxicity) to 8 (higher toxicity) (Starner, 2007; 2008) based on the lowest Benchmark
  - USEPA OPP aquatic life benchmarks
  - Benchmark equivalents, from FOOTPRINT PPDB

Toxicity score	The lowest Benchmark value (ppb)
8 (very high)	<=0.001
7	(0.001, 0.01]
6	(0.01, 0.1]
5	(0.1, 1]
4	(1,10]
3	(10,100]
2	(100,1000]
1 (very low)	>1000

only one with 8:
gamma-cyhalothrin

Phase 1: Use scores

- [priority score]=[toxicity score]*[use score]
- Use score=1 (lower use) to 5 (higher use), dependent on user-defined regions and seasons

chem_code	chemname	use
970	POTASSIUM N-METHYLDITHIOCARBAMATE	6200902
5820	GLYPHOSATE, POTASSIUM SALT	3905396
1855	GLYPHOSATE, ISOPROPYLAMINE SALT	3232614
2629	KAOLIN	2237689
503	PROPANIL	2128464
1929	PENDIMETHALIN	1828874
253	CHLORPYRIFOS	1225664
677	CHLOROTHALONIL	994390
211	MANCOZEB	935848
629	ZIRAM	890609
1601	PARAQUAT DICHLORIDE	856215
1868	ORYZALIN	613030
1973	OXYFLUORFEN	580854
3946	GLUFOSINATE-AMMONIUM	504060
597	TRIFLURALIN	475117
367	MALATHION	463661
104	CAPTAN	418941
636	2,4-D	387744
531	SIMAZINE	375704

Percentage	Use score
2%	5 (very high)
4%	4
8%	3
16%	2
70%	1 (very low)

default values, and
can be changed by users

Phase 2, Refined priority list

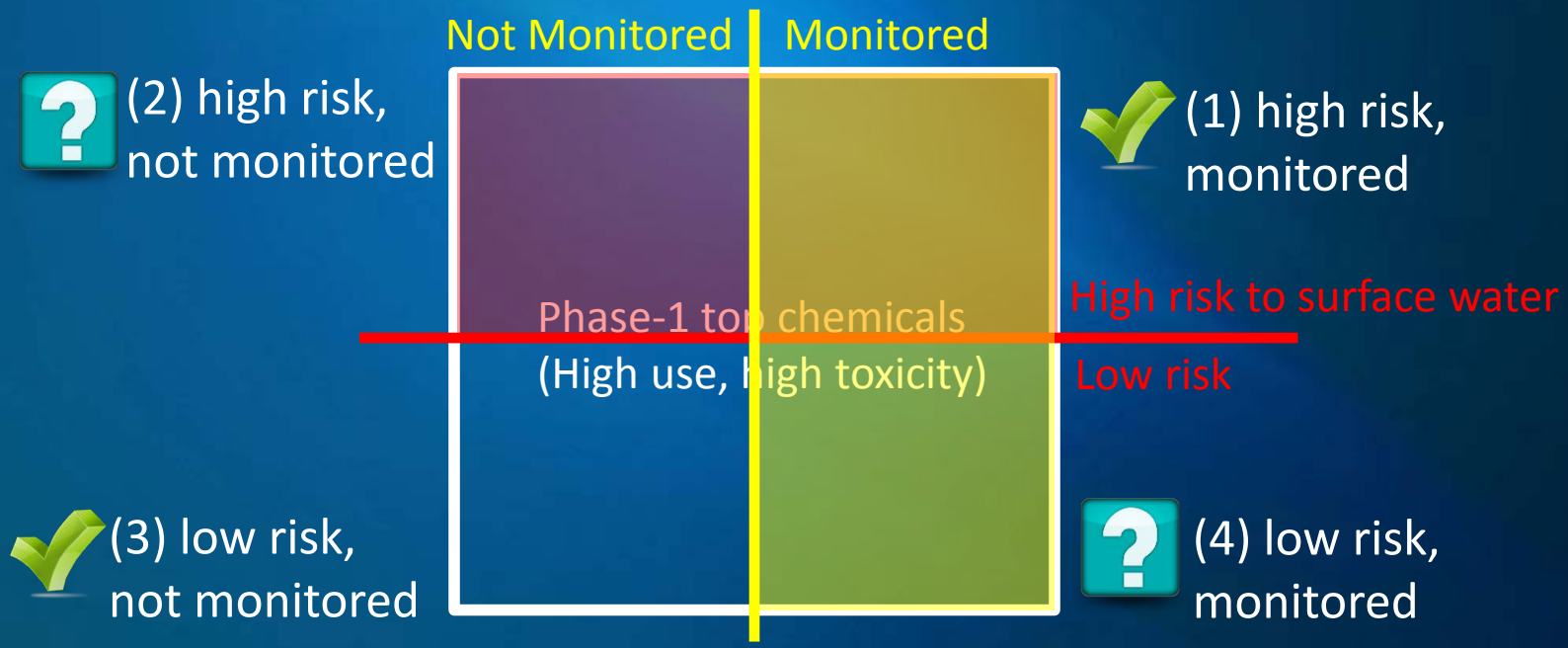
- Results for statewide agricultural uses 2010-2012

Phase 2: Monitoring recommendation

chem_code	CHEMNAME	use	usescore	benchmark	toxscore	finalscore	toxflag	Phase2
253	CHLORPYRIFOS	1225664.4	5	0.05	6	30		True
1601	PARAQUAT DICHLORIDE	856215.1	5	0.396	5	25		True
2008	PERMETHRIN	109891.1	3	0.01	7	21		True
2297	LAMBDA-CYHALOTHRIN	46526.9	3	0.0035	7	21		True
1929	PENDIMETHALIN	1828873.6	5	5.2	4	20		True
677	CHLOROTHALONIL	994390.2	5	1.8	4	20		False
629	ZIRAM	890609.6	5	9.7	4	20		False
1973	OXYFLUORFEN	580854.7	4	0.29	5	20		True
367	MALATHION	463661.7	4	0.3	5	20		True
2300	BIFENTHRIN	115280.9	3	0.075	6	18		True
597	TRIFLURALIN	475117.7	4	7.52	4	16		True
231	DIURON	323798.9	4	2.4	4	16		True
5133	S-METOLACHLOR	271979.6	4	8	4	16		True
383	METHOMYL	241613.7	4	2.5	4	16		True
503	PROPANIL	2128463.9	5	16	3	15		True

