Constituents of Emerging Concern

Current Regulatory Framework and Results on Russian River Watershed Pilot Study

Jeremiah Puget – Regional Water Board
Dr. Alvina Mehinto – Southern CA Coastal Water Research Project
Dr. Rebecca Sutton – San Francisco Estuary Institute
Jennifer Sun – San Francisco Estuary Institute

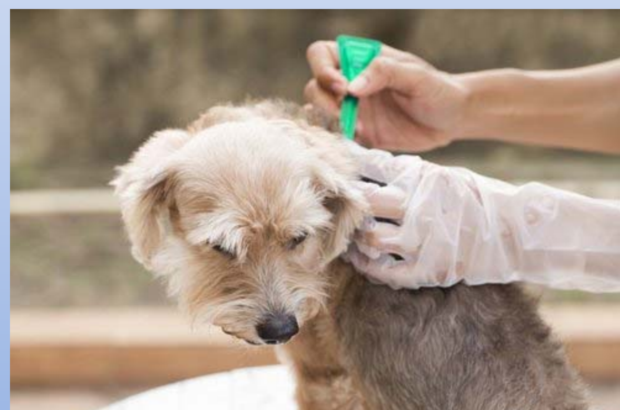
Item No. 7
North Coast Regional Water Quality Control Board
February 8, 2018

CALIFORNIA Water Boards

Presentation Outline

- Background on Statewide Efforts *(15 min.)*
- Russian River Pilot Study Results
  - Water & Sediment - Analytical & BioAnalytical Screens
    - Dr. Alvina Mehinto – SCCWRP *(15 min.)*
  - Fish Tissue
    - Dr. Rebecca Sutton- SFEI *(15 min.)*
  - Pesticides
    - Jennifer Sun – SFEI *(15 min.)*
- Next Steps
- Questions and Comments

Constituents of Emerging Concern



Challenges to Current Monitoring

- Too many chemicals to monitor
  - Over 100,000 known chemicals
  - More discovered every year

- No standardized analytical methods for unexpected and/or unknown chemicals incl. metabolites, byproducts

- Relevant toxicity data often unavailable
  - Chronic sub-lethal toxicity is of concern
  - Toxicity potential of chemical mixtures understudied

Pathways to the Environment

Treated Wastewater

- Permitted Discharges
- Recycled Water
- Biosolids

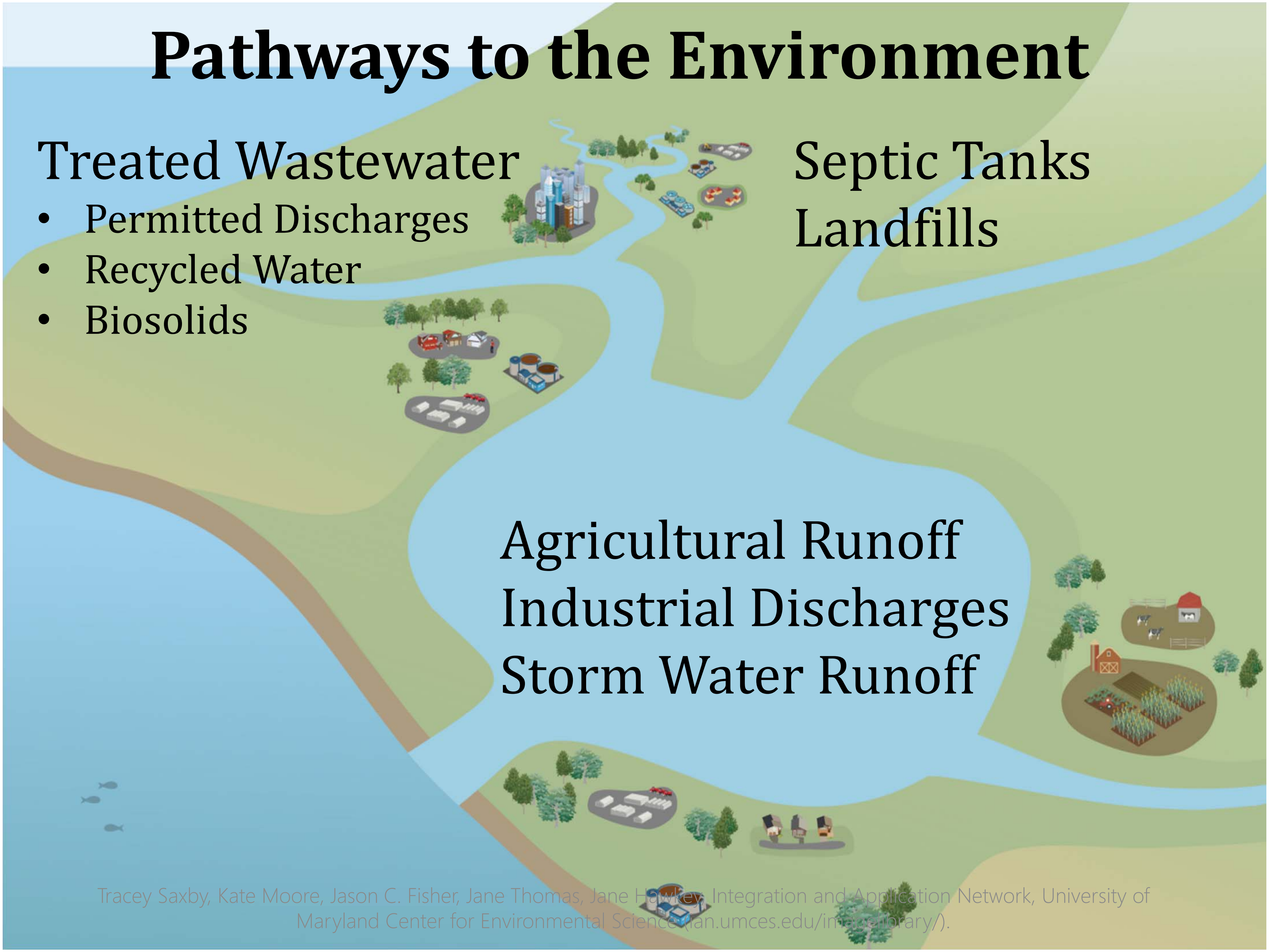
Septic Tanks

Landfills

Agricultural Runoff

Industrial Discharges

Storm Water Runoff

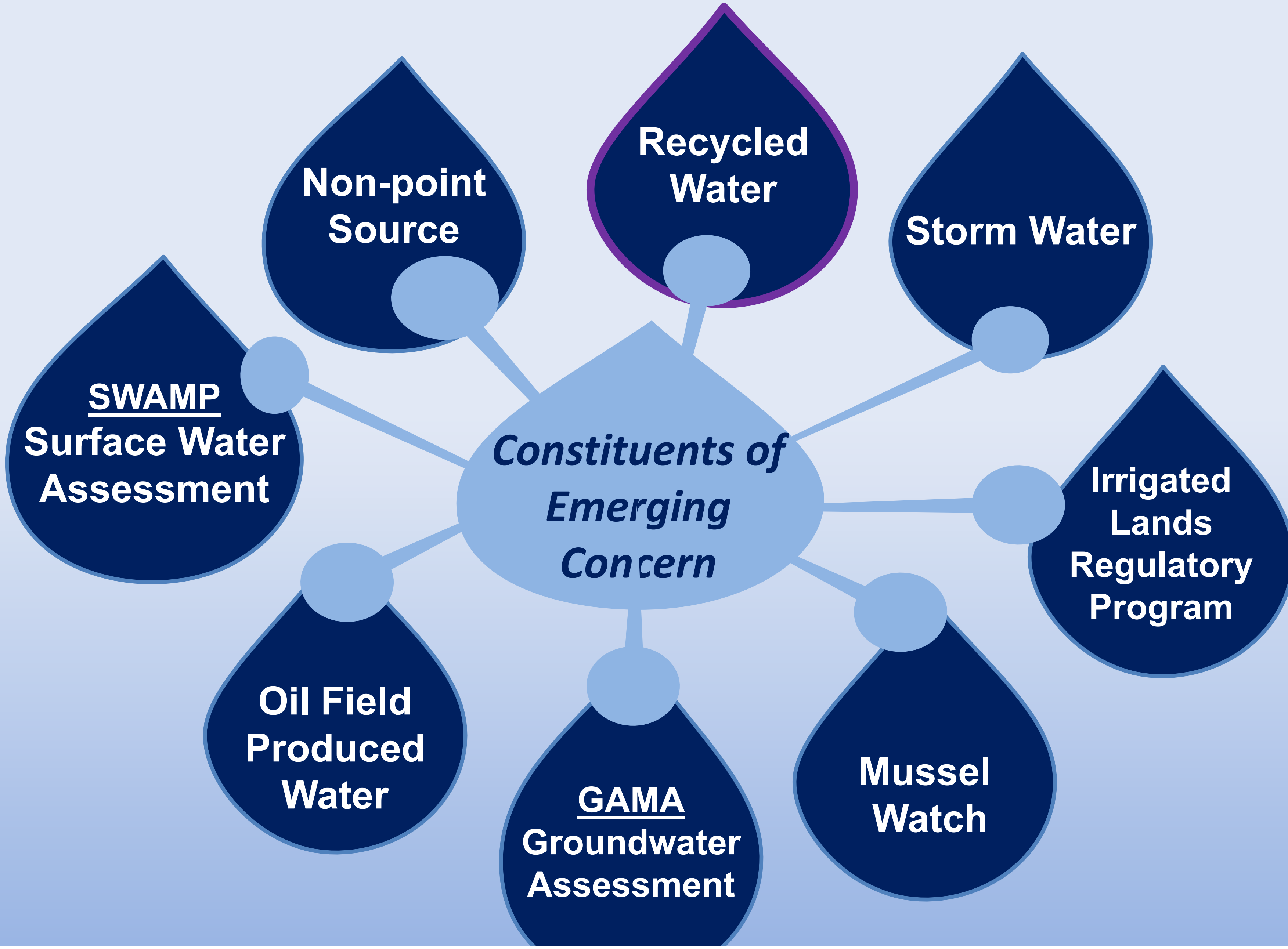


Tracey Saxby, Kate Moore, Jason C. Fisher, Jane Thomas, Jane Hawkey, Integration and Application Network, University of Maryland Center for Environmental Science (ian.umces.edu/imagelibrary/).

Regulatory Framework for CECs

- Recycled Water Policy (2009)
  - CEC Expert Panel (2010)
  - *Monitoring Strategies for Chemicals of Emerging Concern in Recycled Water (2010)*
  - *Monitoring Strategies for Chemicals of Emerging Concern in California's Aquatic Ecosystems (2012)*
- Policy Amendment (2013)
  - Included monitoring and reporting of recycled water used for groundwater recharge projects
- Current Policy Amendment (2018/2019)
  - *Updated CEC Panel Recommendations for Recycled Water (Draft report is currently available for public review)*

Regulatory Framework for CECs



State Water Board Role

- Identify and improve the knowledge base
- Work with DWQ, DDW, Regions, and Expert Panel to develop and implement monitoring strategies for recycled water and other types of discharges
- Track and help evaluate effectiveness of regulatory interventions
- Direct pilot monitoring in ambient recommended by expert panel

CALIFORNIA Water Boards
STATE WATER RESOURCES CONTROL BOARD
REGIONAL WATER QUALITY CONTROL BOARDS

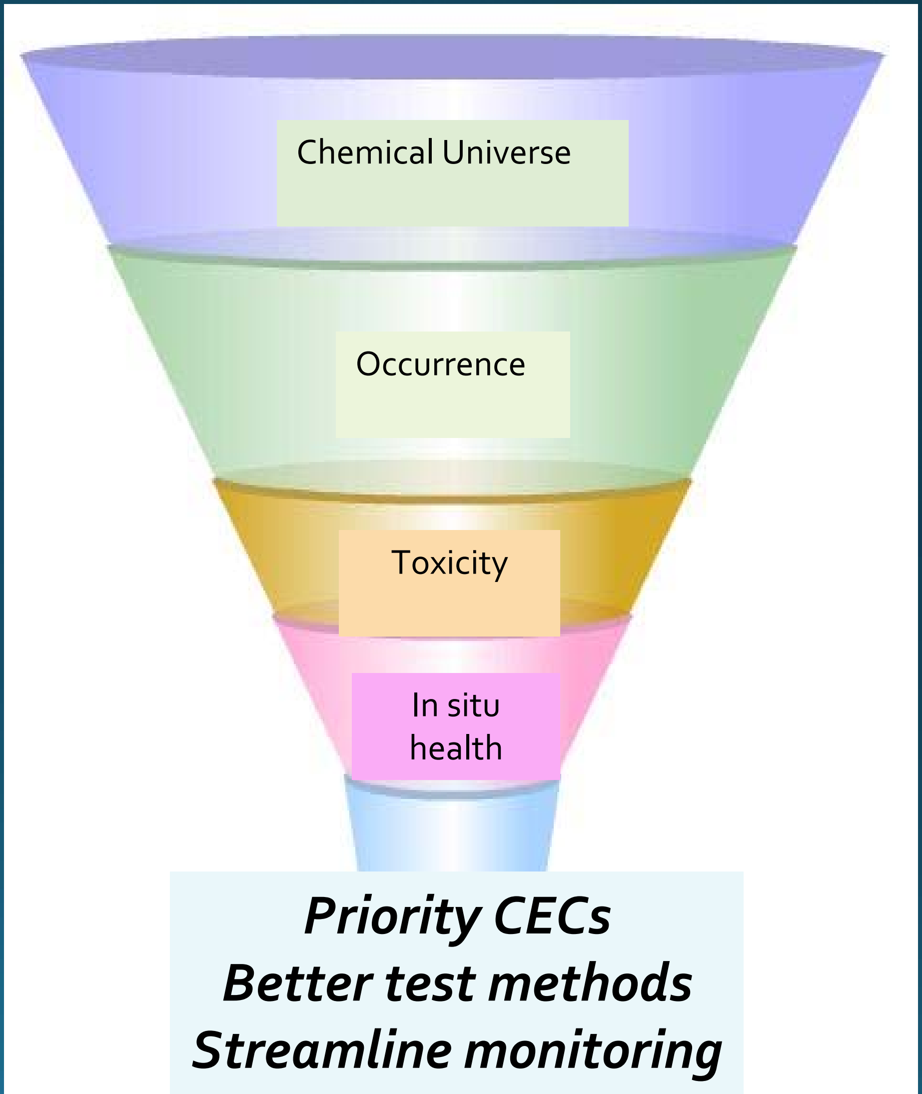
CEC Initiative

Origin of the Ecosystem Panel

- State of knowledge regarding CECs is incomplete
- Regulatory requirements need to be based on best available peer-reviewed science
- Experts needed to guide future monitoring activities
- All members of Recycled Water Panel retained, with the addition of experts in marine resources & antibiotic resistance

Is there a better way to monitor CECs?

