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PILOT MONITORING OF CONSTITUENTS OF EMERGING CONCERN (CECS) IN THE RUSSIAN RIVER WATERSHED (REGION 1)

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Surface Water Ambient Monitoring Program

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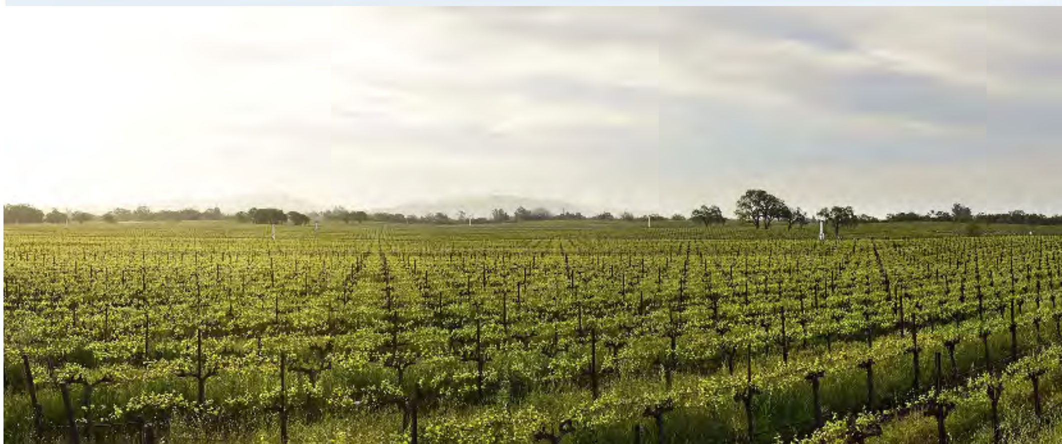
Pilot Monitoring of Constituents of Emerging Concern (CECs) in the Russian River Watershed (Region 1)



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SCCWRP Technical Report **1020**

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EXECUTIVE SUMMARY

In 2015, the Surface Water Ambient Monitoring Program (SWAMP) released guidance for monitoring of contaminants of emerging concern (CECs) in ambient waters across California. Among the recommendations provided to SWAMP by the State's Expert Panel on CECs in aquatic ecosystems was monitoring of a list of priority CECs that included selected hormones, pharmaceuticals and personal care products, current use pesticides, and other chemicals found in consumer and commercial products, in water, sediment and tissue. The Panel also recommended evaluation of bioanalytical tools and non-targeted analysis to improve current water quality monitoring. In response, the North Coast Regional Water Quality Control Board commissioned a pilot study to screen for CECs in the Russian River watershed (RRW). As the region's most populous watershed, the RRW is home to forested, suburban and agricultural lands, with direct discharges from known point sources of CECs restricted to high flow conditions. This study consisted of 3 tasks: 1) targeted analysis and bioanalytical screening of CECs in water and sediment samples from the RRW; 2) targeted analysis of CECs in fish tissue; and 3) prioritization and initial monitoring of an expanded list of pesticides applied to agricultural lands within the RRW.

For Task 1, river water and sediment samples collected at 8 stations during wet weather conditions (for water) and during dry weather (for sediment) in 2016 were screened for endocrine bioactivity using 2 in vitro bioassays (IVBs) and analyzed for 31 CECs by GC-MS and LC-MS. In addition, final effluents from 2 wastewater treatment plants (WWTPs) were collected and screened using IVBs and targeted chemical analysis. Samples were collected, processed and analyzed in accordance with quality assurance/quality control (QA/QC) guidelines for statewide CEC pilot monitoring studies approved by SWAMP, and as reflected in the quality assurance project plan (QAPP).

Targeted chemical analysis of 11 CECs in aqueous samples and 20 CECs in sediment samples indicated that while some were frequently detectable, concentrations of most CECs were below monitoring trigger levels (MTLs) established by the State's Expert Panel. Exceptions were observed for the current use pesticides bifenthrin, permethrin and fipronil in sediment. The highest occurrence of these pesticides, primarily associated with suburban/urban applications (e.g. ant, termite and pet flea control), were found at stations near Santa Rosa, the largest city in the RRW. Analysis of the aqueous and sediment samples using standardized IVBs that screen for estrogenic and glucocorticoid activity were uniformly low, indicating little cause for concern for endocrine related toxicity across the RRW. Excellent agreement between targeted chemical monitoring of known estrogens, the status quo approach for exposure assessment, and the estrogen IVB results suggests that this assay shows promise as an effective screening tool for receiving water environments.

For Task 2, edible tissue from multiple sport fish species collected from locations across the RRW in August 2015 were composited by species (n=13) and analyzed for polybrominated diphenyl ethers (PBDEs) and perfluorinated alkyl substances (PFASs) using GC-MS and LC-MS in accordance with SWAMP QA/QC guidelines for statewide CEC pilot monitoring. Seven of 13 PBDE congeners analyzed were detected in fish tissue; with the sum of PBDE concentrations ranging from 0.1 to 30 ng/g (median: 3 ng/g). BDE 47, a ubiquitous tetrabrominated congener, was detected in all 13 samples. Perfluorooctanesulfonic acid (PFOS) was detected in all 13

samples at concentrations ranging from 1 to 11 ng/g (median: 4 ng/g). Three additional PFASs were detected: perfluorodecanoate (in 7 samples), and perfluoroundecanoate and perfluorododecanoate (both in 4 samples).

Summed PBDE concentrations measured in RRW fish tissue composites were well below thresholds of concern for human consumption established by the Office of Environmental Health Hazard Assessment (OEHHA). Whereas OEHHA has not established fish consumption thresholds for PFASs, the levels of PFOS were well below an advisory level issued by the State of Minnesota (40 ng/g for a consumption rate of one meal per week). The upper range of PFOS measured, however, exceeded an advisory level issued by the State of Michigan (9 ng/g for 16 or more meals per month), suggesting potential concern for humans practicing very high consumption rates. While fish tissue levels of PBDEs and PFOS/PFASs are currently of limited concern to human consumers, they may be of higher concern to the health of wildlife predators (e.g. birds and/or mammals).

For Task 3, river water and sediment samples collected at 5 sites representing agricultural and mixed use sub-watersheds during wet weather conditions (for water) and during dry weather (for sediment) in 2016 were analyzed for more than 100 pesticide analytes by the USGS California Water Science Center (CWSC) laboratory. Water samples fractionated into particulate and dissolved phases prior to analysis revealed a low proportion of detectable analytes: 22 of 162 in water (dissolved); 0 of 131 analytes in water (particulate); and 6 of 118 analytes in bed sediment. Most (16 of 22) pesticides detected in water (dissolved) were found only at the mixed-use site (Mark West Creek near Santa Rosa), including several that are commonly used in urban settings.

Pesticide concentrations in water were relatively low compared to published aquatic toxicity thresholds. Imidacloprid, a neonicotinoid insecticide, was the lone exception, measuring above a newly established EPA Office of Pesticide Prevention (OPP) chronic invertebrate benchmark (10 ng/L). Pesticide concentrations in sediment were below published (USGS) benchmarks. However, recent toxicity data suggest that fipronil and its degradates could be approaching levels of concern in water and sediment collected near suburban areas in the RRW. Bifenthrin, an urban use pyrethroid pesticide, was detected in sediment below a USGS-calculated sediment toxicity benchmark, but above the MTL developed by the State’s Expert Panel for estuarine waterbodies.