Phase 2: Motivation

- Based on phase-1 top pesticides, to identify pesticides with relatively high risks to surface water and make "monitoring recommendations"



Phase 2: Approaches

- "*Screening justification*" for selected pesticides
  - Select some phase-1 top pesticides (i.e., with high use and high toxicity) but not monitored by SWPP: *Acrolein, Diquat dibromide, Paraquat dichloride, Sulfometuron-methyl*
  - Analyze label, use, toxicity, properties, & monitoring results
  - Identify factors to include/exclude a pesticide

Example: Justification report for *Acrolein* (Ensminger, 2014)

Justification for assigning screening code:

Non-persistent in water
Transport to surface water unlikely due to application method
Holding period longer than aquatic half life (aquatic AIs)
Non-persistent in soil
Decreasing Use

More info in CDPR internal share drive: SWPP\Monitoring Priority\Justification\

Phase 2: Approaches

- "*Screening justification*" for selected pesticides
- Identified factors
  - Registered use patterns
  - Application methods
  - Monitoring results
  - Physiochemical properties

Phase 2: Approaches

- "*Screening justification*" for selected pesticides
- Identified factors
- Mathematic representations of the identified factors
  - Observed *high water toxicity*: the 99.9th percentile of measured concentrations > the lowest benchmark
  - *High-risk application method*: spray, chemigation, water applications, broadcast, or turf treatment
  - *High mobility in water*: KOC>4,000
  - …
  - *16 variables* (Table 2, phase-2 document), based on SWPP registration evaluation model and FOOTPRINT PPDB

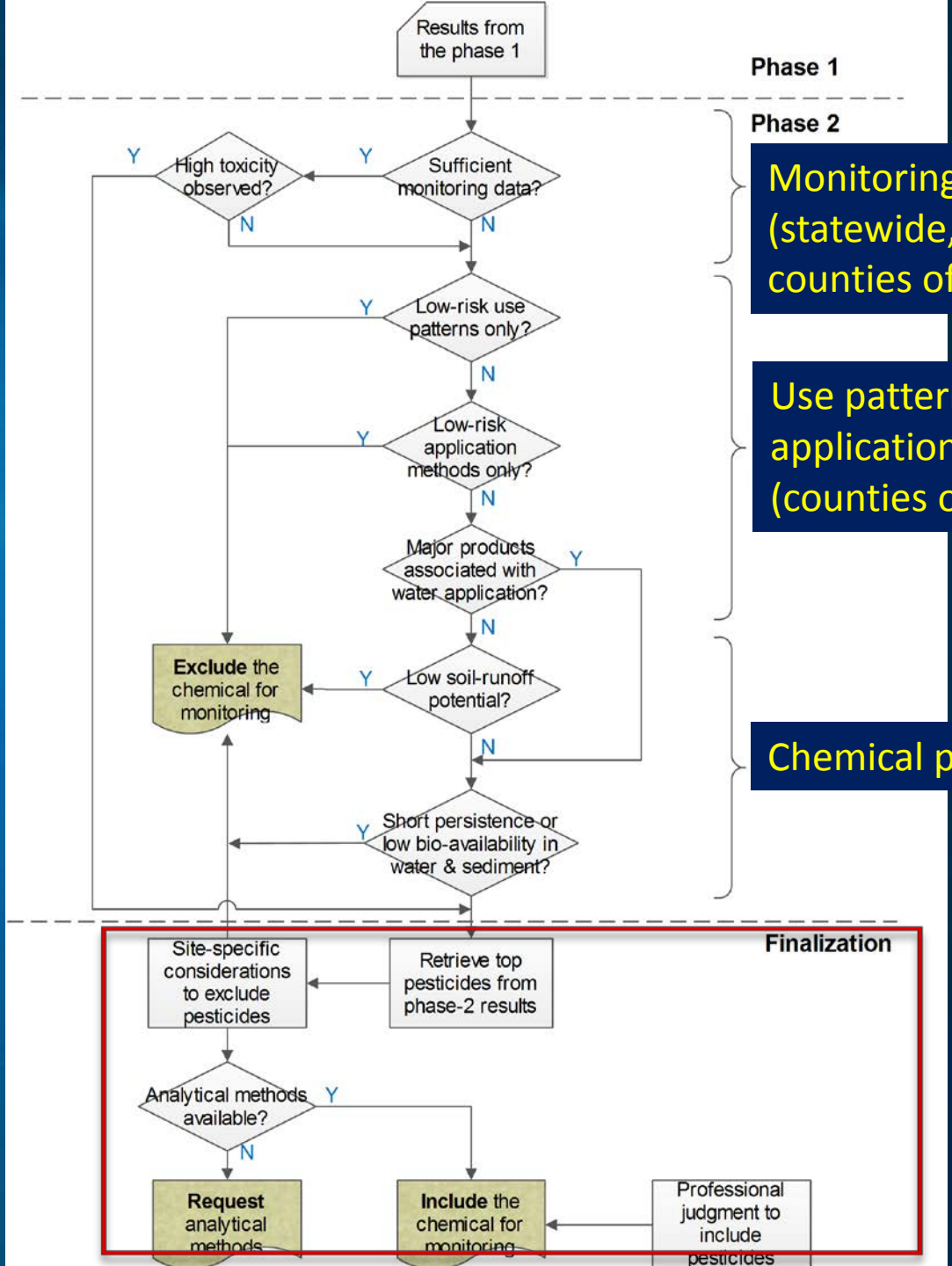
Phase 2: Data

- Monitoring data: SURF (DPR), NWIS (USGS), CEDEN (CWRCB)
- Pesticide use and product info: PUR
- Toxicity data
  - Aquatic toxicity: USEPA aquatic life benchmark, FOOTPRINT PPDB (parent and degradate)
  - USEPA drinking water standards, USEPA human health benchmark
- Chemical properties: FOOTPRINT PPDB (parent and degradate)