- Adaptive management
  - Collect and *interpret* data
  - *Adjust* target parameters, monitoring effort
  - Test promising *new* technologies



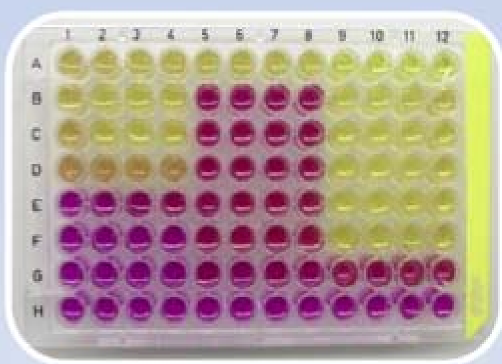
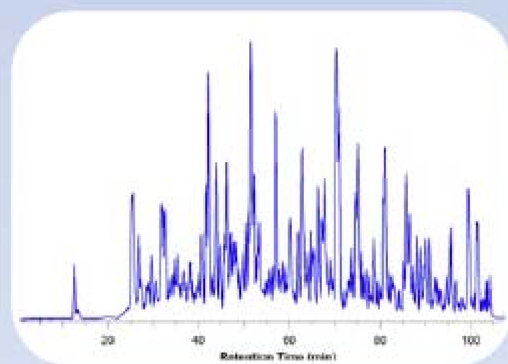
Is there a better way to monitor CECs?

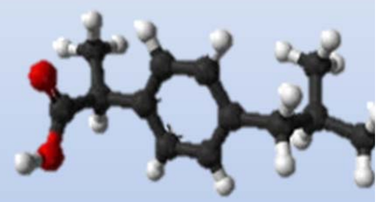
- New monitoring tools
  - *bioanalytical tools* to screen for toxicants by mode of action
  - *non-targeted analysis* to identify toxicants that elude targeted methods

- Develop monitoring thresholds
  - *Monitoring Trigger Levels* (MTLs)
  - Measured environmental concentrations (MEC)
  - Predicted environmental concentrations (PEC)

- Research initiatives
  1. Developing of *bioanalytical screening tools*;
  2. Filling *data gaps* on CEC sources, fate, occurrence and toxicity; and
  3. Assessing the *relative risk* of CECs and other monitored chemicals.

CEC Monitoring Methods

Biological	Chemical
 Bioassessment	 Targeted
 Bioanalytical	 Non-targeted



?

Russian River CEC Pilot Study

SCCWRP
Established 1969

SWAMP
Surface Water Ambient Monitoring Program

SFEI

Russian River CEC Pilot Study

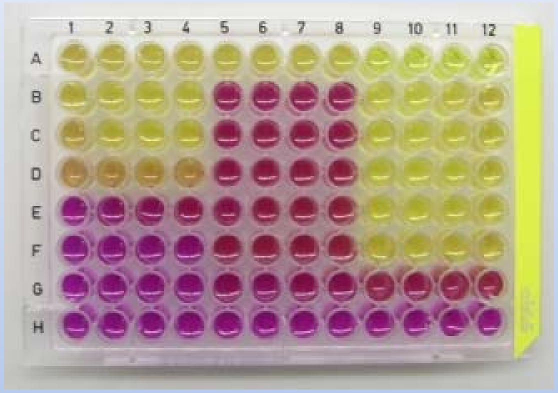
- Are CECs in WWTP effluent and storm water runoff present?
- What is the relative contribution of treated wastewater effluent and storm water runoff to CEC loading into the watershed?
- Do bioanalytical tools effectively screen for the occurrence of CECs?
- What is the extent and magnitude of CECs are in the water column, sediments and fish tissue?
- Which pesticides applied in the Russian River watershed are of highest priority for monitoring

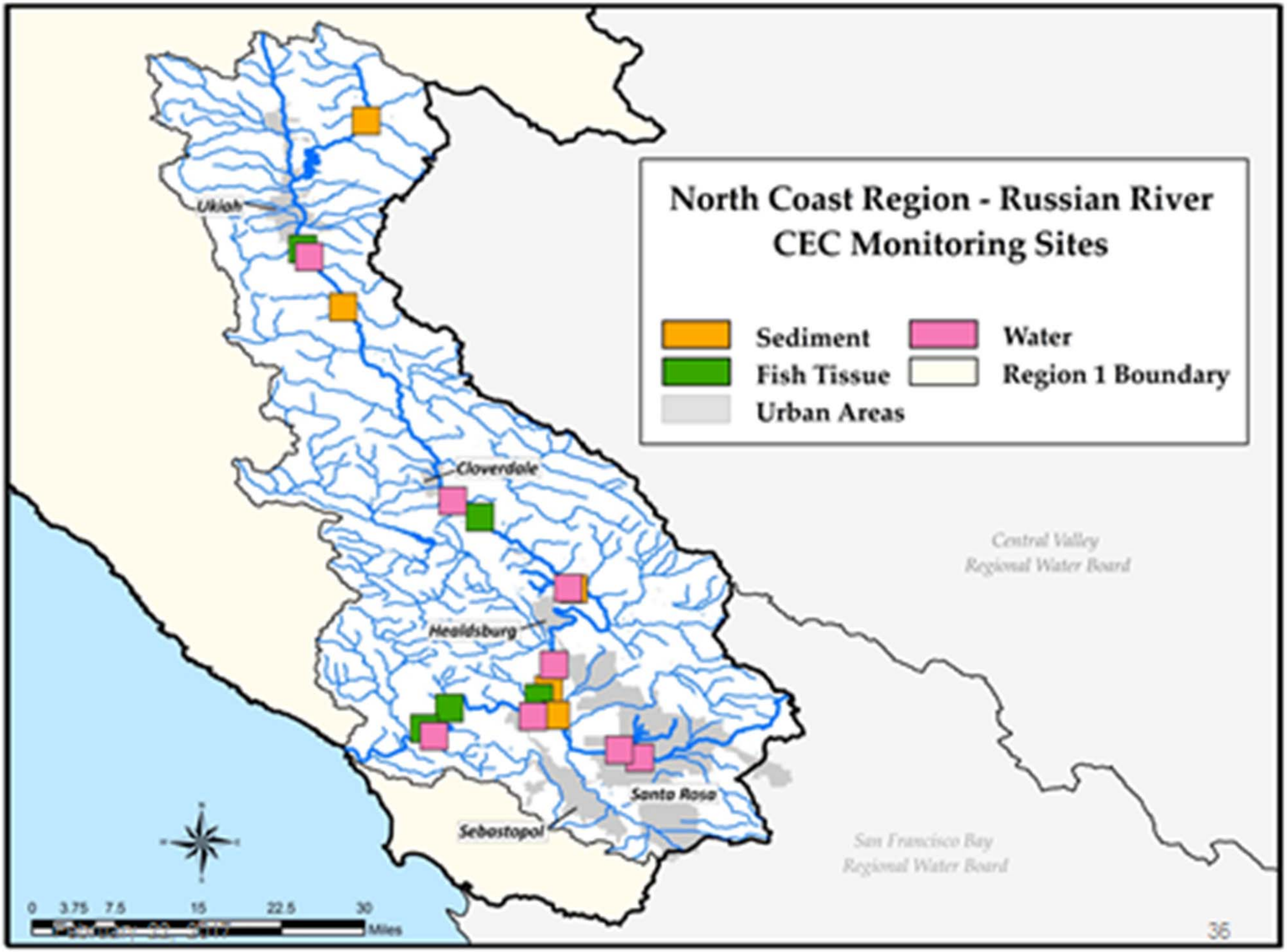
Tools for Russian River CEC Study

Targeted Chemistry

Bioanalytical

BioAssessment



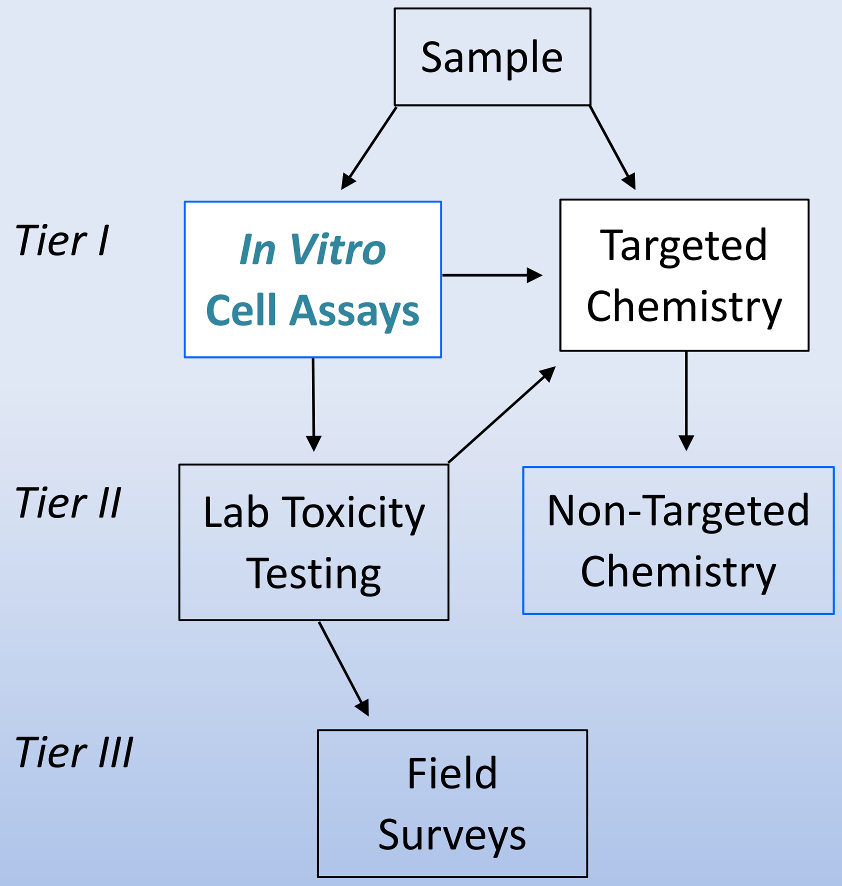

North Coast Region - Russian River
CEC Monitoring Sites
Sediment
Water
Fish Tissue
Region 1 Boundary
Urban Areas
Ukiah
Cloverdale
Healdsburg
Santa Rosa
Sebastopol
Central Valley
Regional Water Board
San Francisco Bay
Regional Water Board
0 3.75 7.5 15 22.5 30
Miles
36