The results of this integrated screening investigation suggest low to moderate concern for potential CEC impacts in the RRW. Current use pesticides such as the pyrethroids bifenthrin and permethrin, fipronil and its degradates, and imidacloprid were detected at levels of moderate concern in sub-watersheds near Santa Rosa, and should be considered for future monitoring in the RRW. Fish tissue levels of PBDEs and PFASs were lower than is found in highly urbanized watersheds, and did not exceed current human consumption advisory levels, with the exception of a PFOS advisory designed to protect those consuming high levels of fish. Low frequency, periodic monitoring (e.g. every 5 years) of these and other persistent, bioaccumulative CECs is recommended to ensure that levels do not rise unexpectedly in the future. Initial bioanalytical screening results suggest that the potential for endocrine disruption in aquatic organisms of the RRW is low. Moreover, the agreement between IVB results and conventional targeted chemistry supports the utility of cell-based screening of water quality.

It should be noted that the scope of this study was limited in space, time and bioanalytical endpoints measured. Wet weather sampling was performed during a single event and at a limited number of sites. The number of commercially available IVBs currently standardized for water quality monitoring remains small, but efforts to expand the bioanalytical toolbox, along with advances in sampling and diagnostic tools are being supported by the State Water Board. Future opportunities to better characterize spatial and temporal patterns of CEC occurrence and bioanalytical response in the North Coast region would be well served in taking advantage of the targeted approaches and new tools described herein that are being test-driven statewide to improve current monitoring of aquatic systems.

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INTRODUCTION

Constituents of emerging concern (CECs) are a diverse group of relatively unmonitored and unregulated chemicals, substances and biological materials that have been shown to occur at trace levels in municipal wastewater discharges, storm water runoff, ambient receiving waters, and drinking water supplies. CECs include pharmaceuticals, personal care products, current registered pesticides and other commercial and industrial compounds. There are 129 priority chemicals currently regulated by the USEPA under the Safe Drinking Water Act and Clean Water Act, but there is little to no regulation of tens of thousands of CECs. An increasing number of studies report the occurrence of CECs in drinking water sources and in aquatic environments.

Current monitoring programs focus on a list of 150-200 contaminants that were identified as priority pollutants decades ago. However, thousands of chemicals in use by industry, agriculture, and households are eventually discharged into the environment. Some of these chemicals persist in the environment, accumulate in sediments and tissues, and are toxic to aquatic life or impact aquatic life in some other way. Because the production of chemicals will change in the future, while behavior, fate and effects are largely unknown, prioritizing CECs for monitoring in the environment is an important first step in protecting the beneficial uses of receiving waters. For many CECs, insufficient information is available to characterize the concentrations present in local surface waters or to determine thresholds above which ecologically significant effects would be expected.

In 2010, the State Water Board sponsored a panel of experts to address the issues associated with CECs in the State's aquatic systems that receive discharge of treated municipal wastewater effluent and stormwater. Evaluation of discharge (controlled and/or incidental) from agricultural operations was not considered by the Panel. These experts recommended 16 CECs for monitoring in aquatic ecosystems throughout California (Anderson et al. 2012). Three model ecosystems were identified to represent the majority of regulated, urban-impacted receiving waters in the State, including (1) effluent dominated rivers; (2) coastal embayments; and (3) ocean discharge of treated municipal wastewater. Moreover, SCCWRP in collaboration with the State's Expert Panel and the Water Boards devised an updated, tiered monitoring and assessment framework that is applicable for all CECs (Maruya et al. 2015). This framework features new monitoring methods, including bioanalytical screening tools to address the wide range of CECs, and non-targeted chemical analysis (NTA) to better identify bioactive contaminants (Dodder et al. 2015). Although they show promise in modernizing monitoring, the latter technologies have yet to be fully evaluated for receiving water monitoring.

In response, the North Coast Regional Water Quality Control Board (RWQCB) commissioned a 3-year pilot study to characterize the occurrence, fate and impact of CECs in the Russian River watershed (RRW). While the RRW is not considered a model "effluent-dominated river," it receives discharges of municipal wastewater effluent during the wet season, as well as stormwater runoff from agricultural and urban areas. The study was comprised of three elements or "Tasks": 1) bioanalytical and targeted chemical screening of river water and sediment, and final effluent from wastewater treatment plants (WWTPs) within the watershed; 2) analysis of CECs in fish tissue; and 3) prioritization and initial monitoring of current use pesticides. This pilot study was among the first of its kind for the RRW and for the North Coast region. The results of this study are interpreted against the latest, science-based thresholds of concern, including those recommended by the Expert Panel, to assist managers in identifying the need for future CEC monitoring in the North Coast region, and if warranted, in what matrices and at which locations within the RRW.

TASK 1: BIOANALYTICAL AND TARGETED CHEMICAL SCREENING OF WATER AND SEDIMENT

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Materials and Methods

Surface water and surficial bed sediment were collected from multiple stations within the RRW during March (water) and September (sediment) of 2016. In addition, final effluents from WWTPs serving the cities of Cloverdale and Ukiah were collected in April 2016. A complete list of samples collected is given in **Table 1-1**.

Table 1-1. Sample identification matrix for targeted CEC analysis and bioanalytical screening of water, sediment and WWTP effluent samples from the Russian River watershed.

Station	Matrix	Sample Date	Targeted Chem ID
14RR0898	Aqueous (river)	3/5/2016	2016-0007
Riverfront	Aqueous (river)	3/5/2016	2016-0011
Pull Out	Sediment (river)	9/30/16	2016-0350
Mirabel	Aqueous (river)	3/5/2016	2016-0015
Mirabel	Sediment (river)	9/30/16	2016-0351
Piner Creek	Aqueous (river)	3/5/2016	2016-0019
Piner Creek	Sediment (river)	9/30/16	2016-0352
114LY0010	Aqueous (river)	3/5/2016	2016-0023
Lytton Springs Creek	Sediment (river)	9/30/16	2016-0353
Santa Rosa Creek	Aqueous (river)	3/5/2016	2016-0027
Santa Rosa Creek	Sediment (river)	9/30/16	2016-0354
Airport	Aqueous (river)	3/5/2016	2016-0031
Airport	Sediment (river)	9/30/16	2016-0355
El Roble	Aqueous (river)	3/5/2016	2016-0035
El Roble	Sediment (river)	9/30/16	2016-0356
Monte Rio	Sediment (river)	10/1/16	2016-0357
114RRCLEF	Aqueous (effluent)	4/13/2016	2016-0063
114RRUKEF	Aqueous (effluent)	4/14/2016	2016-0067
Lab Blank	Aqueous	3/5/2016	2016-0039
Field Blank	Aqueous (river)	3/5/2016	2016-0043
Field Duplicate[1]	Aqueous (river)	3/5/2016	2016-0047
Lab Blank	Sediment (river)	9/30/16	2016-0411

[1] 114LY0010

Study design. Grab samples of river water were collected from 8 stations, stretching from Ukiah at the top of the watershed to Monte Rio (CA) at the bottom of the watershed (**Figure 1-1**), by RWQCB personnel on March 5, 2016. River water sampling was timed to capture runoff during a wet weather event. Twenty-four hour composite samples of final effluent from the Cloverdale and Ukiah WWTPs were collected on April 13 and 14, 2016, respectively. The city of Ukiah WWTP is permitted to discharge disinfected tertiary effluent into the RRW during the wet season (November through May), whereas the city of Cloverdale WWTP discharges its disinfected secondary effluent into percolation ponds, and not directly into the mainstem of the Russian River. Bed sediment was collected from the same eight stations by RWQCB personnel on September 30 and October 1, 2016. Sediment sampling was timed to represent dry weather/quiescent conditions.

Figure 1-1. Map of water and sediment sampling stations in the Russian River watershed.