Phase 2: Results

- Phase-2 *monitoring recommendations*
  - “TRUE”: the pesticide potentially causes surface water toxicity and should be included for monitoring
  - “FALSE”: excluded for monitoring
- Phase-2 *notes*: reasons to exclude

Phase 2: Flowchart



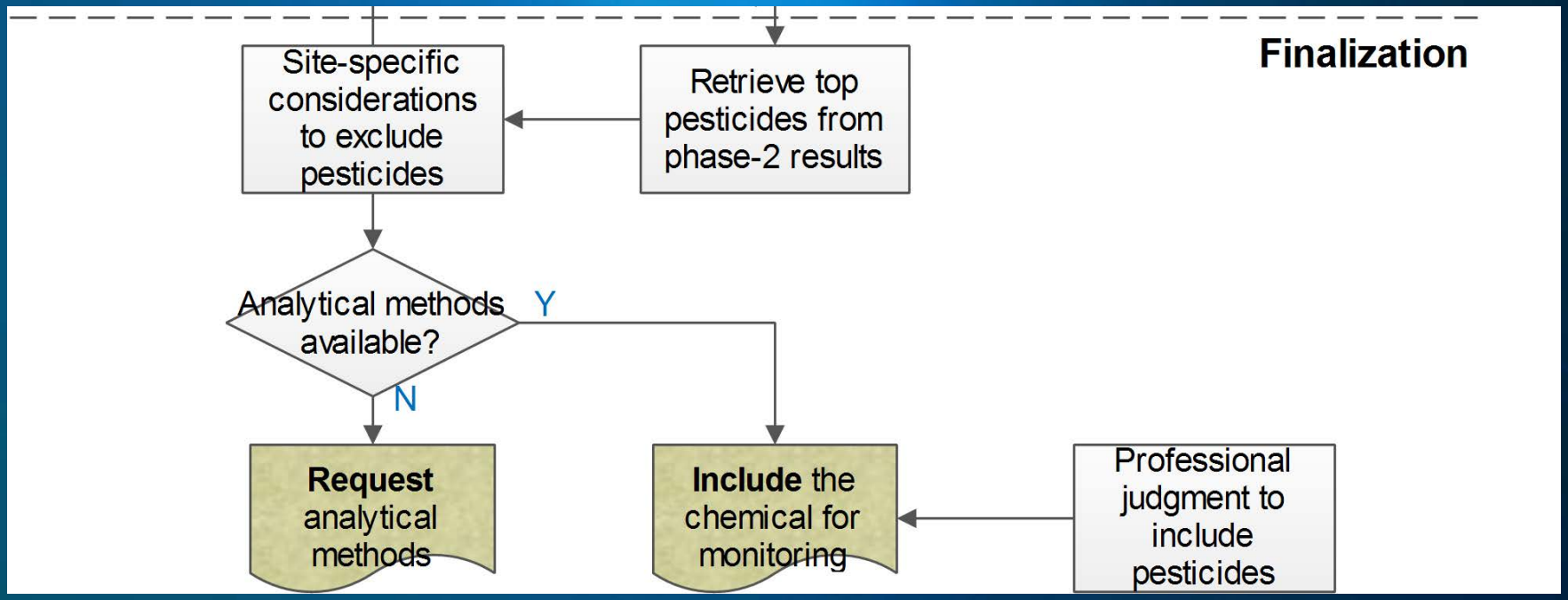
Monitoring data (statewide, and in the counties of interest)

Use patterns and application methods (counties of interest)

Chemical properties

Phase 2: Finalization

- The final list of pesticides for a specific monitoring study/site will be based on
  - Model-based monitoring recommendations
  - Site-specific considerations and professional judgment



Phase 2: Finalization

- The final list of pesticides for a specific monitoring study/site will be based on
  - Model-based monitoring recommendations
  - Site-specific considerations and professional judgment

- Why?
  - Model considers many of the important factors, but not ALL
  - Spatial resolution: monitoring site (a point) *vs.* region-aggregated data
  - Scope, objectives, and resources of a monitoring project
  - Any additional considerations by the project PI(s)

Phase 2: Finalization

- Suggested procedures
  1) Estimate total # of pesticides to be monitored (e.g., 20)
  2) Run the prioritization model and retrieve top recommended pesticides (e.g., 20~25)
  3) Generate the final list by
     A. Removing some of the top candidates
     B. Adding some additional pesticides

- Expectation: the model could explain majority (80~90%) of the final list

Validation 1

- Urban and right-of-way, Sacramento and Placer, 2010-2012
- Top 20 results
- Highlighted are pesticides currently monitored in the corresponding SWPP study (Ensminger, 2014)