Screening for CECs in Water and Sediment from the Russian River Watershed

Dr. Alvina Mehinto, Dr. Keith Maruya

Southern California Coastal Water Research Project

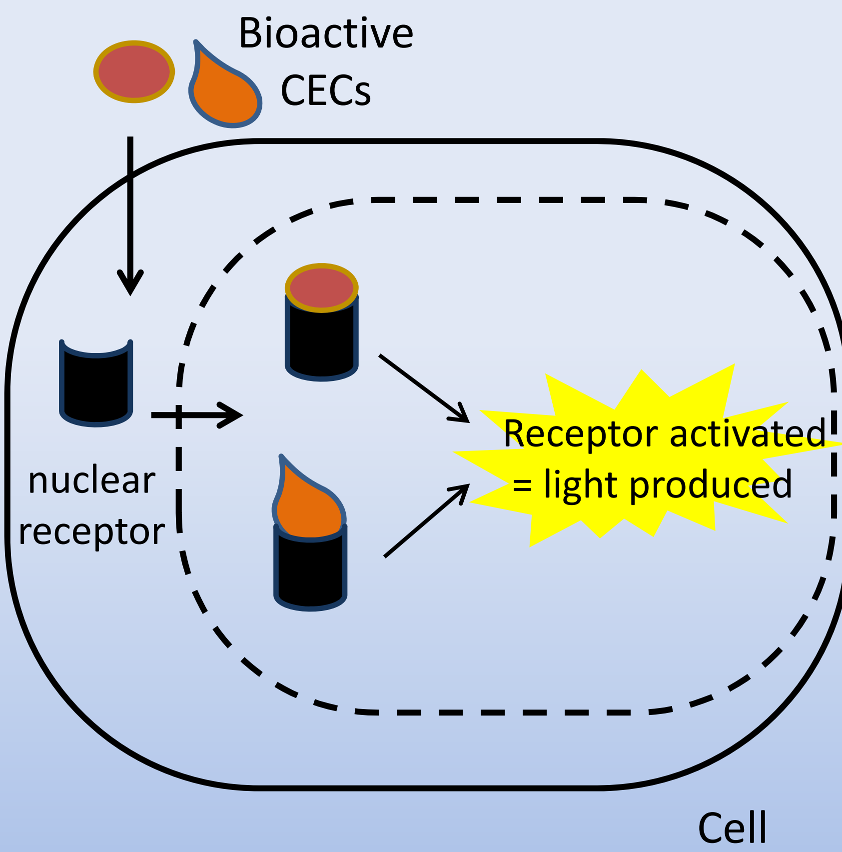
Effect-Based Monitoring



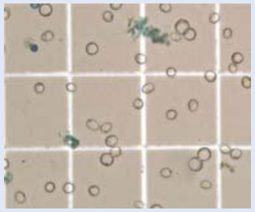
- Framework currently considered by the State Water Board
- New tools proposed to:
  - *Streamline existing monitoring approaches*
  - *Enhance capabilities to identify new and/or unknown contaminants*
  - *Identify ecologically relevant impacts*

What Are Cell Assays?

- Cells engineered to respond to specific classes of CECs
- Light intensity is proportional to the concentration of bioactive chemicals
- Results expressed relative to a known/reference chemical
    - *Bioanalytical equivalent concentration (BEQ, ng/L)*

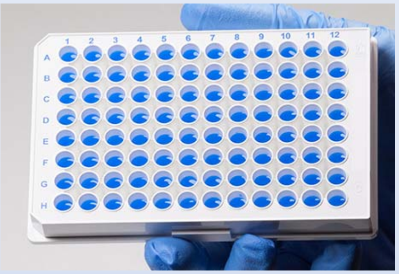


What Are Cell Assays?

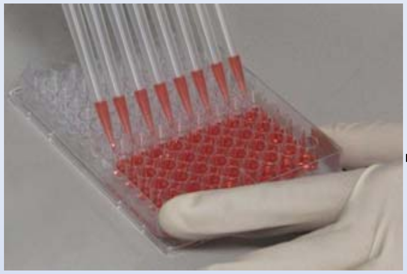


Cell culture

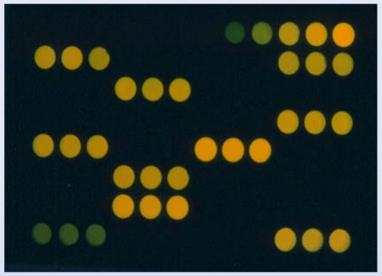
Sample extraction



Add cells + samples
Incubate plate



Add substrate
Then incubate



Measure fluorescence

Advantages of Cell Assays

- Rapid method to screen for hundreds of contaminants simultaneously in one assay
- Integrated measure of known and unknown chemicals acting via a common mode of action
    - *Potential for linkage to toxicity*
- Technology adopted by pharmaceutical, cosmetic and industrial companies to develop their products

Objectives and Study Design

What is the extent and magnitude of **endocrine active CECs** in water and sediment in the Russian River Watershed?

- Water, sediment and effluent samples collected
- Sample analyses:
  - *Cell assay bioscreening (estrogen and glucocorticoid receptor)*
  - *Targeted analyses of known CECs*

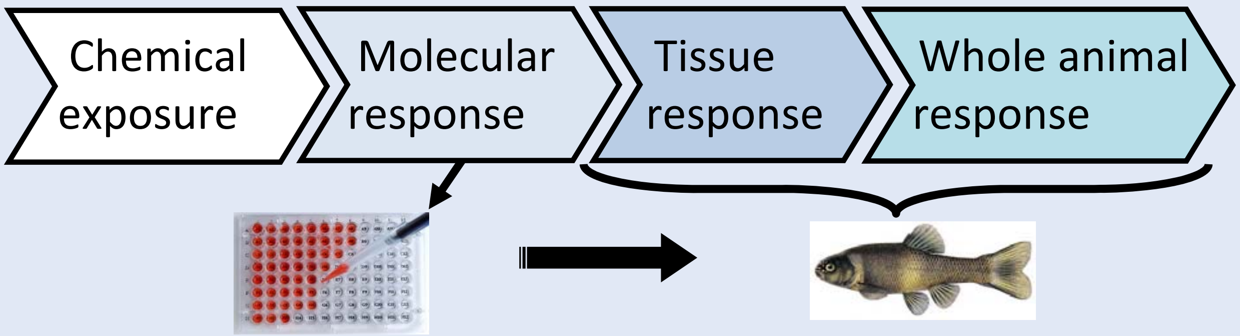
Estrogenic Screen of Water Samples

	Effluent #1	Effluent #2	Mirabel	Piner Creek	Santa Rosa Crk	El Roble
ER Bioscreen (ng E2 equiv/L)	<0.5	**1.9**	<0.5	<0.5	<0.5	<0.5
	Targeted chemical analyses (ng/L)					
17b-estradiol (E2)	<0.5	**0.6**	<0.5	<0.5	<0.5	<0.5
estrone	<0.5	**11.0**	0.5	0.6	<0.5	<0.5
bisphenol A	<10	12.0	<10	55.0	16	<10
4-nonylphenol	60.8	247	25.4	53.3	62	63
Chem. equiv. (ng/L)	<0.5	**1.6**	<0.5	<0.5	<0.5	<0.5

Estrogenic Screen of Sediment Samples

	Lytton Spring	Mirabel	Piner Creek	Santa Rosa Crk	El Roble
ER Bioscreen (ng E2 equiv./g)	<0.01	<0.01	**0.09**	<0.01	<0.01
	Targeted chemical analyses (ng/g)				
17b-estradiol (E2)	<0.12	<0.12	**0.23**	<0.12	<0.12
estrone	<0.12	0.14	**1.3**	0.4	0.28
bisphenol A	1.4	1.9	15	4.6	<1.0
4-nonylphenol	20	34	29	18	18
bifenthrin	<0.2	<0.2	130	1.96	<0.2
Chem. equiv. (ng/L)	<0.1	<0.1	**0.36**	<0.1	<0.1

Linking Bioactivity to Toxicity



- Understanding cell assay effect thresholds is key
- Fish studies have shown that exposure to 2 – 4 ng E2/L had no effect on growth and survival
  - *Effluent BEQ of 1.9 ng E2/L (without dilution) = low concern*
  - *River water BEQ < 0.5 ng E2/L = no concern*

Conclusions

- CECs present low to moderate concern in the Russian river

➢ *Water concentrations of pharmaceuticals below MTLs*

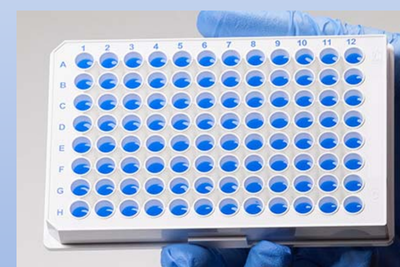
Analyte	Max. measured conc. (ng/L)	Monitoring trigger level (ng/L)
Diclofenac	< 10	100
Estrone	0.56	6
Ibuprofen	< 10	100

➢ *Some pesticide concentrations in sediment were > MTLs*

Analyte	Max. measured conc. (ng/g)	Monitoring trigger level (ng/g)
Bifenthrin	130	0.052
Fipronil	3.4	0.09
Permethrin	4.9	0.073

Conclusions

- CECs present low to moderate concern in the Russian river
- Cell assays provided a reliable and integrated measure of estrogenic chemicals
- Routine application of cell assays could provide a cost-effective strategy to prioritize sites requiring more chemical and toxicity testing



CECs in Sport Fish

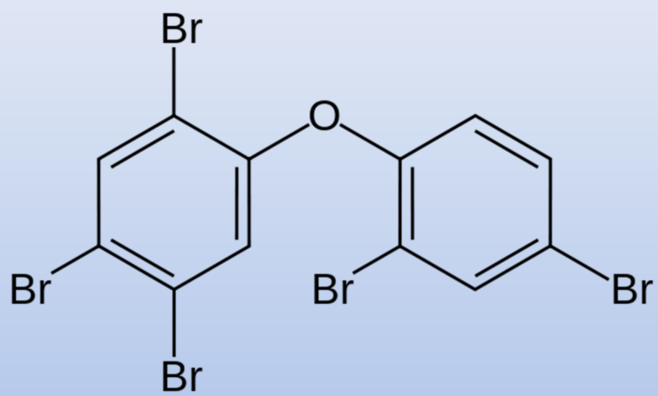
R1 CEC Pilot Monitoring

Rebecca Sutton, Thomas Jabusch, Jay Davis

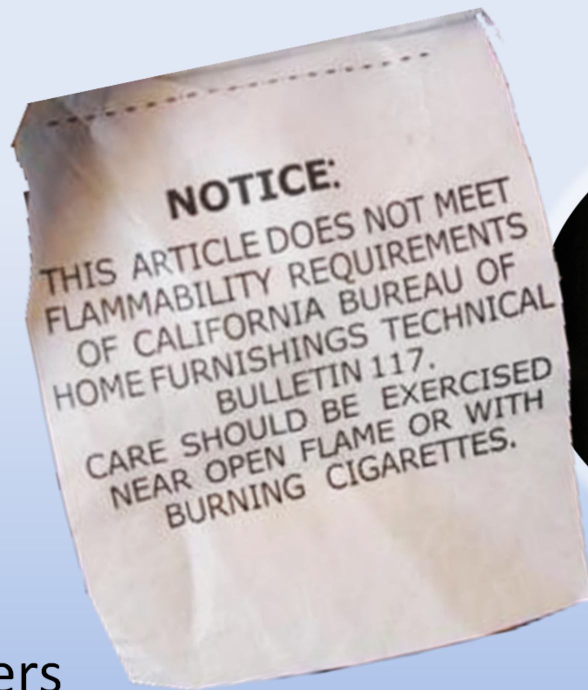
San Francisco Estuary Institute

Study Objectives

MQ3. What is the extent and magnitude of **PBDE** and **PFOS** contamination in fish tissue in the Russian River Watershed?



Polybrominated diphenyl ethers (PBDEs)



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Study Objectives

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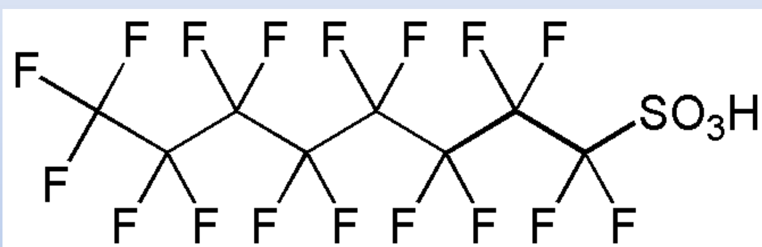

Perfluorooctane Sulfonate (PFOS)

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Study Design

6 popular fishing sites

Sacramento Pikeminnow (5)

Sacramento Sucker (5)

Redear Sunfish (1)

Smallmouth Bass (1)