Sample collection. Surface water and WWTP effluent samples were collected in pre-cleaned 1-L and 4-L amber bottles with preservative supplied by the contractor. Surface water sampling was performed during daylight hours and in sequence from top to bottom of the RRW. Bed sediment was collected, where present and accessible, using a pre-cleaned polyethylene scoop and placed in 250 mL glass jars with Teflon-lined lids. All samples were kept in the dark on ice and water samples were shipped via overnight courier to SCCWRP within 48 hours of collection, accompanied by signed chain of custody forms. For each sampling event, a field blank for water collection was prepared by pouring 1-L of Milli-Q grade water into a pre-cleaned 1-L amber bottle with preservative.

Analytical methods. Water and sediment samples were processed and analyzed using the GeneBLAzer estrogen and glucocorticoid receptor assays (ER-α and GR, respectively) adapted for water quality assessment by SCCWRP and collaborators (Mehinto et al. 2016; Mehinto et al. 2017). Briefly, water samples were pre-filtered using GF/A membranes prior to extraction of target CECs using Oasis HLB solid phase extraction (SPE) cartridges. After loading each cartridge with sample filtrate, target CECs were eluted with methanol, concentrated with gaseous nitrogen and exchanged to dimethylsulfoxide (DMSO). Target CECs were isolated from sediment using accelerated solvent extraction (ASE) with dichloromethane (DCM) under elevated temperature and pressure. Sediment extracts in DCM were exchanged to DMSO for subsequent IVB analysis. Briefly, division-arrested human kidney (HEK 293T) cells were diluted in assay media, seeded into 96-well plates and exposed to serial dilutions of sample extracts (final DMSO concentration $\leq$ 0.5%). After incubation for 16 hours at 37^{o}C and 5% CO_2, a loading substrate was added, and after a second incubation period of 2 hours at room temperature, bioactivity was measured using a microplate reader. All sample extracts were analyzed in triplicate at 1.25 to 10 times their original sample concentration. Assay-specific dose-response curves based on serial dilutions of 17β-estradiol (E2) for ER-α and dexamethasone (DEX) for GR, were utilized to express the results as bioanalytical equivalent concentrations (BEQs) in ng/L (water) or ng/g dry wt (sediment).

For targeted chemical analysis, Expert Panel recommended CECs, including hormones, pharmaceuticals and personal care products, and current use pesticides, were analyzed in aqueous and sediment samples by the Water Quality Research Lab, Sanitation Districts of Los Angeles County (LACSD-WQRL), and SCCWRP (**Table 1-2**). Five different methods based on LC-MS/MS and GC-MS/MS and developed in house by LACSD-WQRL were used to analyze 10 CECs in aqueous and sediment sample extracts. PPCPs were extracted from two 200 mL aliquots of aqueous sample using Oasis HLB cartridges, and extracts (one each for ESI+ and ESI- mode) analyzed by HPLC MS/MS. Steroids and alkylphenols were extracted from a 500-mL aliquot of aqueous sample using Strata-X cartridges, followed by analyses using HPLC MS/MS. Galaxolide and fipronil were extracted from a 500-mL aliquot of aqueous sample using a C18 cartridge, followed by analysis using GC/MS in SIM mode. Pyrethroids were extracted from a 1-L aliquot of aqueous sample using a C18 cartridge, followed by analysis using HPLC MS/MS. PFOS was analyzed by direct injection HPLC/MS-MS. Both the filtrate and filter (GF/A) components of aqueous phase samples were analyzed by LACSD-WQRL, and all methods used isotope dilution techniques for all analytes. All sediment samples were extracted using QuEChERS, followed by the corresponding instrumental technique as described above for aqueous sample extracts. SCCWRP analyzed 12 CECs (8 pyrethroids and 4 fipronil-related analytes) in sediment using a GC-MS-based method, after extraction of a 5 g freeze dried aliquot using accelerated solvent extraction (ASE).

Table 1-2. List of target CECs and participating labs.

Analyte	WQRL-LACSD	SCCWRP
Estrogen receptor (ER)-BEQ		aqueous, sediment
Glucocorticoid receptor (GR)-BEQ		aqueous, sediment
17β-estradiol (E2)	aqueous, sediment	
4-nonylphenol	aqueous, sediment	
bifenthrin	aqueous, sediment	sediment
bisphenol A	aqueous, sediment	
diclofenac	aqueous, sediment	
estrone	aqueous, sediment	
galaxolide	aqueous, sediment	
ibuprofen	aqueous, sediment	
PFOS	aqueous, sediment	
permethrin	aqueous, sediment	sediment
triclosan	aqueous, sediment	
fipronil		sediment
fipronil desulfinyl		sediment
fipronil sulfide		sediment
fenpropathrin		sediment
cyfluthrin		sediment
λ-cyhalothrin		sediment
cypermethrin		sediment
esfenvalerate		sediment
deltamethrin		sediment

Quality assurance/quality control (QA/QC). A performance-based QA/QC approach, adapted from the Statewide CEC Pilot Study Guidance (Dodder et al. 2015)**,** was followed to ensure analytical data of the highest quality. Data quality for IVBs was validated against criteria for calibration, blank, DMSO control, cytotoxicity (cell viability) and sample dose response. Instrumental methods for analysis of individual CECs were selected and/or optimized to meet minimum reporting limits (RLs) recommended by the State's Expert Panel. These data were validated against criteria for instrument calibration, analysis of blanks, matrix spikes and duplicate samples performed by each of the participating analytical labs. Recoveries of DBOFB and PCB-208 spiked into sediment samples prior to extraction as surrogates to track analyte recovery were 70 ± 5.9% and 89 ± 7.9%, respectively. Concentrations reported were not blank corrected, and were censored if less than five times greater than blank concentrations.

Results and Discussion

IVB response. There was no measurable IVB response in the filtrates (dissolved phase) of river water samples, corresponding to BEQs of <0.4 ng E2/L for the ER-α assay; and <20 ng DEX/L for the GR assay (**Table 1-3**). Similarly, estrogenic and glucocorticoid receptor activities were not detectable in the Cloverdale WWTP effluent. BEQs for the Ukiah WWTP effluent were 1.9 ng E2/L and 61 ng DEX/L. No measurable bioactivity was observed for the lab and field blank, and the IVB response for the duplicate sample from Lytton Springs Creek was also non-detect. Similar to water, sediment samples collected from the RRW showed minimal estrogenic and glucocorticoid receptor response, with non-detectable ER-BEQs (< 0.01 ng E2/g dw) in all but a single sample, as well as non-detectable GR-BEQs (<3.7 ng DEX/L) for all 8 samples (**Table 1-4**). A low level of measurable estrogenicity (0.09 ng E2/g) was observed for the sediment sample from Piner Creek. Levels of IVB response were at or below detection limits in lab blanks for sediment samples.

Table 1-3. Bioassay equivalent concentrations (BEQs) for GeneBLAzer estrogen receptor (ER) and glucocorticoid receptor (GR) assays in aqueous samples (dissolved phase) from the Russian River watershed.

Station/Sample Description	ER-BEQ (ng E2/L)	GR BEQ (ng DEX/L)
River Water[1]		
114RR0898 (Monte Rio)	<0.38	<19
Riverfront	<0.38	<19
Mirabel	<0.38	<19
Piner Creek	<0.38	<20
114LY0010 (Lytton Springs Creek)	<0.38	<20
Santa Rosa Cr	<0.44	<22
Airport	<0.44	<19
El Roble	<0.44	<22
WWTP Effluent		
Cloverdale[2]	<0.52	<17
Ukiah[3]	1.9	61
QA/QC		
Lab Blank	<0.44	<20
Field Blank	<0.44	<22
114LY0010-Duplicate	<0.44	<22

E2 – 17β-estradiol; DEX – dexamethasone; < denotes not detected (value is reporting limit)
[1] collected on 3/5/16
[2] collected on 4/13/16
[3] collected on 4/14/16

Table 1-4. Bioassay equivalent concentrations (BEQs) for GeneBLAzer estrogen and glucocorticoid receptor assays in sediment samples from the Russian River watershed.