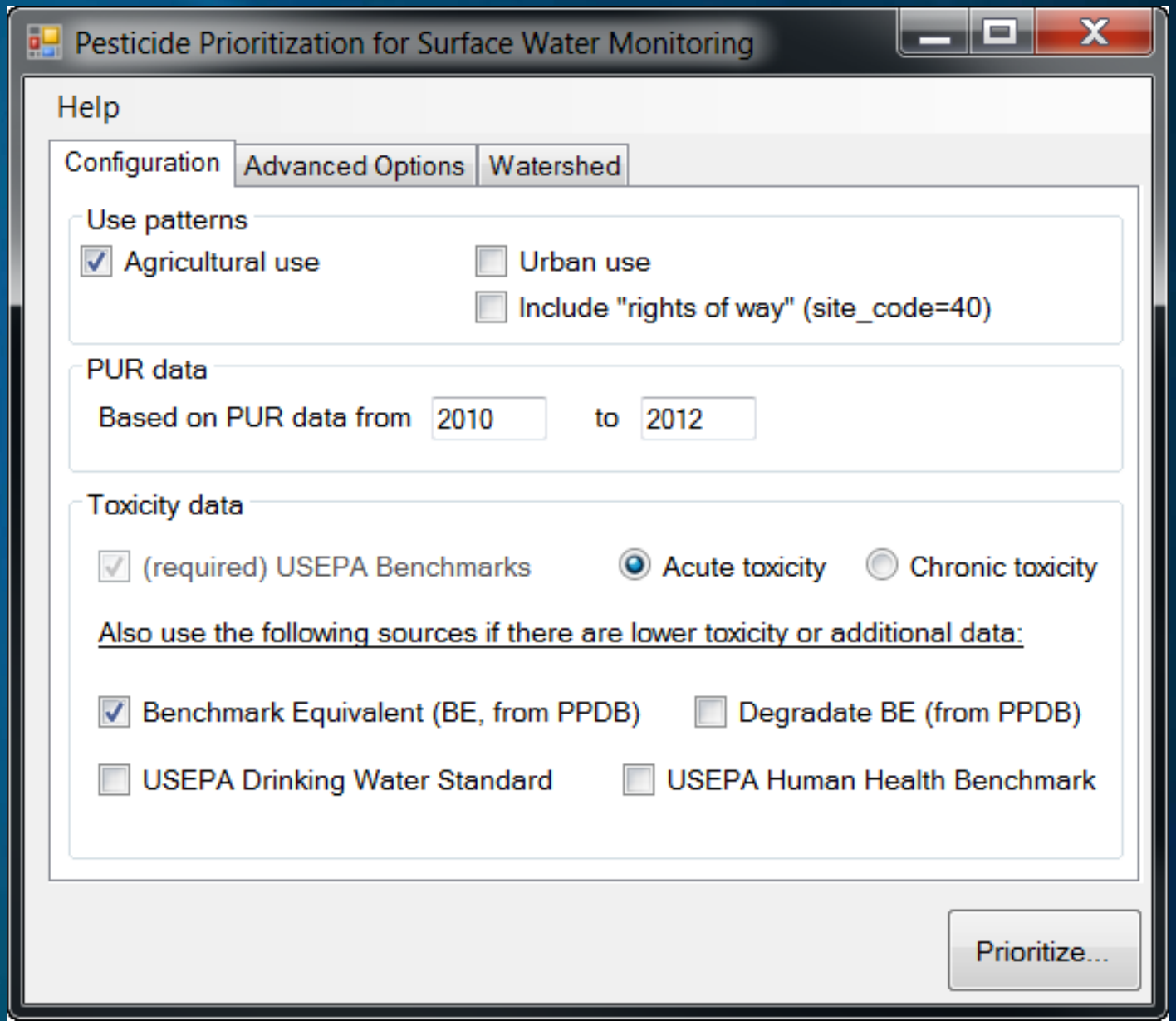
Chem_code	CHEMNAME	finalscore	Phase2
2008	PERMETHRIN	35	TRUE
2300	BIFENTHRIN	30	TRUE
2223	CYFLUTHRIN	24	TRUE
3995	FIPRONIL	20	TRUE
~~677~~	~~CHLOROTHALONIL~~	~~16~~	~~FALSE~~
1929	PENDIMETHALIN	16	TRUE
2236	PRODIAMINE	16	TRUE
2171	CYPERMETHRIN	15	TRUE
105	CARBARYL	15	TRUE
~~229~~	~~DIQUAT DIBROMIDE~~	~~15~~	~~FALSE~~
1973	OXYFLUORFEN	15	TRUE
2149	SULFOMETURON-METHYL	15	TRUE
367	MALATHION	15	TRUE
~~5802~~	~~FLUMIOXAZIN~~	~~15~~	~~FALSE~~
2297	LAMBDA-CYHALOTHRIN	14	TRUE
1868	ORYZALIN	12	TRUE
2170	TRICLOPYR, BUTOXYETHYL ESTER	12	TRUE
3849	IMIDACLOPRID	12	TRUE
2308	DITHIOPYR	12	TRUE
~~3919~~	~~HALOSULFURON-METHYL~~	~~12~~	~~FALSE~~
231	DIURON	12	TRUE
3938	CHLORFENAPYR	12	TRUE
~~3~~	~~ACROLEIN~~	~~12~~	~~FALSE~~
3010	DELTAMETHRIN	12	TRUE
2143	CHLORSULFURON	12	TRUE