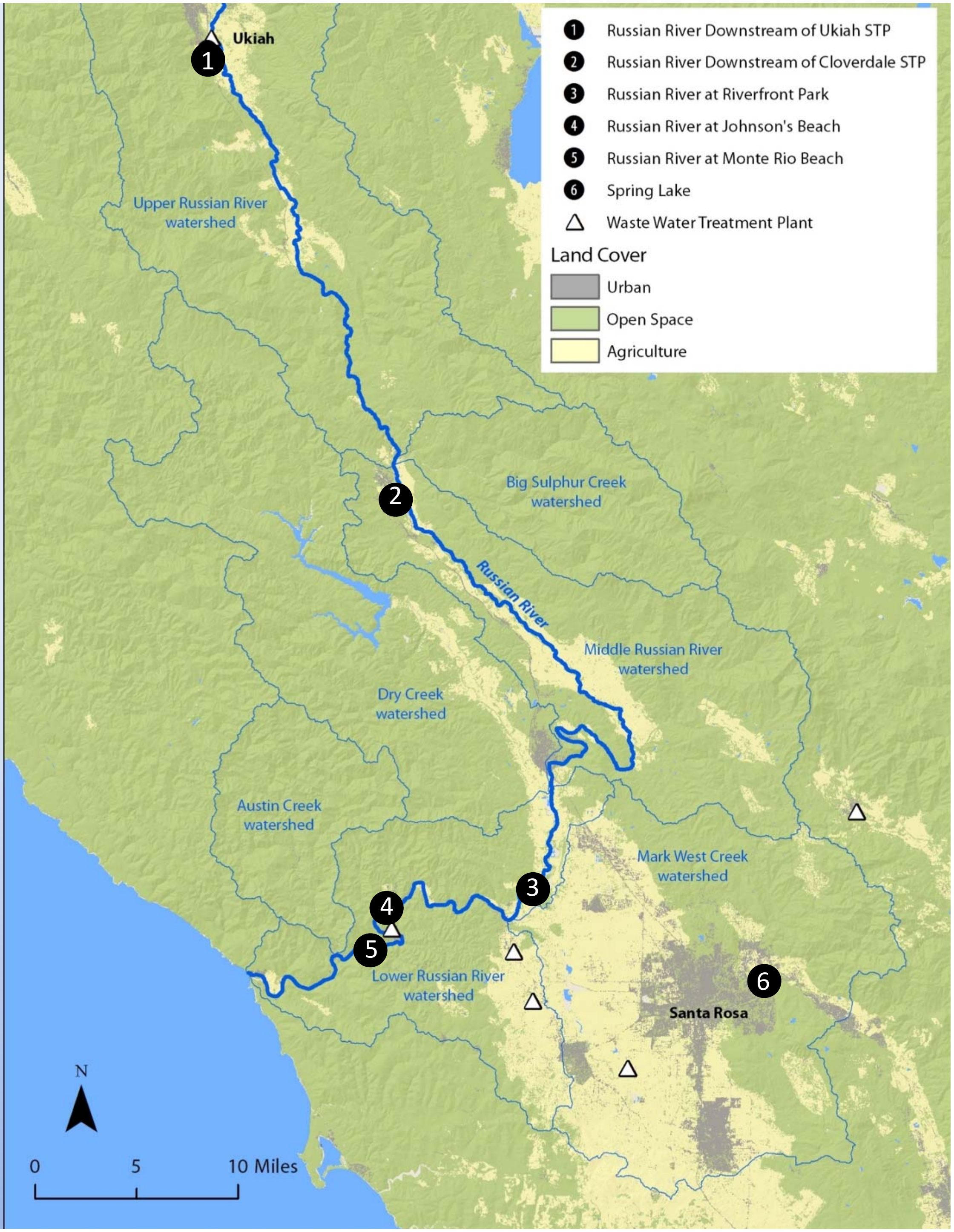
Largemouth Bass (1)

PBDEs (13 analytes)

PBDE 15, 28, 33, 47, 49, 66, 75, 99, 100, 153, 154, 155, 183

PFASs (13 analytes)

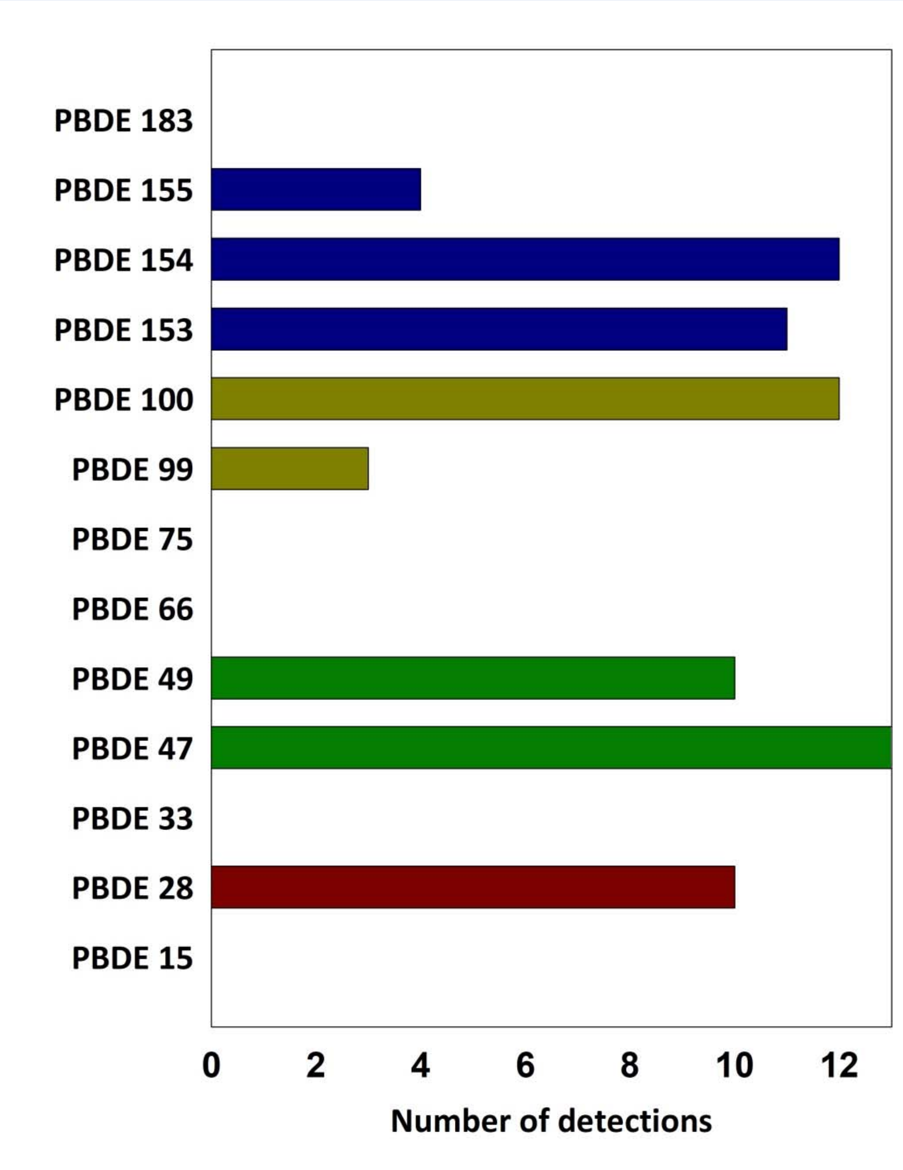
PFBA, PFBS, PFPA, PFHx, PFHxS, PFHpA, PFOA, **PFOS**, PFOSA, PFNA, PFDA, PFUA, PFDoA

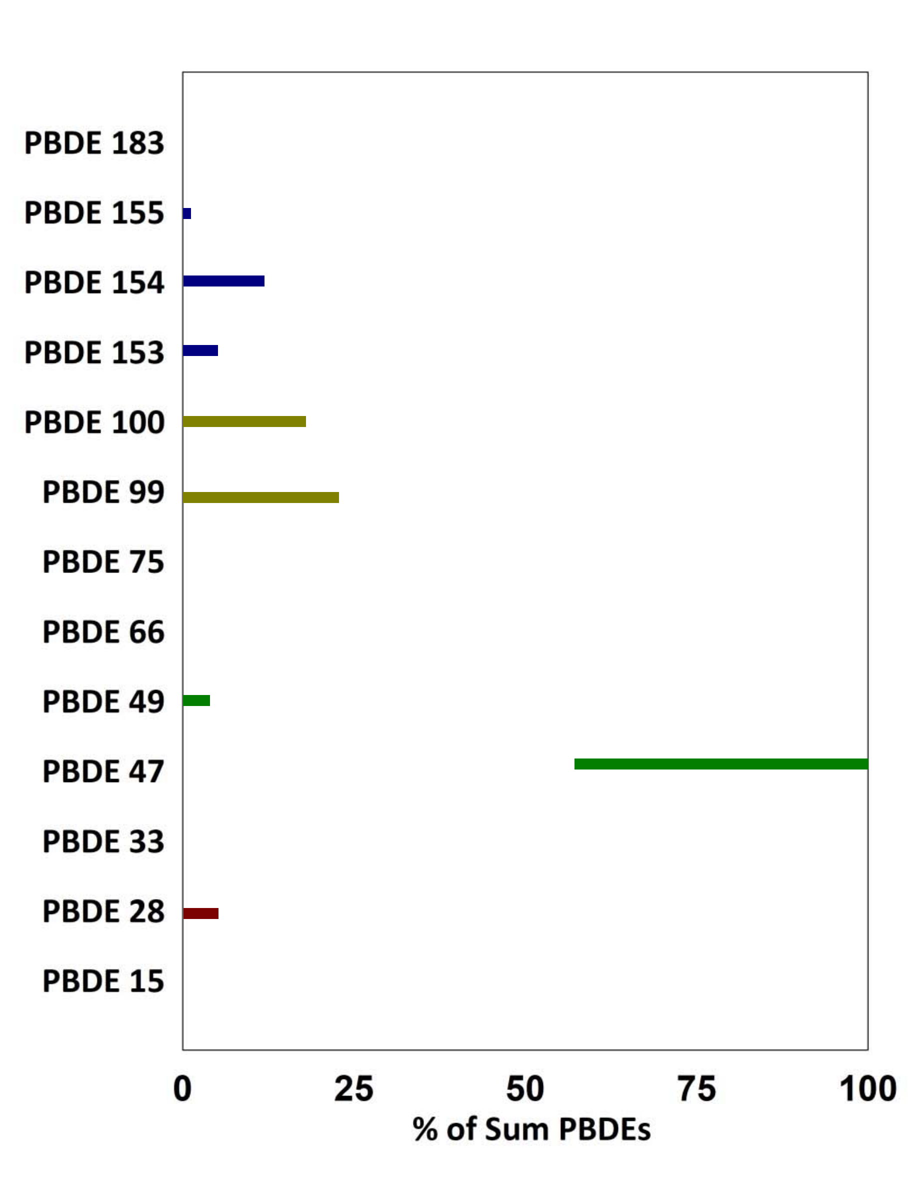


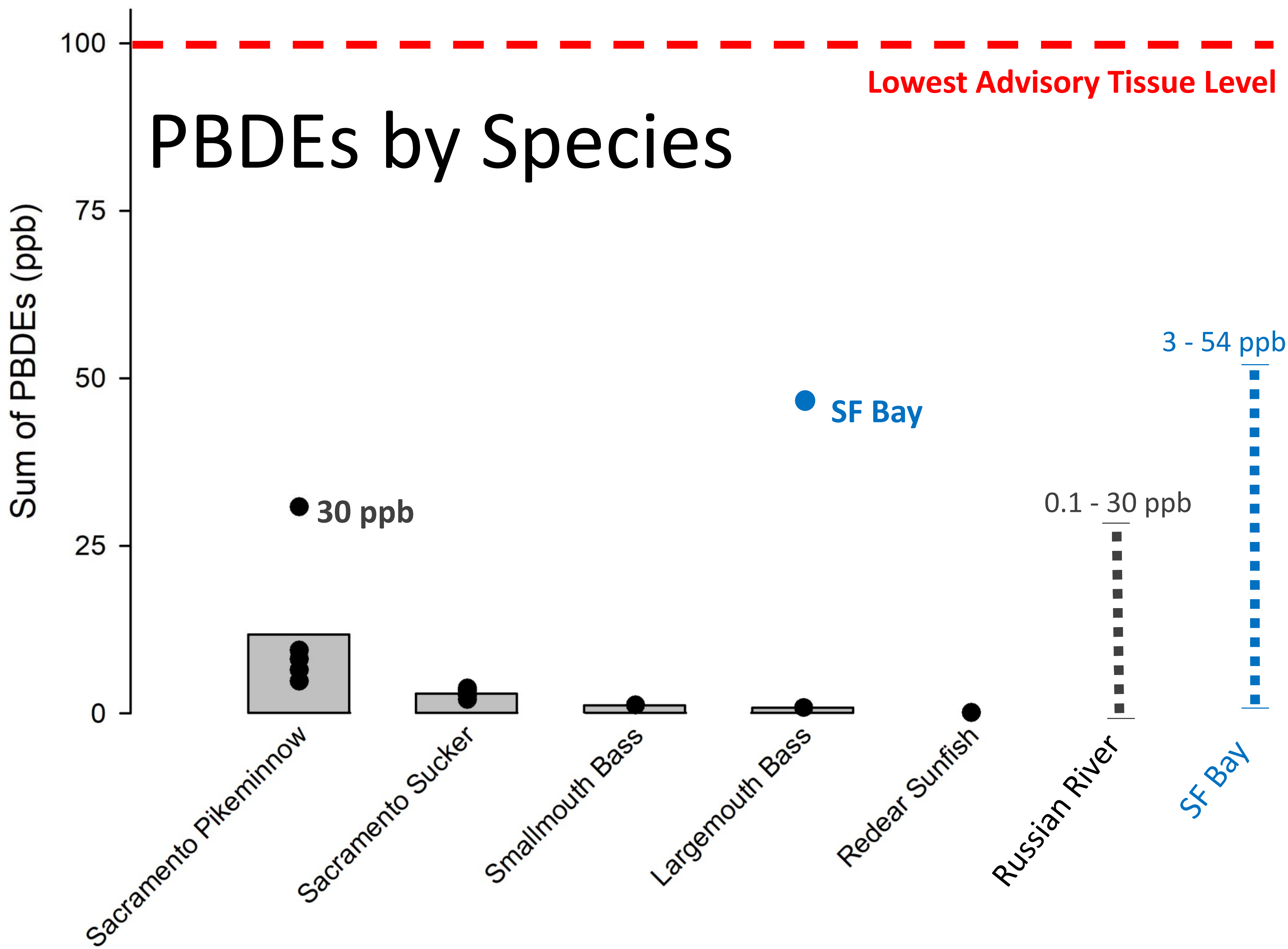
Safe to Eat Thresholds

	California: Advisory Tissue Levels			
	3 servings/week	2 servings/week	1 serving/week	No Consumption
PBDEs	< 100 ppb	100-210 ppb	210-630 ppb	> 630 ppb
	Minnesota: Meal Advice Categories			
	Unrestricted	1 meal/week	1 meal/month	DO NOT EAT
PFOS	≤ 40 ppb	> 40-200 ppb	> 200-800 ppb	> 800 ppb
	Michigan: Fish Consumption Screening Values			
	16 meals/month	12 meals/month	8 meals/month	4 meals/month
PFOS	≤ 9 ppb	> 9-13 ppb	> 13-19 ppb	> 19-38 ppb