Station/Sample Description	ER-BEQ (ng E2/g)	GR-BEQ (ng DEX/g)
El Roble	< 0.01	< 3.74
Airport	< 0.01	< 3.74
Lytton Springs Creek	< 0.01	< 3.74
Pull Out	< 0.01	< 3.74
Santa Rosa Creek	< 0.01	< 3.74
Piner Creek	0.09	< 3.74
Mirabel	< 0.01	< 3.74
Monte Rio	< 0.01	< 3.74
Lab Blank 1	0.01	< 3.74
Lab Blank 2	< 0.01	< 3.74

E2 – 17β-estradiol; DEX – dexamethasone; < denotes not detected (value is reporting limit)

In contrast to the non- or barely detectable IVB response for RRW samples, ER- and GR BEQs for water and sediment collected during dry weather in 2016 from the Los Angeles and San Gabriel river watersheds in the metropolitan southern California region were more frequently detectable and higher in magnitude (Maruya 2017). Stream flow in these two watersheds during the summer is dominated by discharge from multiple WWTPs, with the occurrence of wastewater derived CECs strongly linked to these discharges (Sengupta et al. 2014; Maruya et al. 2016). The frequency and magnitude of IVB screening response for the RRW samples was similar with that reported for inland surface waters in southern California, also sampled in 2015-16 (Mehinto et al. 2017). The level of estrogenicity measured for the Ukiah WWTP effluent (1.9 ng E2/L) was identical to that reported for final effluent from the Los Coyotes WWTP that discharges to the San Gabriel river in southern California, and was well within the range of ER-BEQs reported for 3 WWTP effluents that included the Los Coyotes facility (0.7 to 1.9 ng E2/L) using the same (GeneBLAzer) cell assay (Maruya 2017). The level of GR-BEQs for the Ukiah WWTP effluent (61 ng DEX/L) was lower but within the same order of magnitude as those reported previously for WWTP effluent (94-98 ng DEX/L) (Maruya 2017). In contrast, BEQs reported for effluents from 4 WWTPs representing both southern and northern California exhibited a wider range of response, e.g. < 25 to 392 ng DEX/L and 2.3 to 17 ng E2/L (Mehinto et al. 2016). All of the WWTPs cited above, similar to the Cloverdale and Ukiah WWTPs, employ either secondary or tertiary treatment.

Target CEC concentrations. Aqueous concentrations (dissolved phase) of the 12 target CECs in river samples are summarized in **Table 1-5**. Galaxolide and 4-nonylphenol were detected at all 8 stations, but were also detected in both lab procedural and field blanks (**Table 1-6**). Sample concentrations of galaxolide and 4-nonyphenol were 1-4 times the estimated blank concentration, indicating that blank contributions were not trivial. No other target CEC was detected in aqueous dissolved phase blanks. Diclofenac, ibuprofen, 17β-estradiol (E2) and triclosan were not detected in any river water sample. Perfluorooctane sulfonate (PFOS) was detectable in all but one (Riverfront) sample, whereas the pesticides fipronil, permethrin and bifenthrin, the plastics component bisphenol A and the natural hormone degradate estrone were detected in some but not all samples. Samples with the largest number of detectable CECs were Piner Creek (8 of 12); Santa Rosa Creek (7 of 12) and Mirabel (6 of 12). The maximum concentrations observed were also measured in samples from these 3 stations, all of which are located in the southeastern portion of the RRW nearest to the city of Santa Rosa. With 1-2 exceptions (e.g., bisphenol A and PFOS), maximum river water concentrations in the present study were lower than those reported for the effluent dominated Los Angeles and San Gabriel rivers (Maruya 2017). Concentrations of current use pesticides in stormwater runoff from Suisun Bay in the San Francisco Bay Delta region and from the Pacific Northwest were reported to be an order of magnitude or greater than reported in the present study, reaching 14.6 ng/L for bifenthrin (Weston et al. 2015a) and 27 ng/L for fipronil (Weston et al. 2015b). It should be noted that these higher concentrations represent whole (unfiltered) runoff, since liquid-liquid extraction was utilized with no mention of a pre-filtration step in these comparative studies.

Table 1-5. Dissolved phase aqueous concentrations (in ng/L) of target CECs in the Russian River watershed.

SAMPLE ID	2016-0007	2016-0011	2016-0015	2016-0019	2016-0023	2016-0027	2016-0031	2016-0035
COLLECTION DATE	3/5/2016	3/5/2016	3/5/2016	3/5/2016	3/5/2016	3/5/2016	3/5/2016	3/5/2016
SAMPLE DESCRIPTION	114RR0898	RIVERFRONT	MIRABEL	PINER CR	114LY0010	STA RSA CR	AIRPORT	EL ROBLE
ANALYTE								
17β-estradiol	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50
4-nonylphenol[1]	37.4	81.9	25.4	53.3	25.1	62	76	63
bifenthrin	<0.10	<0.10	<0.10	0.2	<0.10	0.10	<0.10	<0.10
bisphenol A	<10	<10	<10	55.0	<10	16	<10	<10
diclofenac	<10	<10	<10	<10	<10	<10	<10	<10
estrone	<0.50	<0.50	0.5	0.6	<0.50	<0.50	<0.50	<0.50
ibuprofen	<10	<10	<10	<10	<10	<10	<10	<10
PFOS[2]	1.28	<1.0	11.5	9.5	2.0	5.8	1.65	1.15
permethrin	<0.1	<0.1	0.2	0.1	<0.1	0.12	<0.10	<0.10
triclosan	<10	<10	<10	<10	<10	<10	<10	<10
fipronil	<2.0	<2.0	4.8	4.7	<2.0	6.6	<2.0	2.3
galaxolide	150	130	370	190	120	150	230	330
No. CECs Detected	3	2	6	8	3	7	3	4

[1] technical mixture

[2] perfluorooctane sulfonate

< not detected (value is reporting limit)

Table 1-6. Dissolved phase aqueous concentrations (in ng/L) of target CECs in wastewater effluent and QA/QC samples.