Validation 2

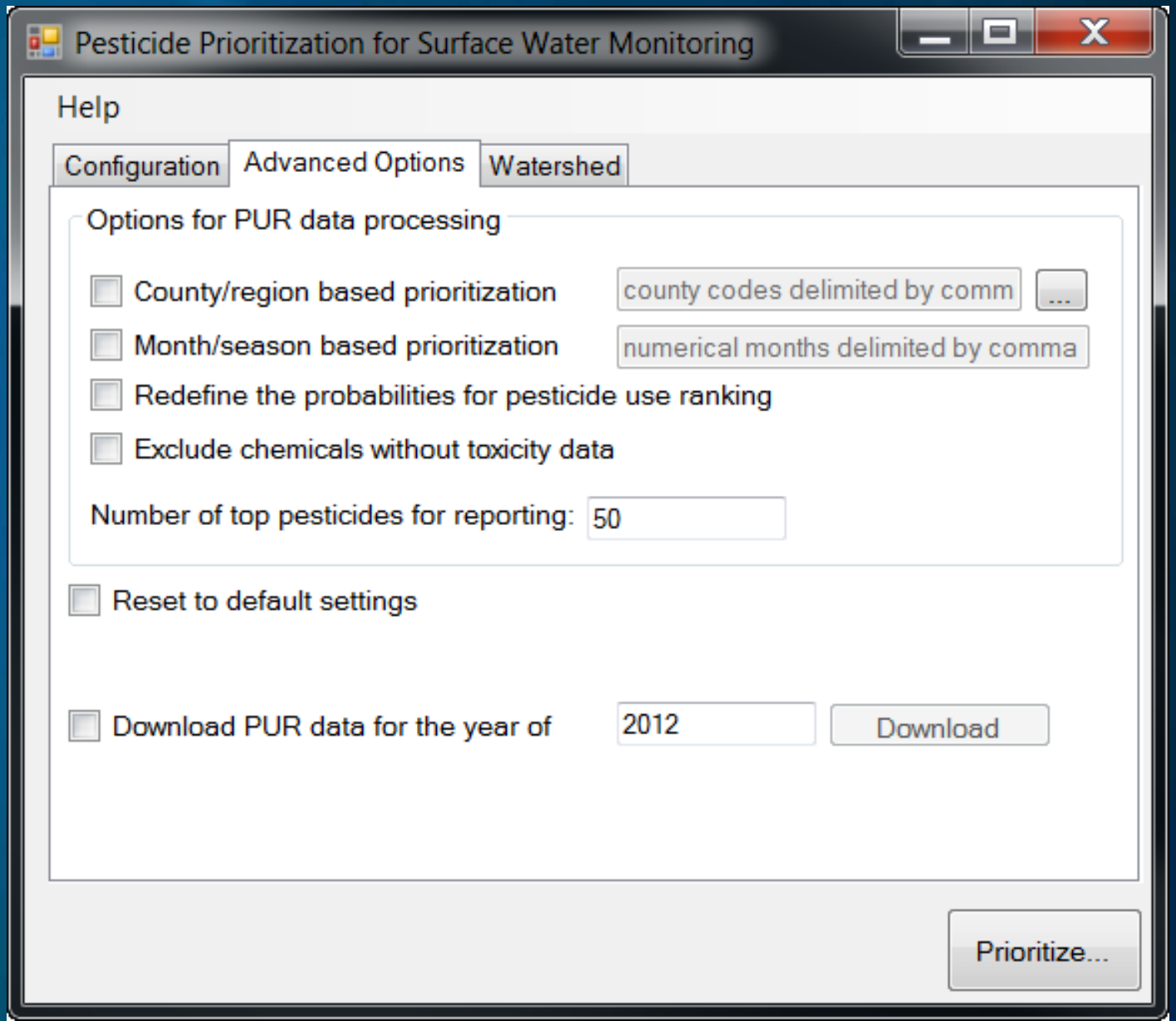
- Agriculture, Imperial, 2010-2012
- Top 20 results
- Highlighted are pesticides currently monitored in the corresponding SWPP study (Deng, 2014)

Chem_code	CHEMNAME	finalscore	Phase2
253	CHLORPYRIFOS	24	TRUE
2008	PERMETHRIN	21	TRUE
1929	PENDIMETHALIN	20	TRUE
597	TRIFLURALIN	20	TRUE
367	MALATHION	20	TRUE
383	METHOMYL	16	TRUE
45	ATRAZINE	15	TRUE
2297	LAMBDA-CYHALOTHRIN	14	TRUE
636	2,4-D	12	TRUE
216	DIMETHOATE	12	TRUE
~~834~~	~~BROMOXYNIL OCTANOATE~~	~~12~~	~~FALSE~~
~~677~~	~~CHLOROTHALONIL~~	~~12~~	~~FALSE~~
361	LINURON	12	TRUE
2321	ESFENVALERATE	12	TRUE
2300	BIFENTHRIN	12	TRUE
2223	CYFLUTHRIN	12	TRUE
70	BENSULIDE	10	TRUE
~~229~~	~~DIQUAT DIBROMIDE~~	~~10~~	~~FALSE~~
2171	CYPERMETHRIN	10	TRUE
1973	OXYFLUORFEN	10	TRUE
1601	PARAQUAT DICHLORIDE	10	TRUE
198	DIAZINON	10	TRUE
~~211~~	~~MANCOZEB~~	~~9~~	~~FALSE~~
3849	IMIDACLOPRID	9	TRUE