PBDE Results

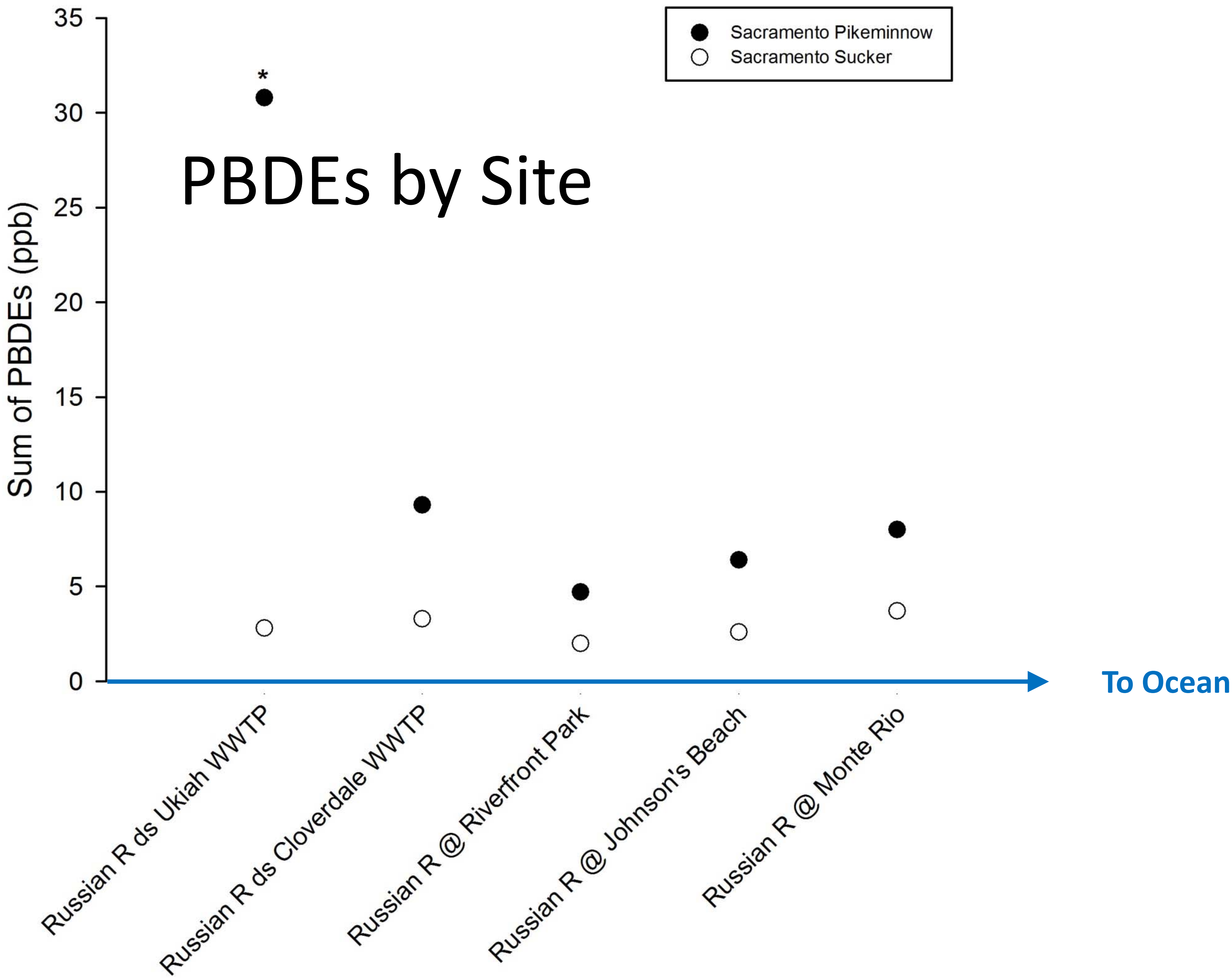




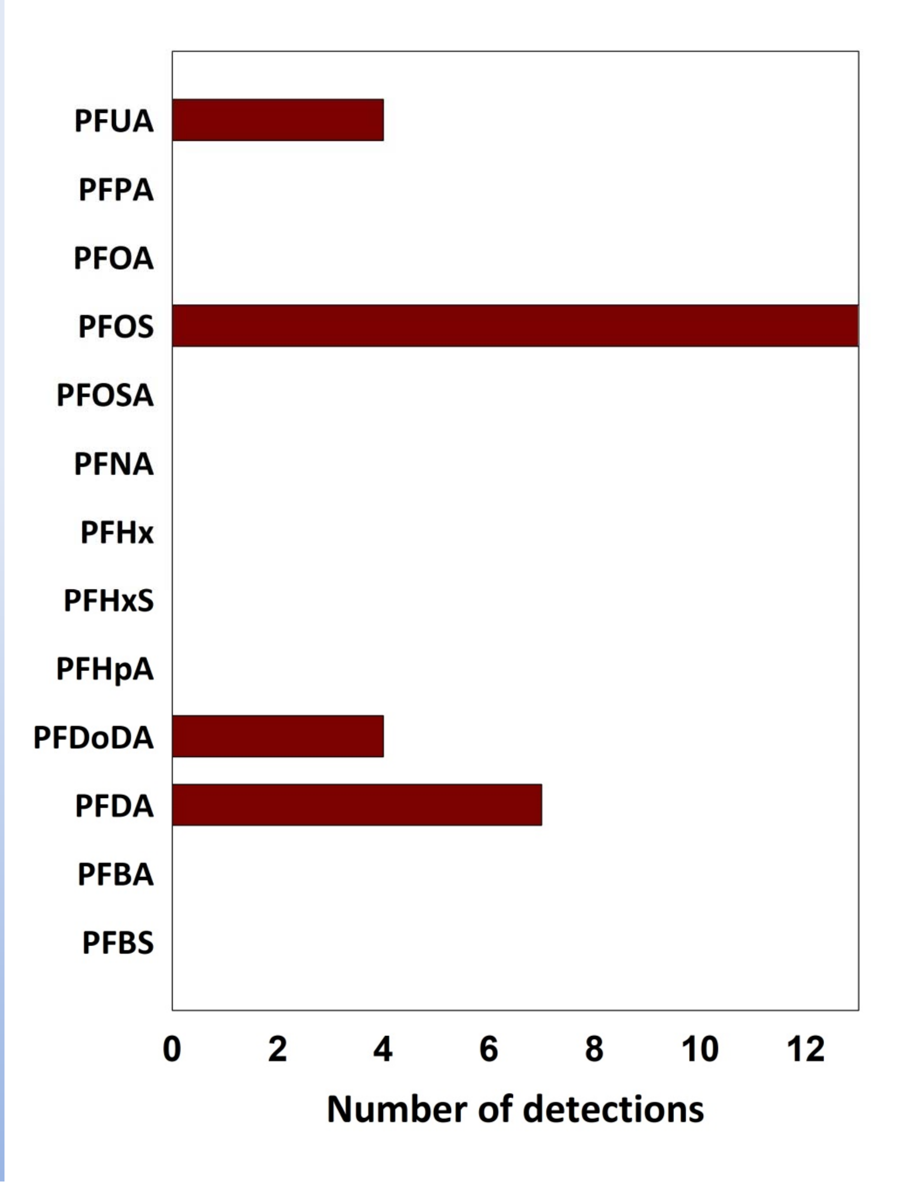


PBDEs by Species
Lowest Advisory Tissue Level
Sum of PBDEs (ppb)
100
75
50
25
0
30 ppb
SF Bay
0.1 - 30 ppb
3 - 54 ppb
Sacramento Pikeminnow
Sacramento Sucker
Smallmouth Bass
Largemouth Bass
Redear Sunfish
Russian River
SF Bay

PBDEs by Site



PFOS & Other PFASs Results



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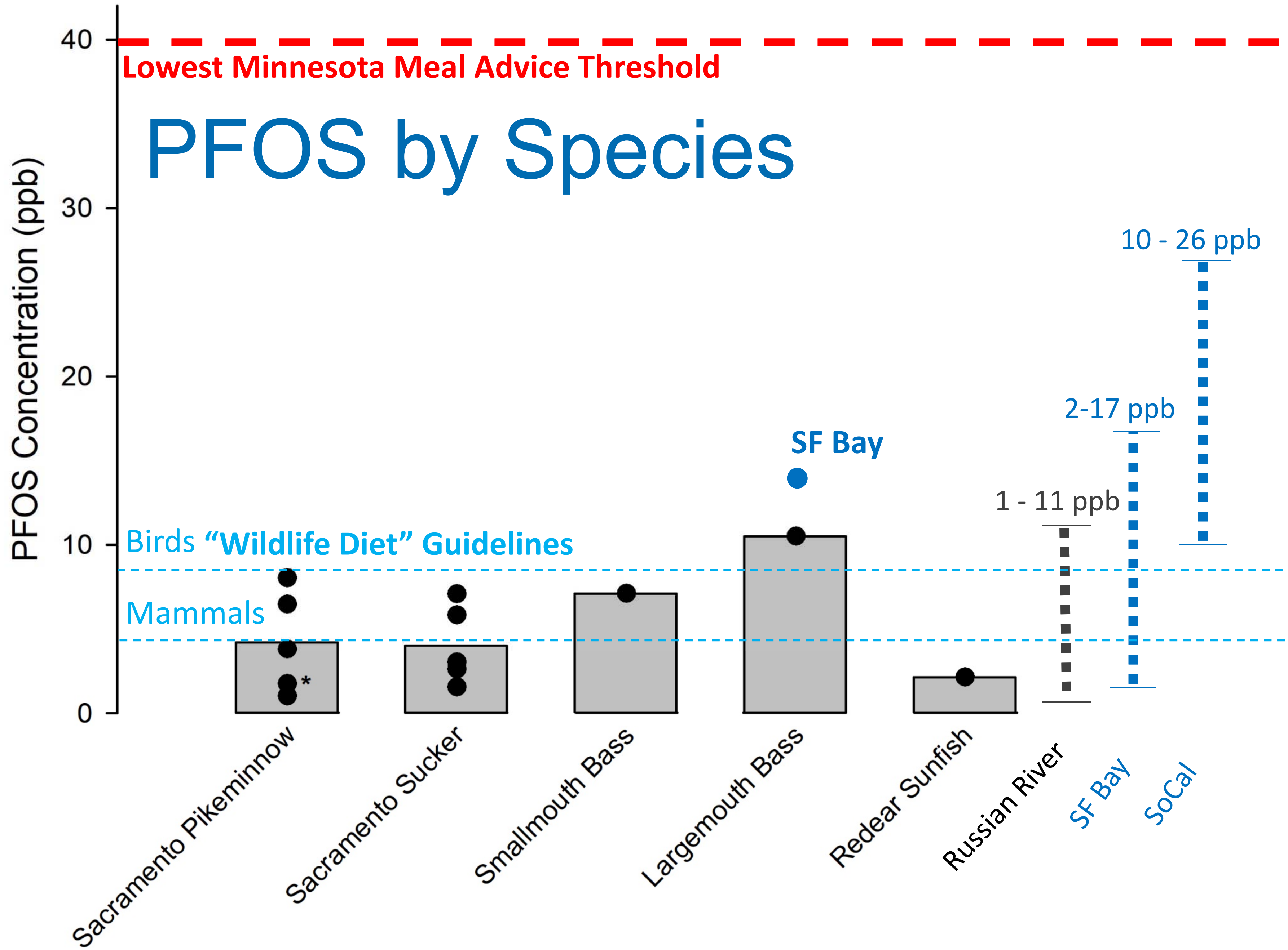
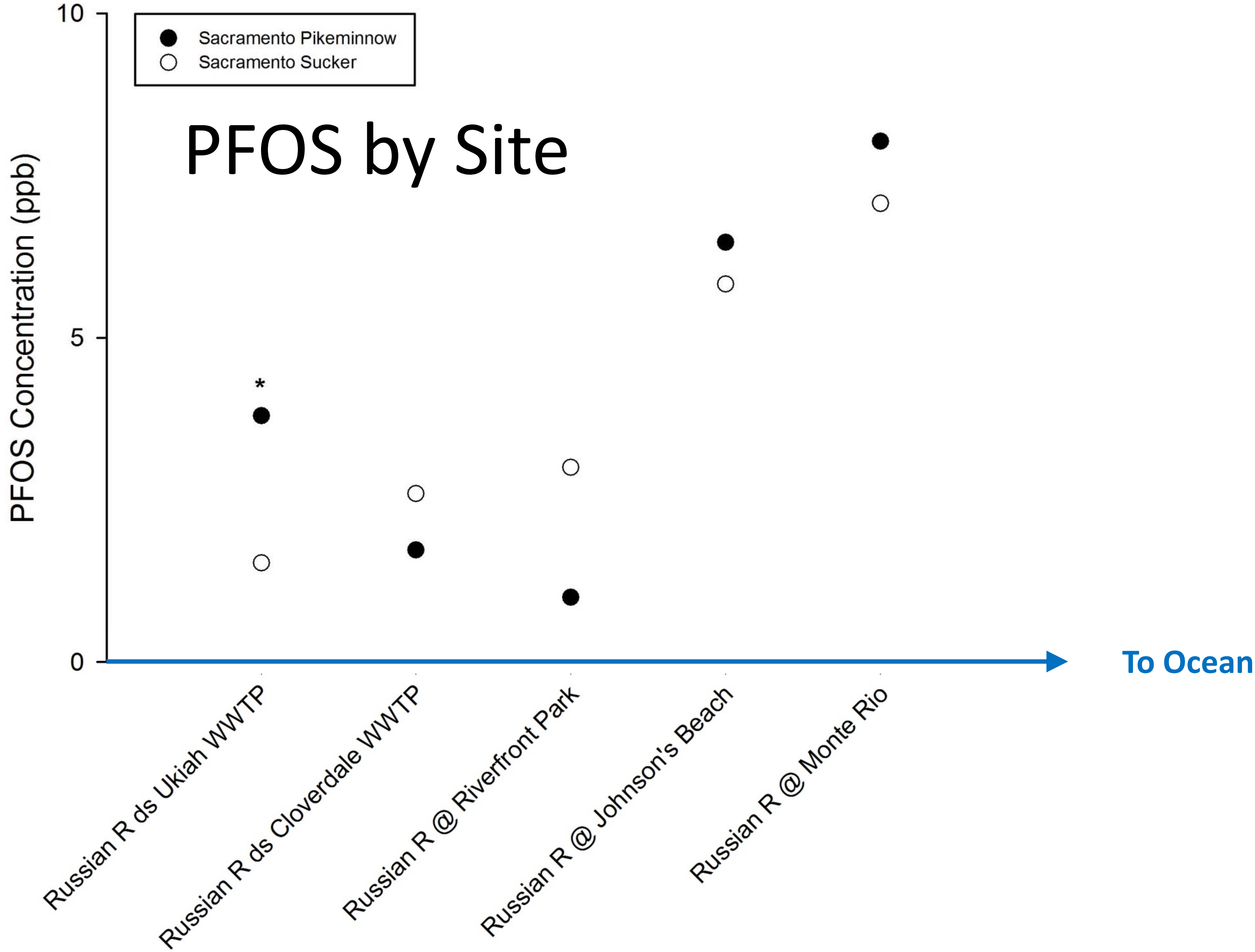