SAMPLE ID	2016-0039	2016-0043	2016-0047	2016-0063	2016-0067
COLLECTION DATE	3/5/2016	3/5/2016	3/5/2016	4/13/2016	8/2/2016
SAMPLE DESCRIPTION	LAB BLANK	FLD BLANK	SAMPLE DUPL	EFF-CLVDALE	EFF-UKIAH
ANALYTE					
17β-estradiol	<0.50	<0.50	<0.50	<0.50	0.6
4-nonylphenol[1]	24.2	30.2	41.7	60.8	247
bifenthrin	<0.10	<0.10	<0.10	<0.10	0.14
bisphenol A	<10	11	<10	36.0	12.0
diclofenac	<10	<10	<10	<10	46.0
estrone	<0.50	<0.50	<0.50	<0.50	11.0
ibuprofen	<10	<10	<10	<4.0	611
PFOS[2]	<1.0	<1.0	1.82	1.0	5.0
permethrin	<0.10	<0.10	<0.10	0.35	1.9
triclosan	<10	<10	<10	<10	22.0
fipronil	<2[s]	<2.0	<2.0	<4.0	40.0
galaxolide	120	81.0	110	1300	16000
No. CEC Detected	2	3	3	5	12

[1] technical mixture

[2] perfluorooctane sulfonate

< not detected (value is reporting limit)

For effluent, all 12 target CECs were detected in the sample from the Ukiah WWTP, whereas 5 of 12 analytes were detectable in the sample from the Cloverdale WWTP (Table 1-6). For all target CECs except bisphenol A, concentrations were also higher, and in some cases more than 10 times greater, in the Ukiah WWTP effluent. Although individual CECs were not measured in WWTP effluent in the CEC pilot study on effluent dominated rivers in southern California (Maruya 2017), water column samples from stations located just downstream of WWTP outfalls discharging to these systems are subject to little attenuation and thus can be compared to samples of discharged final effluent. A comparison of CEC concentrations at these near outfall stations with concentrations in the Cloverdale and Ukiah WWTP effluent show that selected CECs (e.g., estrone, galaxolide and ibuprofen) occur at levels 3-30 times higher in the disinfected tertiary Ukiah WWTP effluent. CEC concentrations measured in the disinfected secondary Cloverdale WWTP effluent were comparable or lower than concentrations reported in the effluent dominated rivers. Interestingly, the effluent quality from the Ukiah WWTP was poorer relative to the Cloverdale WWTP, and also compared to effluent from other WWTPs discharging to rivers in southern California.

Sediment concentrations for the 20 target CECs are summarized in **Table 1-7**. Similar to aqueous dissolved phase results, the detection frequency and concentrations of CECs were greatest in sediments from Piner Creek, Santa Rosa Creek and Mirabel. Even more pronounced than in water, maximum concentrations for 9 of 20 analytes were measured in the Piner Creek sediment sample, followed by 4 of 20 analytes in the Santa Rosa Creek sample. Only triclosan was detectable in the sediment blank, at a concentration at the RL (1.0 ng/g).

The most noteworthy concentration of 99 ng/g for bifenthrin in the Piner Creek sediment sample was twice the maximum reported sediment concentration from effluent dominated rivers in southern California (Maruya 2017), and was comparable to concentrations reported in Ballona Creek sediment, an urban estuary in Los Angeles county that receives no intentional discharge of WWTP effluent (Lao et al. 2010). In contrast, sediments collected from the base of 100 watersheds in California reported total pyrethroid concentrations up to 1000 ng/g, with bifenthrin as the most frequently detected compound (69% of samples) at concentrations exceeding the LC50 for *Hyalella azteca* in 15% of samples tested (Siegler et al. 2015). A survey of more than 150 sediment samples from coastal habitats across southern California revealed that the greatest pyrethroid concentrations were located near sources of runoff from urban watersheds. Bifenthrin and cyfluthrin were detected in 32 and 15% of all samples, respectively, whereas the other six pyrethroids were detected in ≤5% of samples. Permethrin and bifenthrin had the highest concentrations at 132 and 65 ng/g, respectively (Lao et al. 2012). Similar patterns were observed in urban watersheds of the San Francisco Bay Area though concentrations and abundances were greater than measured in the present study, based on data compiled from the nine Bay Area counties in the State's Department of Pesticide Regulation (DPR) SURF database. Bifenthrin and permethrin were the two most commonly monitored pyrethroids and were also detected in the greatest percentage of Bay Area samples monitored (detected in 27% and 28% of samples), with maximum concentrations of 159 and 126 ng/g, respectively. Cyfluthrin was detected in about 17% of samples, with a maximum concentration of 539 ng/g. Deltamethrin, lambda cyhalothrin, and s-cypermethrin were monitored less frequently and were detected in roughly 15% of samples each (cyfluthrin was detected in 17% of samples).

Table 1-7. Sediment concentrations (in ng/g) of target CECs in the Russian River watershed (Fall 2016).

SAMPLE ID	2016-411	2016-350	2016-351	2016-352	2016-353	2016-354	2016-355	2016-356	2016-357
COLLECTION DATE		9/30/2016	9/30/2016	9/30/2016	9/30/2016	9/30/2016	9/30/2016	9/30/2016	10/1/2016
STATION	BLANK	PULL OUT	MIRABEL	PINER CR	LYT SPG CR	STA RSA CR	AIRPORT	EL ROBLE	MONTE RIO
MOISTURE (%)		32.0	42.6	70.3	10.0	69.4	63.6	60.9	25.8
ANALYTE									
17β-estradiol	<0.12	<0.12	<0.12	0.23	<0.12	<0.12	<0.12	<0.12	<0.12
4-nonylphenol[1]	<6.2	29	34	29	20	18	8	18	23
bifenthrin (LACSD)	<0.05	<0.05	<0.05	99	<0.05	0.73	<0.05	<0.05	<0.05
bifenthrin (SCCWRP)	<0.20	<0.20	<0.20	130	<0.20	1.96	<0.20	<0.20	<0.20
bisphenol A	<1.0	1.8	1.9	15	1.4	4.6	2.1	<1.0	<1.0
diclofenac	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
estrone	<0.12	<0.12	0.14	1.3	<0.12	0.4	<0.12	0.28	0.34
ibuprofen	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
PFOS[2]	<0.125	<0.12	0.38	4.1	0.26	1.9	0.76	0.59	<0.125
permethrin (LACSD)	<0.05	<0.05	<0.05	2.0	<0.05	0.4	0.2	<0.05	0.14
permethrin (SCCWRP)	<1.7	<1.7	<1.7	4.9	<1.7	<1.7	<1.7	<1.7	<1.7
triclosan	1.0	<1.0	6.8	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
fipronil desulfinyl	<0.025	<0.025	<0.025	0.033	<0.025	0.034	<0.025	<=0.013	<0.025
fipronil sulfide	<0.021	<0.021	<0.021	0.043	<0.021	0.036	<=0.018	<=0.021	0.048
fipronil	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	3.4
fipronil sulfone	<0.11	<0.11	<0.11	<=0.073	<0.11	0.19	<0.11	<0.11	0.112
fenpropathrin	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14
□-cyhalothrin	<0.047	<0.047	<0.047	0.21	<0.047	<=0.03	<0.047	<0.047	<0.047
cyfluthrin	<0.075	<0.075	<0.075	2.2	<0.075	3.3	<0.075	<0.075	<0.075
cypermethrin	<0.067	<0.067	<0.067	0.49	<0.067	2.2	<0.067	<0.067	<0.067
esfenvalerate	<0.03	<0.03	<0.03	0.36	<0.03	0.04	<0.03	0.88	<0.03
deltamethrin	<0.16	<0.16	<=0.15	2.1	<0.16	<0.16	<0.16	0.2	<0.16

[1] technical mixture

[2] perfluorooctane sulfonate

Overlap between target CEC lists for sediment allowed for a direct comparison of concentrations reported by WQRL-LACSD and SCCWRP for the pyrethroids bifenthrin and permethrin. Good agreement was achieved for the elevated concentration of bifenthrin in the Piner Creek sample (within 25%), with higher variability between the lower concentrations reported for permethrin and for bifenthrin in the Santa Rosa Creek sample. As no standard reference material currently exists for pyrethroids (and most CECs), it cannot be determined which value is more accurate. Interlaboratory comparison exercises for CECs in ambient monitoring programs would assist in flagging outlier data points for analytes with no certified concentrations, i.e. that may have greater uncertainty in measured concentrations.