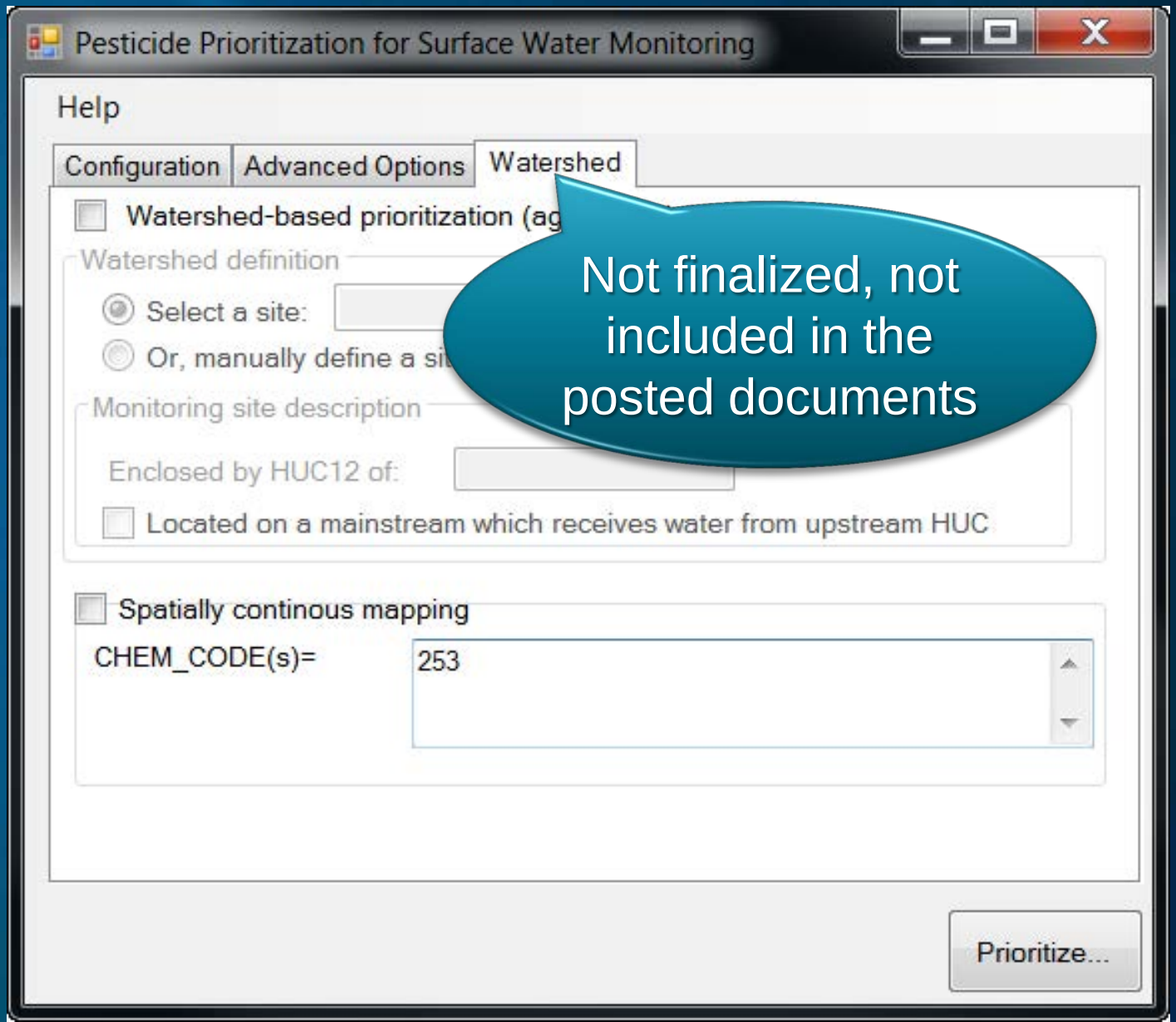
Graphical user interface (GUI)



Graphical user interface (GUI)



Graphical user interface (GUI)



Not finalized, not included in the posted documents

Demonstration 1, a simple test

- Region: statewide
- Settings: agricultural, annual data of 2010-2012
- Toxicity data: acute aquatic benchmarks for parent AI's

Demonstration 1, a simple test

- Results

Phase 1: use and toxicity

Phase 2: Monitoring recommendation

chem_code	CHEMNAME	use	usescore	benchmark	toxscore	finalscore	toxflag	Phase2
253	CHLORPYRIFOS	1225664.4	5	0.05	6	30		True
1601	PARAQUAT DICHLORIDE	856215.1	5	0.396	5	25		True
2008	PERMETHRIN	109891.1	3	0.01	7	21		True
2297	LAMBDA-CYHALOTHRIN	46526.9	3	0.0035	7	21		True
1929	PENDIMETHALIN	1828873.6	5	5.2	4	20		True
677	CHLOROTHALONIL	994390.2	5	1.8	4	20		False
629	ZIRAM	890609.6	5	9.7	4	20		False
1973	OXYFLUORFEN	580854.7	4	0.29	5	20		True
367	MALATHION	463661.7	4	0.3	5	20		True
2300	BIFENTHRIN	115280.9	3	0.075	6	18		True
597	TRIFLURALIN	475117.7	4	7.52	4	16		True
231	DIURON	323798.9	4	2.4	4	16		True
5133	S-METOLACHLOR	271979.6	4	8	4	16		True
383	METHOMYL	241613.7	4	2.5	4	16		True
503	PROPANIL	2128463.9	5	16	3	15		True

Demonstration 1, a simple test

- Notes

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

====================
PUR Chem_code: 629
Chemical name: ZIRAM
Short persistence in water, based on hydrolysis or other degradation processes

====================
PUR Chem_code: 211
Chemical name: MANCOZEB
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: 5802
Chemical name: FLUMIOXAZIN
Short persistence in water, based on hydrolysis or other degradation processes

====================
PUR Chem_code: 104
Chemical name: CAPTAN
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: 229
Chemical name: DIQUAT DIBROMIDE
Low bio-availability in water-sediment system

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

Demonstration 2, urban

- Region: Orange County
- Settings: urban and right-of-way, dry season (May to Oct.) of 2010-2012
- Toxicity data: acute aquatic benchmarks for parent AI's and *degradates*

Demonstration 2, urban

- Results

Phase 1: use and toxicity

Phase 2: Monitoring recommendation

chem_code	CHEMNAME	use	usescore	benchmark	toxscore	finalscore	toxfla	Phase2	Degradate
2008	PERMETHRIN	3167.2	5	0.01	7	35		True	False
2297	LAMBDA-CYHALOTHRIN	851.4	4	0.0035	7	28		True	False
2223	CYFLUTHRIN	1793.7	4	0.0125	6	24		True	False
2300	BIFENTHRIN	1579.8	4	0.075	6	24		True	False
677	CHLOROTHALONIL	7695.6	5	1.8	4	20		False	False
3995	FIPRONIL	2245.1	4	0.11	5	20		True	True
3010	DELTAMETHRIN	271.6	3	0.055	6	18		True	False
2170	TRICLOPYR, BUTOXYETHYL ESTER	2870.6	5	70	3	15		False	False
229	DIQUAT DIBROMIDE	443.2	3	0.75	5	15		False	False
2171	CYPERMETHRIN	345.9	3	0.195	5	15		True	False
1973	OXYFLUORFEN	323.9	3	0.29	5	15		True	False
367	MALATHION	241.3	3	0.3	5	15		True	False
211	MANCOZEB	1855.6	4	47	3	12		False	False
636	2,4-D	926.2	4	13.1	3	12		True	False