PFOS by Species
Lowest Minnesota Meal Advice Threshold
PFOS Concentration (ppb)
40
30
20
10
0
Birds "Wildlife Diet" Guidelines
Mammals
SF Bay
1 - 11 ppb
2-17 ppb
10 - 26 ppb
Sacramento Pikeminnow
Sacramento Sucker
Smallmouth Bass
Largemouth Bass
Redear Sunfish
Russian River
SF Bay
SoCal

PFOS by Site



Sacramento Pikeminnow
Sacramento Sucker
PFOS Concentration (ppb)
10
5
0
*
To Ocean
Russian R ds Ukiah WWTP
Russian R ds Cloverdale WWTP
Russian R @ Riverfront Park
Russian R @ Johnson's Beach
Russian R @ Monte Rio

Conclusions

- Fish tissue findings suggest minimal concern
  - Levels of PBDEs and PFOS generally below available consumption thresholds
  - For PFOS, potential for impacts further up the food chain
- Periodic monitoring (e.g., every 5-10 years) is recommended

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Current Use Pesticides

R1 CEC Pilot Monitoring

Jennifer Sun, Rebecca Sutton, Diana Lin

San Francisco Estuary Institute

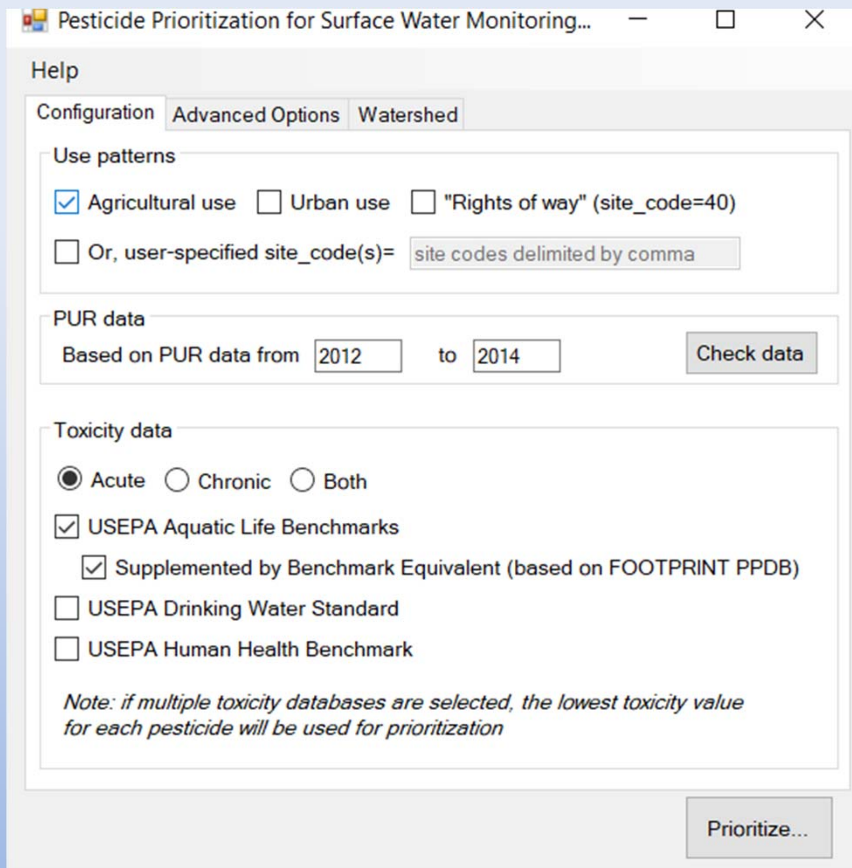
Study Objectives

MQ4. **Which pesticides** applied in the Russian River watershed **are of highest priority** for monitoring?

MQ5. **What is the extent and magnitude** of pesticide contamination in Russian River **water and sediment**?

Pesticide Prioritization

DPR Surface Water Monitoring Program modeling tool



Use

+

Toxicity

+

Pesticide Properties

Prioritization

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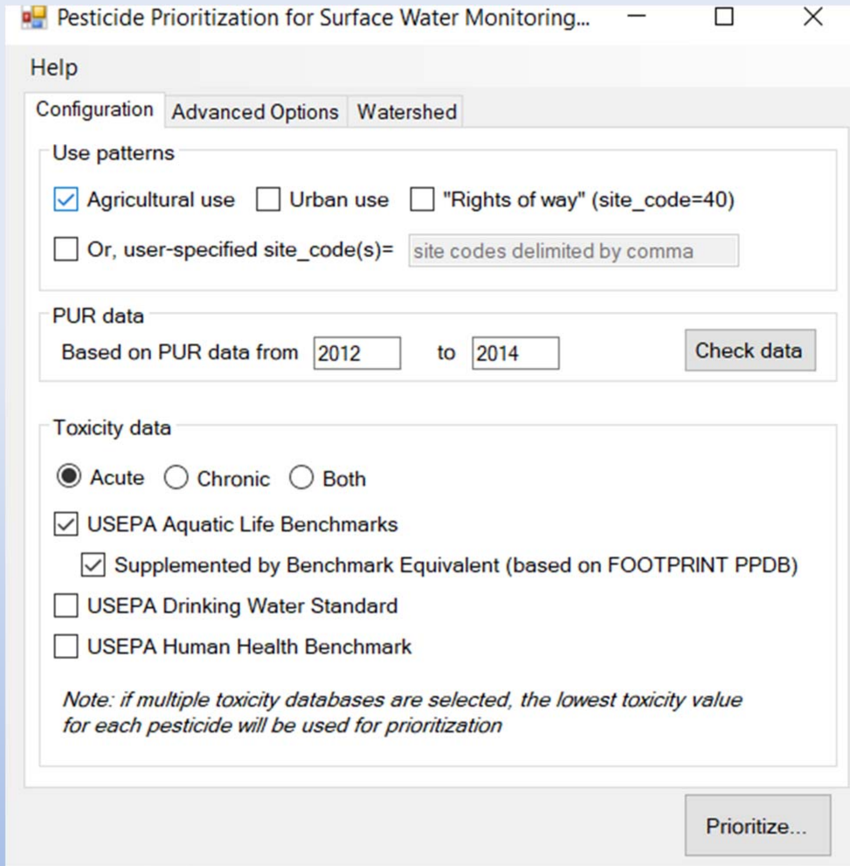
Pesticide Prioritization



DPR Pesticide Use Database (2012-2014 data, monthly)

+

USEPA Aquatic Life Benchmarks or DPR equivalents (acute or chronic)

+

Physical-chemical properties

↓

Prioritized Pesticide list

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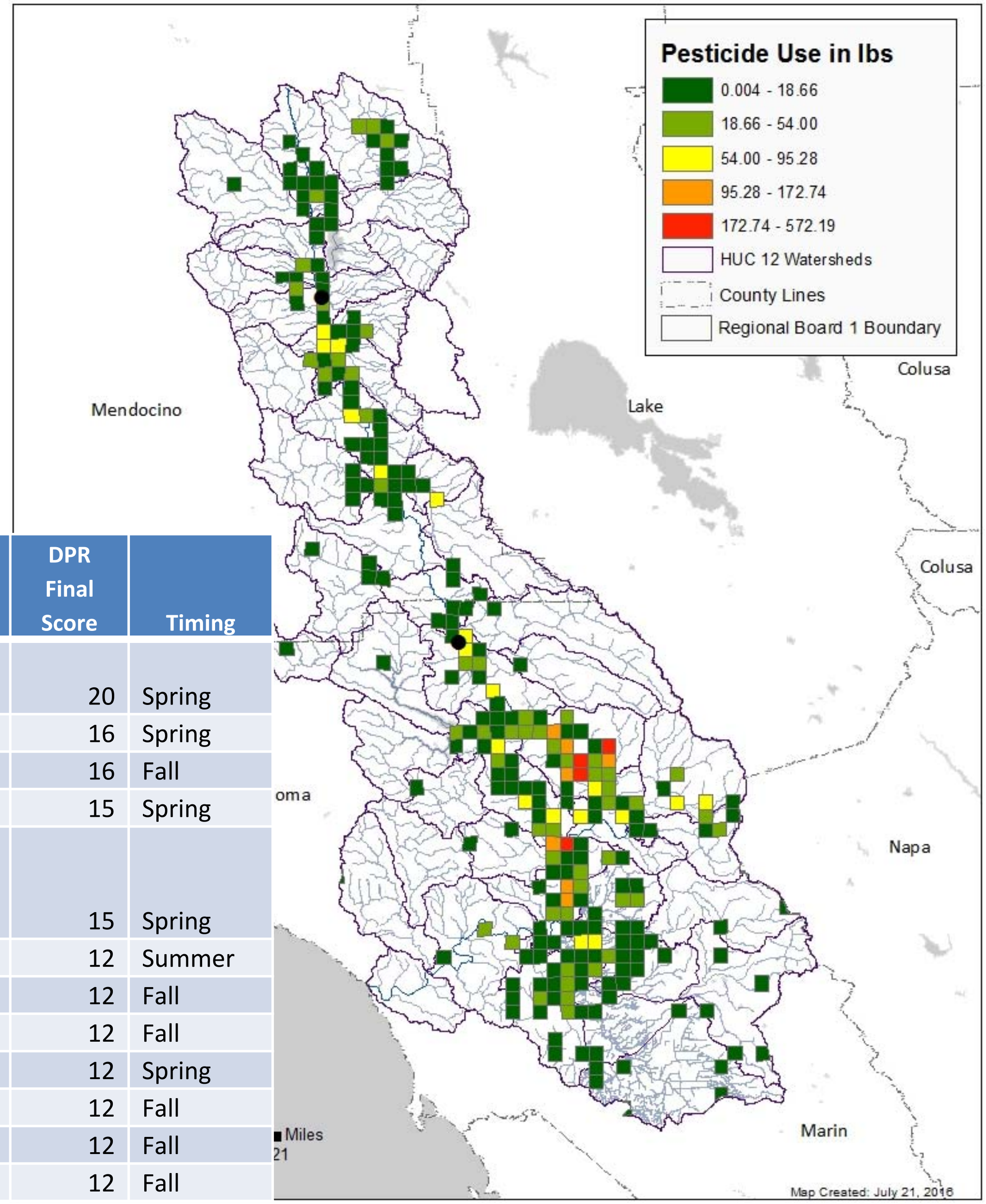
2. **Use Maps**
(Site Selection)