Moisture content is a well-established proxy for porosity, grain size and total organic carbon (TOC), with a positive association between % moisture and TOC (Cao et al. 2015). It is also well established that TOC is a reservoir for hydrophobic organic compounds (HOCs). However, it is important to note that relatively few CECs are considered hydrophobic. Regardless of the mechanism of interaction, finer grained sediments have greater capacity to sorb and/or bind aqueous phase compounds. Consistent with these principles, the sediment sample from Piner Creek contained the greatest moisture content (70%), with Santa Rosa Creek close behind (69%). In contrast, the sediment samples from Lytton Springs Creek (10%), Monte Rio (26%) and Pull Out (32%) would be predicted to be relatively coarse in texture, and as a result, less likely to house HOCs. Correspondingly, maximum CEC concentrations were not observed in any of these sediment samples, except for fipronil in the Monte Rio sediment. The infrequent detection and/or low CEC concentrations measured in the Lytton Springs Creek and Pull Out sediment samples would suggest that these locations would serve as good reference stations for future contaminant investigations.

Monitoring trigger quotients (MTQs). Maximum concentrations in water and sediment from the RRW were compared to monitoring trigger levels (MTLs) established by the State's Expert Panel (**Tables 1-8 and 1-9**). Except for bifenthrin and permethrin, maximum concentrations were greater in the aqueous sample filtrates (dissolved phase) compared to the filter (particulate) phase. As the Panel considered three generic exposure scenarios with only a single freshwater habitat (effluent dominated rivers), and the RRW is not an effluent dominated system as specified under discharge permits, the inclusion of MTQs is for comparison to other waterbodies across the State. Similarly, the Panel did not recommend WWTP effluent as a matrix to apply MTQs; hence, these comparisons are provided for comparison purposes only.

MTQs for CECs in river water were all much less than unity, except for bisphenol A (0.92) and galaxolide (0.81). MTQs computed for WWTP effluent exceeded unity for estrone (1.8) and ibuprofen (6.1). For sediment, the Panel recommended MTLs for only a single CEC (fipronil) in freshwater systems. In part because of the extremely low toxicity threshold for fipronil (0.09 ng/g dw), the MTQ for fipronil in freshwater sediment (38) exceeded unity. Although not directly applicable, comparison of maximum sediment concentrations to MTLs recommended for embayment (estuarine) habitats, which are on average 10 times lower than MTLs for freshwater habitats, resulted in MTQs for bifenthrin and permethrin exceeding unity by factors of 2500 and 67, respectively. Future studies on CECs, particularly those associated with discharge/fate of WWTP effluent, could focus on bisphenol A, galaxolide, estrone and ibuprofen. In watersheds draining or adjacent to suburban landscapes, monitoring should focus on pyrethroids and fipronil.

Table 1-8. Monitoring trigger quotients (MTQs) for CECs in Russian River water. Maximum concentrations and monitoring trigger level (MTL) are in ng/L.

Analyte		Effl-CD		Effl-UK		River		MTL	MTQ	MTQ
	RL	disslvd	filter	disslvd	filter	disslvd	filter		Effl	River
17β estradiol	0.5	<0.50	<0.25	0.6	<0.25	<0.50	<0.50	2	0.30	<0.25
4-nonylphenol	25	60.8	n/a	247	n/a	81.9	n/m	n/a		
bifenthrin	0.1	<0.10	0.47	0.14	0.11	0.16	2.55	n/a		
bisphenol A	10	36	2.3	12	<2.0	55	<2.0	60	0.64	0.92
diclofenac	10	<10	<2.0	46	<2.0	<10	<2.0	100	0.46	<0.12
estrone	0.5	<0.50	<0.25	11	<0.25	0.56	<0.25	6	1.8	0.09
fipronil	2	<4.0	<2.0	40	<2.0	6.6	<2.0			
galaxolide	100	1300	290	16000	980	370	200	700	24	0.81
ibuprofen	10	<10	<2.0	611	<2.0	<10	<2.0	100	6.1	<0.12
PFOS	1	1.02	n/a	5.03	n/a	11.5	n/m			
permethrin	0.1	0.35	1.26	1.85	1.33	0.2	1.75			
triclosan	10	<10	<2.0	22	<2.0	<10	<2.0	250	0.09	<0.05

Table 1-9. Monitoring trigger quotients (MTQs) for CECs in Russian River sediments.

ANALYTE	MTL	MTL	MEC_{max}	MTQ	MTQ
	River	Bay	RR	RR	RR Estuary
17β-estradiol	n/a	n/a	0.23	n/a	n/a
4-nonylphenol[1]	n/a	n/a	34	n/a	n/a
bifenthrin	n/a	0.052	130	n/a	2500
bisphenol A	n/a	n/a	15	n/a	n/a
diclofenac	n/a	n/a	<1.0	n/a	n/a
estrone	n/a	n/a	1.3	n/a	n/a
ibuprofen	n/a	n/a	<1.0	n/a	n/a
PFOS[2]	n/a	n/a	4.1	n/a	n/a
permethrin	n/a	0.073	4.9	n/a	67
triclosan	n/a	n/a	6.8	n/a	n/a
fipronil[3]	0.09	6.5	3.4	38	0.52

[1] technical mixture

[2] perfluorooctane sulfonate

[3] parent, desulfinyl, sulfide or sulfone

MTL - monitoring trigger level (ng/g)

MTQ - monitoring trigger quotient

MEC_{max} - maximum measured environmental concentration (ng/g)

orange highlighting denotes 1<MTQ<100; red highlighting denotes MTQ>100

Thresholds for IVBs in receiving waters have not been established to date. However, data compiled to support development of aquatic life criteria (ALC) for individual estrogenic chemicals suggest lowest observable effect concentrations (LOECs) as low as 0.1 ng/L (USEPA 2008). Nominal concentrations of EE2 spiked into natural lakes that affected reproduction of were 5-6 ng/L (Kidd et al. 2007). Assuming estrogenic potency of E2 and EE2 are essentially equivalent (Jarosova et al. 2014), one can surmise that ER-BEQs reported herein for the RRW would not constitute a high level of concern. Moreover, the largely non-detectable response using the ER-α and GR assays did not warrant further identification of bioactive agents using targeted or non-targeted chemical analysis, or an urgent need to conduct whole animal toxicity tests or field investigations, e.g. those identified as Tier II monitoring tools in a recently published CECs monitoring and assessment framework under consideration for adoption by State Water Board staff (Maruya et al. 2015).

Screening utility of the ER-α IVB. Concentrations of E2 measured by LC-MS/MS were compared to BEQs estimated using the ER-α IVB for aqueous samples (**Table 1-10**). For all samples except the Ukiah WWTP effluent, both methods reported non-detectable levels of either E2 (for LC-MS/MS) or total estrogens (for the IVB). Furthermore, the method reporting limits for these assays were nearly identical (~ 0.5 ng E2/L). The concordance of non-detections indicates that 1) the levels of E2 in these samples was confirmed to be < 0.5 ng/L; 2) the levels of integrated estrogenic activity in these samples was also low (as measured by the IVB); and 3) the standardized IVB method does not appear to be subject to false positive response in the media (water and sediment) analyzed.

The positive detections for the Ukiah WWTP effluent afford the opportunity to further validate the IVB results, as well as identify the contributions of estrogenic compounds measured individually by LC-MS/MS. Since estrone was also detected at 11 ng/L, and its estrogenic potency has been reported to be 1-20% of E2 (Jarosova et al. 2014), the integrated BEQ response of 1.9 ng/L can plausibly be attributed to the sum contribution of E2 and estrone (i.e., 0.6 ng/L + 0.1(11 ng/L) = 1.7 ng/L), where 0.1 is the assumed relative potency (10%) of estrone compared to E2. The measured concentrations of bisphenol A and 4-NP, both weak estrogens with potencies much less than 1% of that for E2 (Leusch et al. 2010; Jarosova et al. 2014), were not high enough to affect estrogenic activity as measured by the IVB. A similar comparison of IVB screening results for sediment revealed that the only sample with a detectable ER-α response (Piner Creek; Table 1-4) was also the only sample with detectable concentrations of E2, estrone and bisphenol A (Table 1-7).