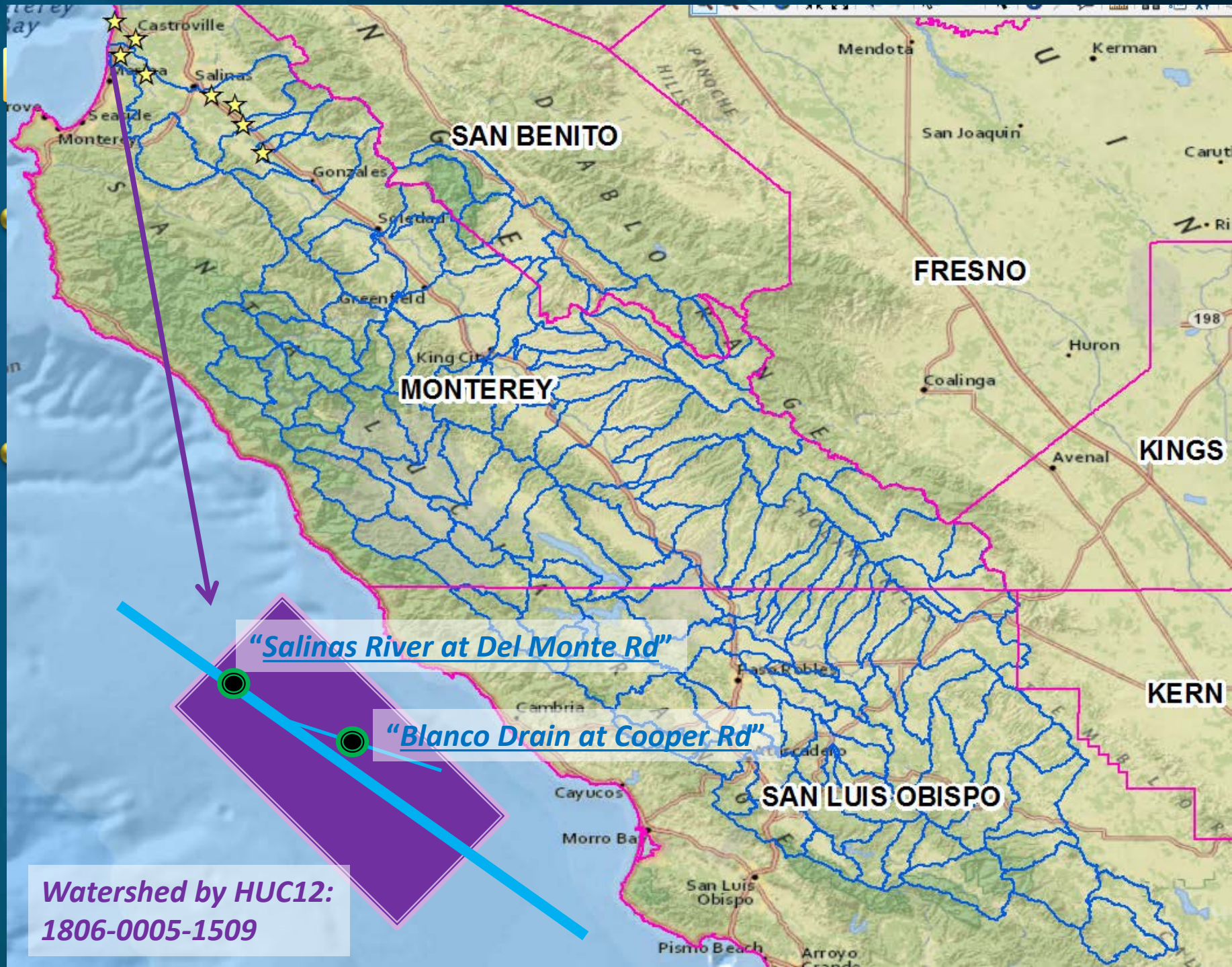
Demonstration 2, urban

- Notes

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

====================
PUR Chem_code: 3995
Chemical name: FIPRONIL
The following degradates for this chemical may be included for monitoring:
fipronil sulfone (the lowest acute benchmark equivalent=12.5)
fipronil sulfide (the lowest acute benchmark equivalent=15)

====================
PUR Chem_code: 2170
Chemical name: TRICLOPYR, BUTOXYETHYL ESTER
All dominant products are registered with low-risk use patterns or low-risk application methods