Imidacloprid: Total Use 2012-2014



1. Prioritization List

(Analytical Lab Selection)

Chemical Name	Water Toxicity Benchmark (ug/L)	DPR Use Score	DPR Toxicity Score	DPR Final Score	Timing
Ethylene thiourea (MANCOZEB degradate)	2	5	4	20	Spring
PENDIMETHALIN	5.2	4	4	16	Spring
CYPRODINIL	8	4	4	16	Fall
OXYFLUORFEN	0.29	3	5	15	Spring
THPA; 482-HA; APF (FLUMIOXAZIN degradates)	0.49	3	5	15	Spring
CHLORPYRIFOS	0.04	2	6	12	Summer
IMIDACLOPRID	1.05	3	4	12	Fall
PYRACLOSTROBIN	1.5	3	4	12	Fall
SIMAZINE	2.24	3	4	12	Spring
TRIFLOXYSTROBIN	2.76	3	4	12	Fall
DIFENOCONAZOLE	5.6	3	4	12	Fall
QUINOXYFEN	7	3	4	12	Fall

Study Design

5 co-located sites

USGS - CWSC

Sediment

September 2016

118 pesticides

Water

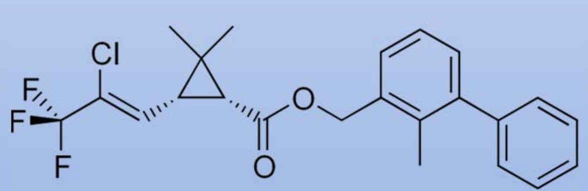
Oct 2016 (“first fall flush”)

162 pesticides (dissolved)

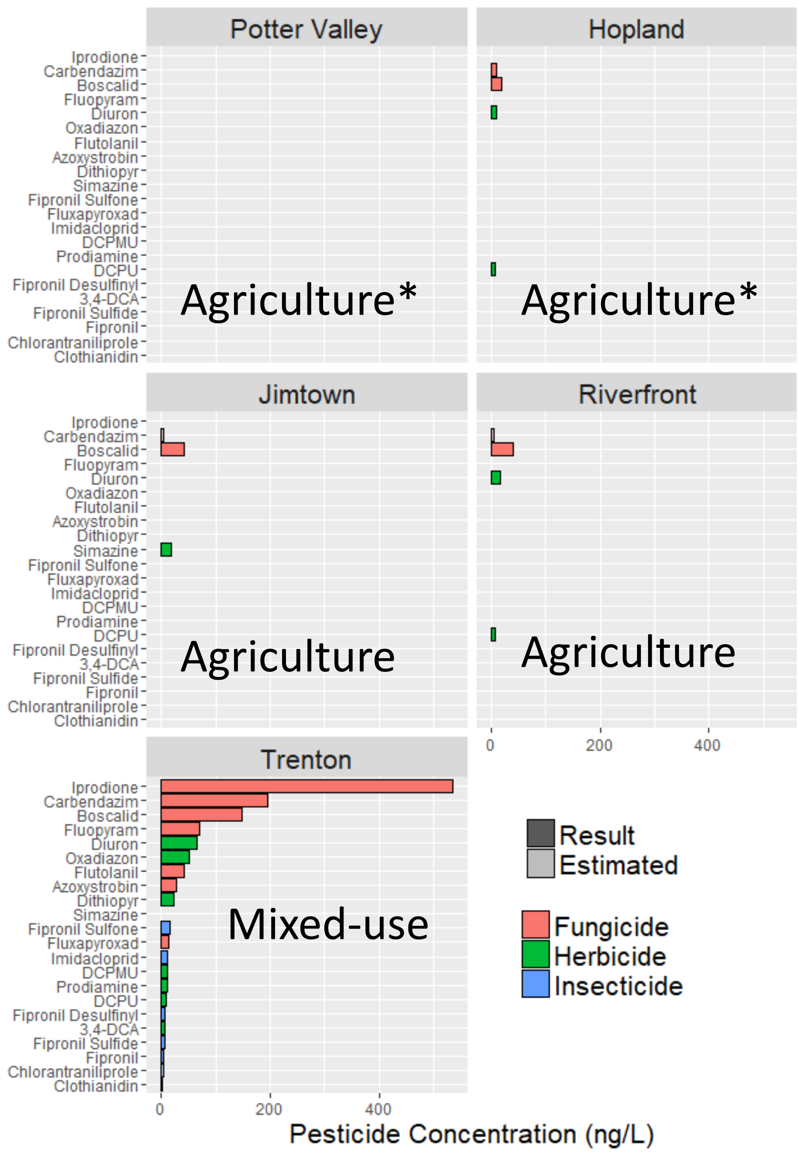
131 pesticides (particulate)

Pesticides in sediment were low

- No exceedances of USGS benchmarks
- Largest number of detections at the mixed use ag- and urban site
- Six pesticides detected
  - Fungicides: boscalid, iprodione
  - Legacy insecticides: DDT, DDD, DDE
  - **Pyrethroid insecticide: bifenthrin**



Pesticides in water were low, but highest in urban-influenced areas



- No pesticides detected in particulate phase
- 16 pesticides detected in dissolved phase

*May have received limited stormwater runoff

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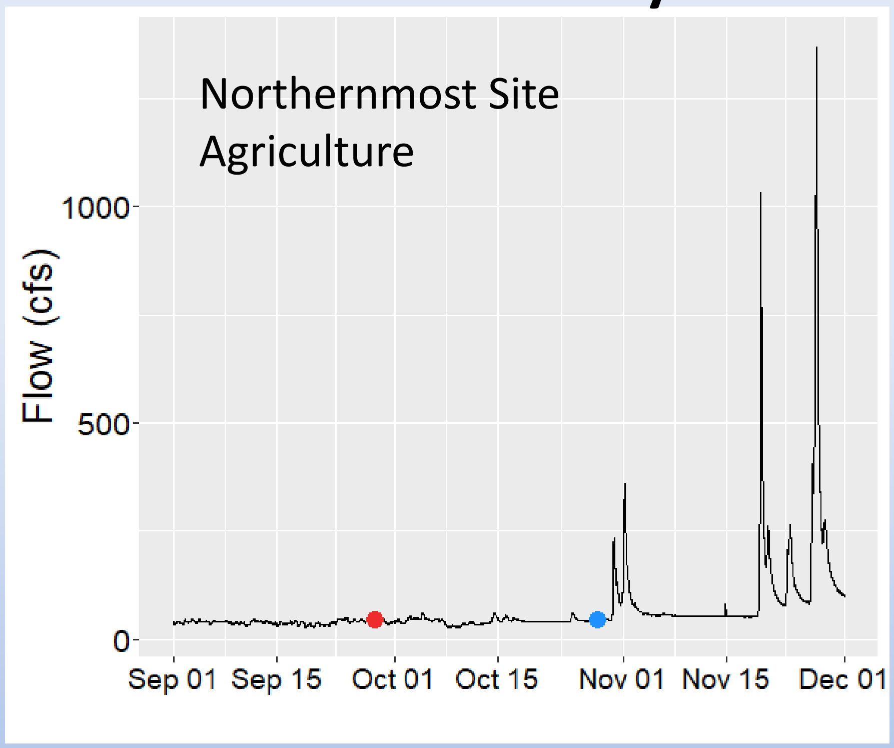
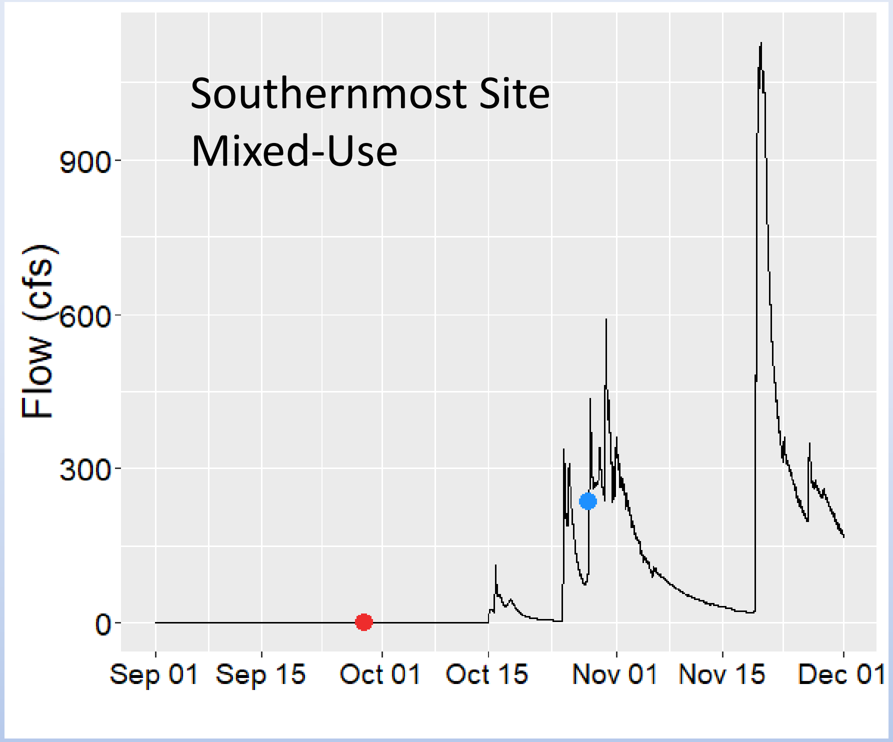
Stormwater runoff may not have been captured at northern sites