Conclusions and Recommendations

The frequency of detection of target CECs in river water samples varied from zero (e.g. for E2, ibuprofen and triclosan) to 100% detection for galaxolide, 4-NP and PFOS. In all cases, however, the measured CEC concentrations did not exceed MTLs established by the Expert Panel for effluent-dominated freshwater systems, suggesting a low concern and thus low priority for future monitoring. Target CECs were detected in WWTP effluent, with concentrations substantially higher in effluent from the Ukiah WWTP compared to the Cloverdale WWTP effluent. As potential sources of CECs into the RRW, periodic (e.g. annually or bi-annually) monitoring of WWTP effluent would provide assurance that future levels and potential loading of high priority CECs are not increasing.

Table 1-10. Comparison of equivalent concentrations of 17β-estradiol (E2) in aqueous (dissolved phase) samples measured by the ER-α in vitro bioassay and by LC-MS/MS. The bioassay equivalent concentration (BEQ) measured by IVB represents an integrated measure of all estrogenic substances present in the sample. The LC-MS/MS data represents only the concentration of E2 present in the sample.

Station ID	ER-α BEQ (ng E2/L)	LC-MS/MS (ng E2 /L)
114RR0898	BDL: <0.38	BDL: <0.5*
Riverfront	BDL: <0.38	BDL: <0.5*
Mirabel	BDL: <0.38	BDL: <0.5*
Piner Creek	BDL: <0.38	BDL: <0.5*
114LY0010	BDL: <0.38	BDL: <0.5*
Santa Rosa Cr	BDL: <0.44	BDL: <0.5*
Lab Blank	BDL: <0.44	BDL: <0.5*
Field Blank	BDL: <0.44	BDL: <0.5*
114LY0010-Dupl	BDL: <0.44	BDL: <0.5*
Cloverdale WWTP Effl	BDL: <0.52	BDL: <0.5*
Ukiah WWTP Effl	1.90	0.6**

* estrone not detected (< 0.56 ng/L)
** 11 ng/L estrone reported

The frequency of detection of target CECs in sediment samples was lower overall than for water samples, with no analytes except for 4-NP exhibiting universal occurrence across all stations. Rather, there was a clear pattern of detectable levels by station, with those located in the southeastern portion of the RRW exhibiting the highest concentrations. The proximity of these stations (Piner Creek, Santa Rosa Creek and Mirabel) to the city of Santa Rosa suggested a higher degree of localized (i.e. suburban) input of CECs. In addition, the elevated moisture content in these samples were suggestive of finer grained, TOC-enriched substrates which capture hydrophobic chemicals more efficiently than coarse-grained, “sandy” sediments. Moreover, the enrichment of bifenthrin and permethrin on suspended particulates in aqueous samples indicated that sediment is indeed the primary matrix of interest for monitoring of these hydrophobic pesticides. In contrast to CEC in water, the MTQs for sediment would support a higher frequency (e.g., annually) and/or greater spatial coverage for monitoring of pyrethroids and fipronil, where measured concentrations exceeded MTLs by a factor of 10 or more.

The GeneBLAzer in vitro bioassay results, expressed as BEQs, suggested a low occurrence of estrogenic chemicals and glucocorticoid steroids (e.g. anti-inflammatory agents found in asthma mediation) in water and sediment from the RRW. The concordance of the analytical chemistry results for the known strong estrogens (e.g., 17β-estradiol, estrone, 4-NP and bisphenol A) provides additional evidence to support the IVB results. Similar to the targeted CEC results, BEQs for the Ukiah WWTP effluent were higher than for the Cloverdale WWTP effluent. Moreover, the measured concentrations of the target estrogens in the WWTP effluent samples were consistent with the magnitude of response observed using the ER-α IVB. The concordance between the bioanalytical and conventional targeted chemical methods indicates that the ER-α and GR IVBs 1) are not prone to false positives; and 2) can be applied as integrative screening tools for groups of CECs that share the same cellular bioresponse.

This initial screening study was limited to single event sampling at a few representative stations and with a small number of commercially available IVBs that have been standardized for water quality measurement. As more bioanalytical tools and expanded chemical methods become available, it would be informative to revisit the RRW in 5-10 years to screen for CECs and their potential for ecological and human health impacts.

References

Anderson P, Denslow N, Drewes JE, Olivieri A, Schlenk D, Scott G, Snyder S. 2012. Monitoring Strategies for Chemicals of Emerging Concern (CECs) in Aquatic Ecosystems: Final Report. Southern California Coastal Water Research Project (SCCWRP) Technical Report 692, Costa Mesa, CA.

Cao Q, Wang R, Zhang H, Ge X, Liu J. 2015. Distribution of organic carbon in the sediments of Xinxue River and the Xinxue River constructed wetland, China. *Plos One* https://doi.org/10.1371/journal.pone.0134713.

Dodder NG, Mehinto AC, Maruya KA. 2015. Monitoring of constituents of emerging concern (CECs) in aquatic ecosystems: pilot study design and QA/QC guidance. Southern California Coastal Water Research Project. Costa Mesa, CA. 95 pgs.

Jarosova B, Blaha L, Giesy JP, Hilscherova K. 2014. What level of estrogenic activity determined by in vitro assays in municipal waste waters can be considered safe? *Environment International* 64:98-109.

Kidd KA, Blanchfield PJ, Mills KH, Palace VP, Evans RE, Lazorchak JM, Flick RW. 2007. Collapse of a fish population after exposure to a synthetic estrogen. *Proceedings of the National Academy of Sciences* 104:8897-8901.

Lao W, Tsukada D, Greenstein DJ, Bay SM, Maruya KA. 2010. Analysis, occurrence and toxic potential of pyrethroids and fipronil in sediments from an urban estuary. *Environmental Toxicology and Chemistry* 29:834-851.

Lao W, Tiefenthaler L, Greenstein DJ, Maruya KA, Bay SM, Ritter K, Schiff K. 2012. Pyrethroids in Southern California coastal sediments. *Environmental Toxicology and Chemistry* 31(7):1649-1656.

Leusch FDL, de Jager C, Levi Y, Lim R, Puijker L, Sacher F, Tremblay LA, Wilson VS, Chapman HF. 2010. Comparison of five in vitro bioassays to measure estrogenic activity in environmental waters. *Environmental Science and Technology 44*:3853–3860.

Maruya KA, Dodder NG, Mehinto AC, Denslow ND, Schlenk D, Snyder SA, Weisberg SB. 2015. A tiered, integrated biological and chemical monitoring framework for contaminants of emerging concern (CECs) in aquatic ecosystems. *Integrated Environmental Assessment and Management* 12:540-547.

Maruya KA, Dodder NG, Sengupta A, Smith DJ, Lyons JM, Heil AT, Drewes JE. 2016. Multi-media screening of contaminants of emerging concern (CECs) in coastal urban watersheds in southern California. *Environmental Toxicology and Chemistry* DOI: 10.1002/etc3348.

Maruya KA. 2017. Screening study for constituents of emerging concern (CECs) in selected freshwater rivers in the Los Angeles Region – Phase 3 Final Report. Southern California Coastal Water Research Project. Costa Mesa, CA. 50 pgs.