====================
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: 2244
Chemical name: HYDROPRENE
All dominant products are registered with low-risk use patterns or low-risk application methods
Low soil runoff potentials, based on vapor pressure
```

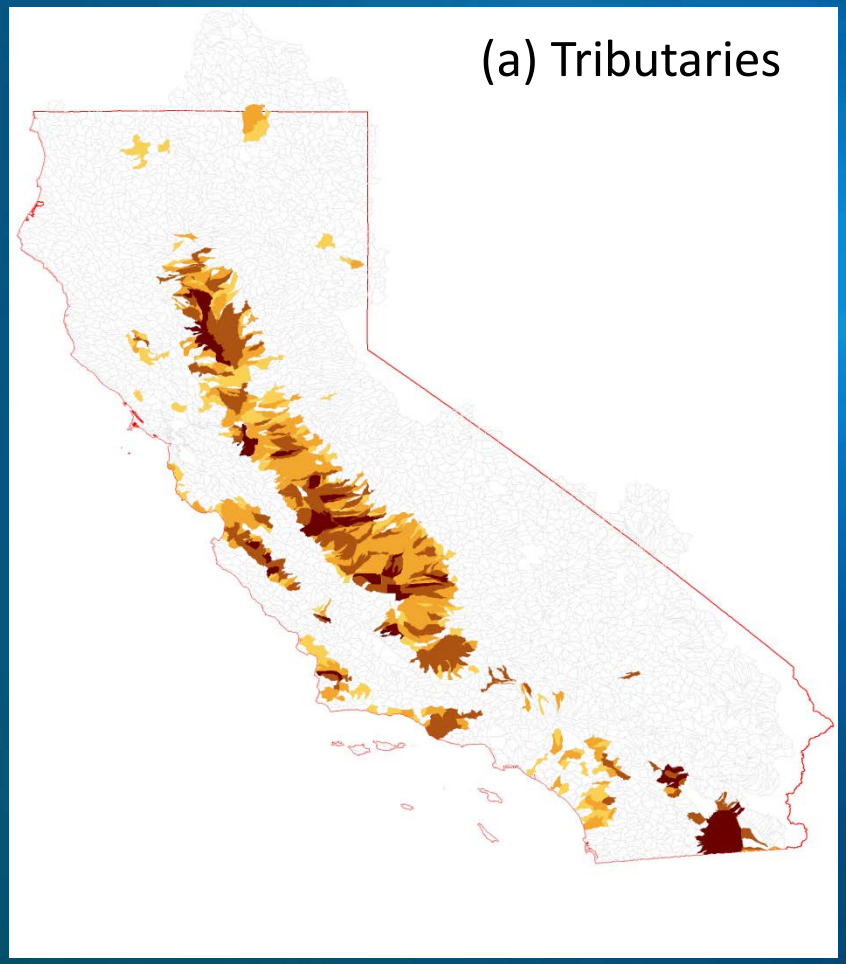
Demonstration 3, watershed

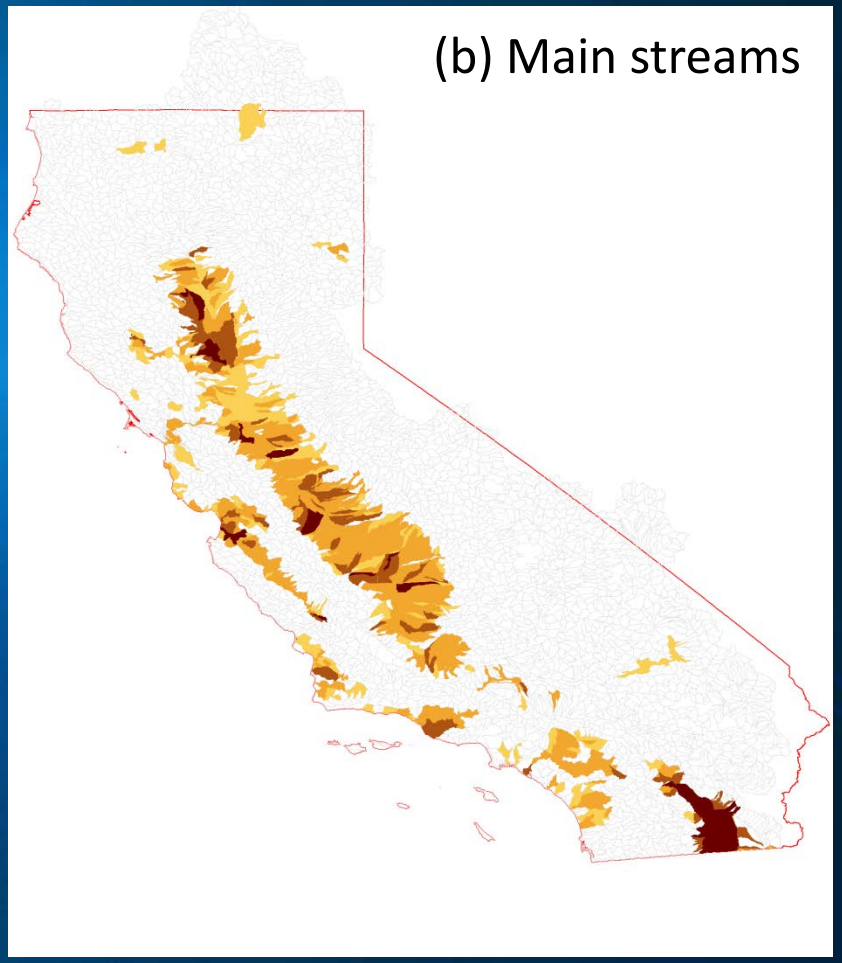
- Region: drainage area of "*Salinas River at Del Monte Rd*" (defined by DPR Study 290, Deng, 2014)
  1) Manual geo-referencing to a USGS 12-dig HUC
  2) (Yes/No) Main stream receiving upstream discharge
- Settings: agricultural, annual data of 2010-2012


Castroville
Salinas
Seaside
Monterey
Gonzales
Soledad
Greenfield
King City
SAN BENITO
MONTEREY
FRESNO
KINGS
KERN
SAN LUIS OBISPO
Mendota
Kerman
San Joaquin
Huron
Coalinga
Avenal
Paso Robles
Cambria
Cayucos
Morro Bay
San Luis Obispo
Pismo Beach
Arroyo Grande
198
"Salinas River at Del Monte Rd"
"Blanco Drain at Cooper Rd"
Watershed by HUC12:
1806-0005-1509

Spatially continuous mapping

Chlorpyrifos, agriculture, annual, 2012
Priority score = use/area/toxicity





Not a monitoring PI?

- A tool for PUR query
  - e.g., urban bifenthrin use in Central Valley (13 counties) during May to August of 2010?
- Compiled toxicity database (aquatic toxicity, drinking water, human health; acute and chronic; parents and degradates)
- Chemical properties: a formatted and up-to-date copy of FOOTPRINT PPDB
- Comprehensive monitoring data for pesticides, based on SURF (DPR), NWIS (USGS), CEDEN (CWRCB)

All indexed by CHEM_CODE!

FAQ

- For a specific pesticide, its [use score] may change? Why not fixed cut values?
- Use data not covered by PUR: indoor uses, homeowner uses, surfactants, etc.?
- More toxicity database such as EcoToxicity? Saltwater species?
- Relative runoff potentials for different crops, use patterns, soil/weather/hydrology conditions?
- Connections with SWPP registration evaluation?
- Model availability?

Questions?

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