Potter Valley



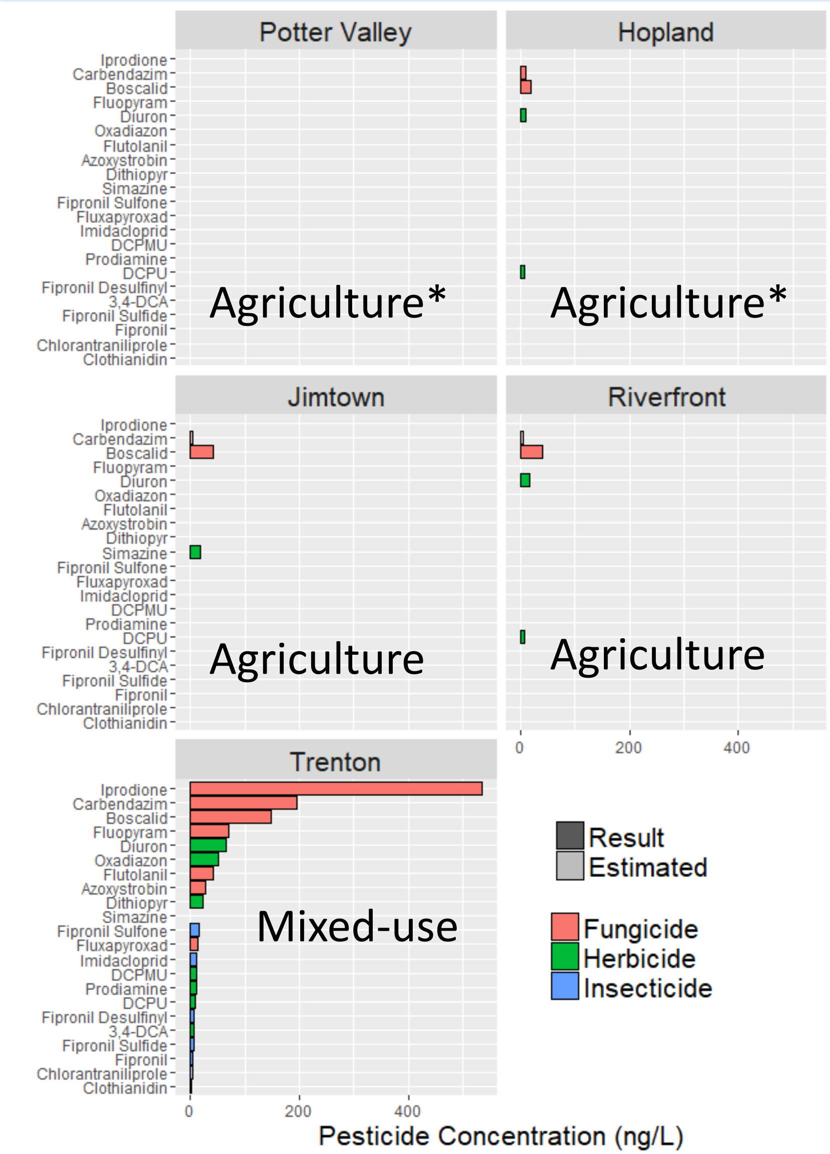
Trenton Road



Sediment Sampling Event

Water Sampling Event

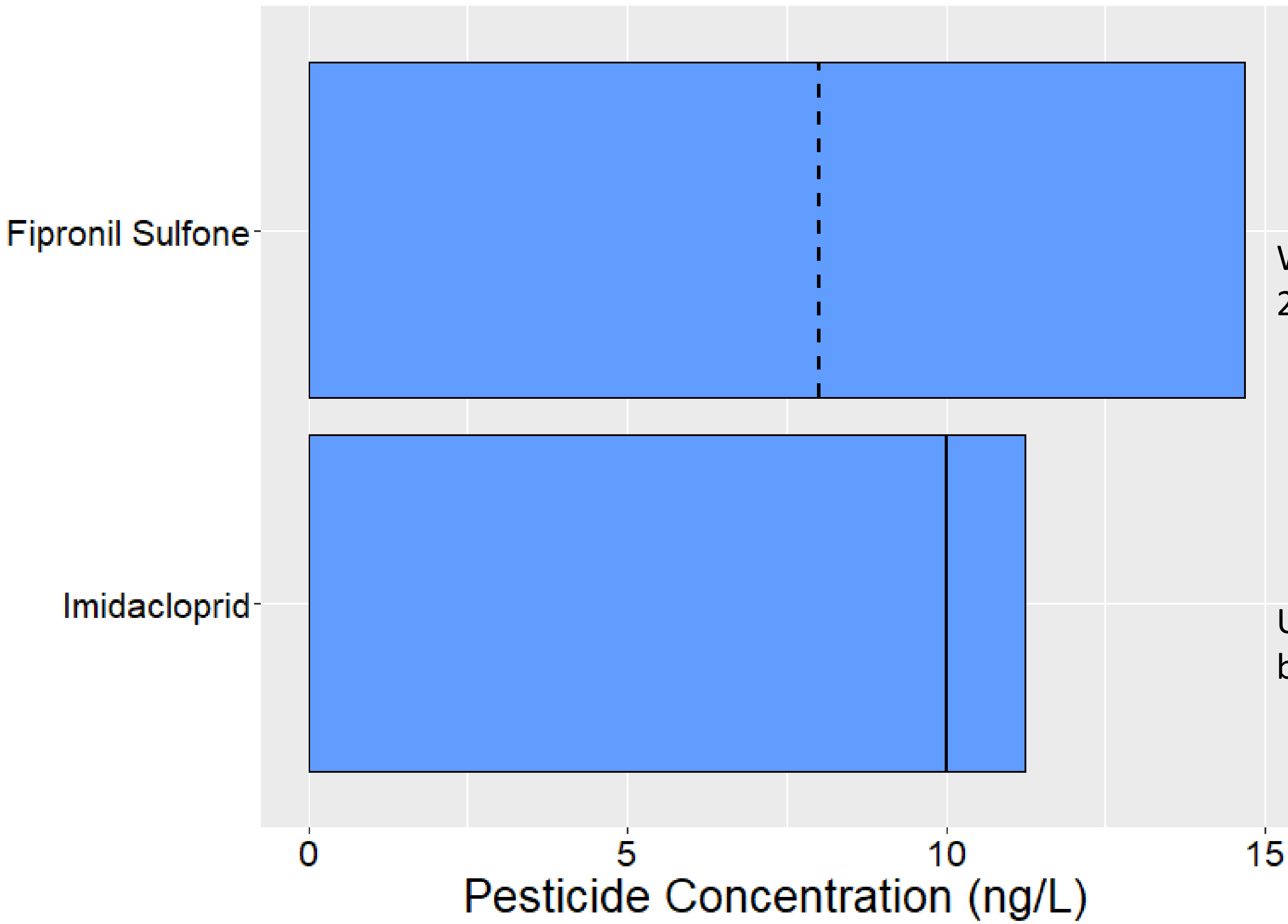
Pesticides in water were low, but highest in urban-influenced areas



- No pesticides detected in particulate phase
- 16 pesticides detected in dissolved phase
- **Fungicides** are most abundant, but not highly toxic
- Several **urban pesticides** detected were not prioritized, esp. toxic **insecticides**

*May have received limited stormwater runoff

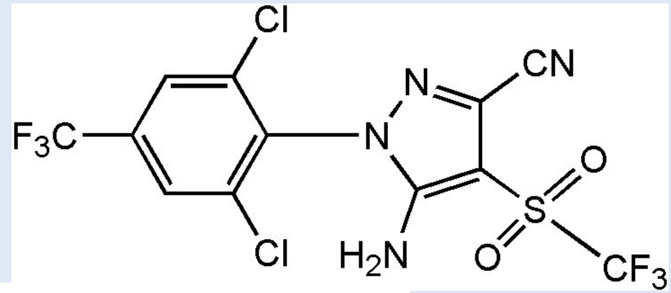
Two urban insecticides exceeded chronic invertebrate thresholds

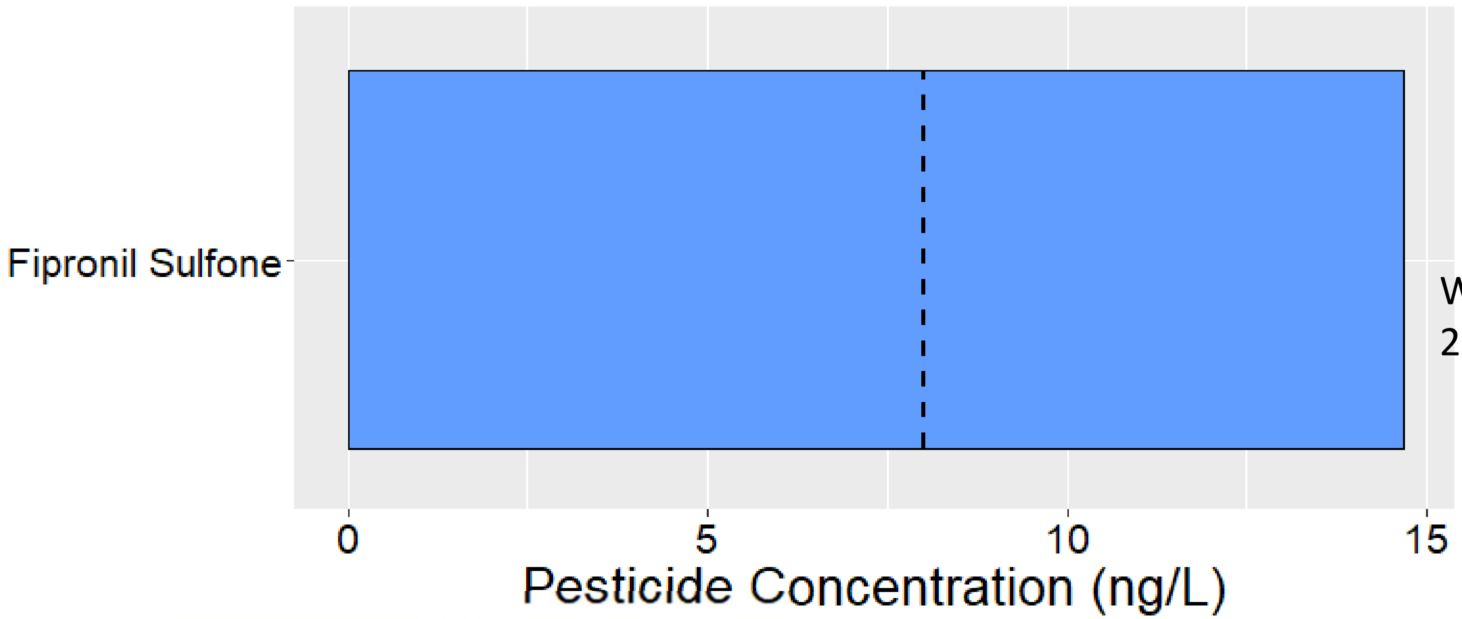


Weston & Lydy et al. 2014

USEPA 2017 revised benchmark

Fipronil Sulfone





Weston & Lydy et al. 2014

Fipronil

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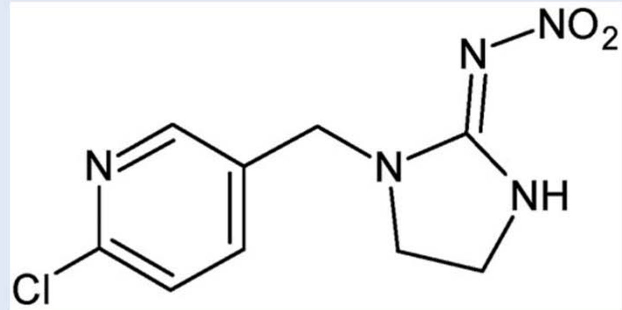
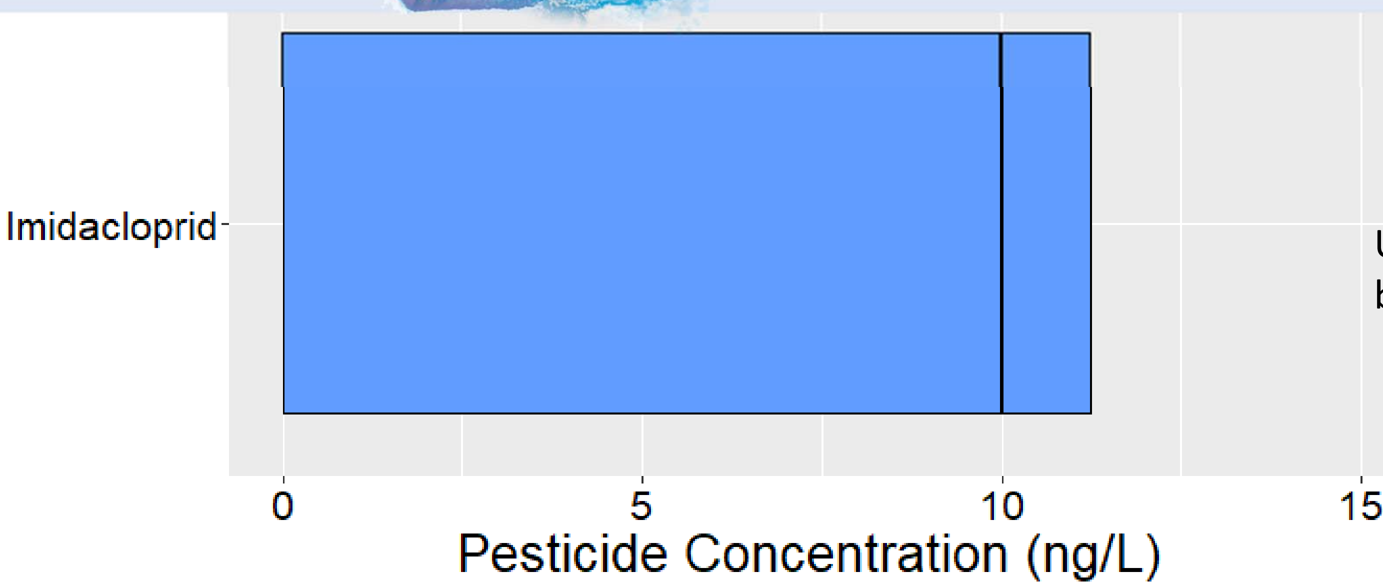
Imidacloprid



polystyrene insulation,
vinyl siding, adhesives, sealants, textiles for outdoor use, pressure-treated wood decking



USEPA 2017 revised benchmark

Conclusions

- Pesticides from **agricultural runoff are not likely a major concern** during the fall, based on this study
  - Pesticide use varies seasonally – this study did not characterize risks from **spring runoff**
  - Pesticide concentrations may be higher nearer to sources
- Some **urban insecticides** currently exceed or are approaching levels of concern
  - **Imidacloprid** exceeded a USEPA chronic invertebrate benchmark
  - **Fipronil degradates** are approaching or exceed chronic invertebrate threshold
  - **Bifenthrin** is approaching a USGS sediment benchmark

Recommended for monitoring in receiving waters by California Statewide CEC Expert Panel

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Pesticide Monitoring Partners

- **USGS** National Water Quality Assessment: Stream Quality Assessment Project
  - 2017 spring monitoring
  - Trenton Road and Riverfront/Pull-Out sites
- **DPR, SWRCB, CASQA:** statewide framework for urban pesticide monitoring

Lessons Learned

- ✓ BioAnalytical tools show promise
- ✓ Initial screening results for water and fish tissue suggest minimal concern for impacts; however, keep an eye on PFOS
- ✓ Urban use insecticides warrant a closer look
- ✓ Continue implementing improved monitoring strategies

Next Steps

What can be done?

- ✓ Prudent usage of products or use alternative products
- ✓ Proper disposal (*Medicines collected regionally*)
- ✓ Improve treatment technologies
- ✓ Implement expert panel recommended monitoring strategies
- ✓ Efficient and proper use of recycled water
- ✓ Implement the Recycled Water Policy

I WANT
YOU

To
Properly
Dispose
Unwanted
Medication

Partnerships

- Other agencies
- Municipalities
- Advocates
- Academia
- Public

✓ Together we can assess conditions and minimize harmful effects

"Hmphh. Happy as clams, indeed.
They're just all on Prozac."

To be continued….

Questions?