Mehinto AC, Jayasinghe BS, Vandervort DR, Denslow ND, Maruya KA. 2016. Screening for endocrine activity in water using commercially available in vitro transactivation bioassays. *Journal of Visualized Experiments*, 118:e54725, DOI:10.3791/54725.

Mehinto AC, Vandervort DR, Lao W, He G, Denison MS, Vliet SM, Volz DC, Mazor RD, Maruya KA. 2017. High throughput in vitro and in vivo screening of inland waters of southern California. *Environmental Science: Processes and Impacts*. 19:1142-1149. DOI: 10.1039/C7EM00170C.

Sengupta A, Lyons JM, Smith DJ, Heil A, Drewes JE, Snyder SA, Maruya KA. 2014. The occurrence and fate of chemicals of emerging concern (CECs) in coastal urban rivers receiving discharge of treated municipal wastewater effluent. *Environmental Toxicology and Chemistry* 33:350-358.

Siegler K, Phillips BM, Anderson BS, Voorhees JP, Tjeerdema RS. 2015. Temporal and spatial trends in sediment contaminants associated with toxicity in California watersheds. *Environmental Pollution* 206:1-6.

U.S. Environmental Protection Agency. 2008. Aquatic life criteria for contaminants of emerging concern – draft (USEPA OW/ORD Working Group 2008). (86 pgs).

Weston DP, Schlenk D, Riar N, Lydy MJ, Brooks ML. 2015a. Effects of pyrethroid insecticides in urban runoff on Chinook salmon, steelhead trout, and their invertebrate prey. *Environmental Toxicology and Chemistry* 34(3):649-657.

Weston DP, Chen D, Lydy MJ. 2015b. Stormwater-related transport of the insecticides bifenthrin, fipronil, imidacloprid, and chlorpyrifos into a tidal wetland, San Francisco Bay, California. *Science of the Total Environment* 527-528:18-25.

TASK 2: CONTAMINANTS OF EMERGING CONCERN IN SPORT FISH FROM THE RUSSIAN RIVER WATERSHED

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Summary

This report summarizes the results from Task 2: monitoring of prioritized CECs in fish tissue. Following the pilot study guidance (Dodder et al. 2015), samples were analyzed for polybrominated diphenyl ethers (PBDEs) and perfluorinated alkyl substances (PFASs). PBDEs and PFASs have been used in a wide variety of applications for many years. PBDEs are additive flame retardants that have been used in polymers, paints, electrical appliances, and polyurethane foams used in furniture and cars. PFASs make surface coatings water and oil resistant and have been extensively used in adhesives, food packaging, electronic devices, cosmetics, surfactants, and fire-fighting foams. In recent years, several PBDEs and PFASs were found to be highly persistent, bioaccumulative, and toxic. Specific water quality objectives have not yet been developed for PBDEs or PFASs, but information on their occurrence and effects in the environment is lacking.

Seven of thirteen analyzed PBDEs were detected in fish tissue. PBDE concentrations in fish tissue samples collected from sites in the Russian River watershed were well below thresholds of concern for human consumption established by the California Office of Environmental Health Hazard Assessment. The ranges of summed PBDE congener concentrations (range: 0.1 – 30 ppb, median: 3 ppb) were somewhat lower than ranges observed in fish from San Francisco Bay (range: 3 – 54 ppb, median: 5 ppb; Sun et al. 2017) and in Southern California coastal urban watersheds, where maximum tissue concentrations varied widely (370 ppb and 7.0 ppb for the Santa Clara River and coastal embayments, respectively; Maruya et al. 2016). The most frequently detected PBDE congener was PBDE 47 (a tetrabromodiphenyl ether, detected in all thirteen analyzed samples). Overall, the PBDE fingerprints are consistent with typical PBDE compositions reported in the literature.

Consistent with studies elsewhere, perfluorooctanesulfonic acid (PFOS) was the dominant PFAS detected in samples from the Russian River. PFOS was detected in all 13 samples analyzed (range: 1 – 11 ppb, median: 4 ppb). OEHHA has not established fish consumption thresholds for PFOS or other PFASs. Observed PFOS concentrations in fish tissue samples from the Russian River watershed reached a maximum of 11 ppb. This value is well below an advisory level issued by the State of Minnesota (40 ppb for a consumption rate of one meal per week). However, it exceeds an advisory level issued by the State of Michigan (no greater than 9 ppb for 16 or more meals per month), suggesting potential concern for human health at high consumption rates. It is also possible that PFOS levels in fish may pose low-level concerns to avian or mammalian predators (ECCC 2013). The maximum concentration of PFOS observed in Russian River sport fish was lower than the maximum observed in San Francisco Bay (18 ppb in a 2009 leopard shark sample) and near the low end of concentrations observed in fish tissue collected in the Santa Clara River and Santa Clara River Estuary in the Los Angeles region (10 to 26 ppb, SCCWRP 2015). Three other PFASs were detected in some samples:

perfluorodecanoate (in seven samples), and perfluoroundecanoate and perfluorododecanoate, each detected in four of the 13 samples.

Regional patterns in PBDE and PFOS accumulation should be interpreted with caution due to the lack of replication at each location, but tissue concentrations in Sacramento pikeminnow and Sacramento sucker (the two fish species that were collected at multiple river stations) do suggest spatial variation.

In Sacramento pikeminnow, the sum of PBDEs was highest at the two sites located downstream of the points of discharge of the Ukiah WWTP and the Cloverdale WWTP . This is consistent with the expectation to find higher concentrations near wastewater discharges. The sum of PBDEs was lower in samples collected at a site located upstream of the Santa Rosa urban area (Russian River at Riverfront Park) than in those collected at sites farther downstream and closer to the coast. The lower reach of the Russian River receives flows from tributaries that are heavily impacted by human activities, which may act as pathways for PBDE pollution. Notably, the highest PFOS concentrations observed for both species were also from the stations closest to the coast and farthest from upstream locations that are closer to expected stormwater and wastewater discharge points.

A potential pollution pathway for PFOS is land application of WWTP biosolids. PFOS can build up in areas where sludge is applied to land (Sepulvado et al. 2011). PFOS is soluble in water and may be readily transported via stormwater runoff.

Fish tissue levels of PBDEs and PFOS/PFASs are currently of limited concern. Periodic monitoring (for example, every five to ten years) is recommended to ensure that levels do not rise unexpectedly in the future.

Background

CECs are increasingly being detected in the environment. They are pollutants not currently included in routine monitoring programs and may be candidates for future regulation depending on their ecotoxicity, potential human health effects, and frequency of occurrence in environmental media. Preliminary research has linked CECs that are known to act as endocrine disruptors to adverse effects in aquatic life. Some CECs accumulate in the food web and may pose a threat to human and wildlife health. Important delivery pathways to surface waters include wastewater effluent and stormwater runoff. However, data about sources and the occurrence of CECs are generally lacking across the state (Anderson et al. 2012).

PBDEs and PFASs have been used in a wide variety of applications for many years. PBDEs are additive flame retardants that have been used in polymers, paints, electrical appliances, and polyurethane foams used in furniture and cars. PFASs make surface coatings water and oil resistant and have been extensively used in adhesives, food packaging, electronic devices, cosmetics, surfactants, and fire-fighting foams. In recent years, however, several PBDEs and PFASs were found to be highly persistent, bioaccumulative, and toxic (e.g., Fisher et al. 2016, Giesy & Kannan 2001, Siddiqi et al. 2003). These findings led the state of California to enact bans on two types of PBDE mixtures (“penta” and “octa”) starting in 2006. Meanwhile, federal actions have led to nationwide, voluntary phase-outs of the production and use of members of both groups of compounds. Specific water quality objectives have not yet been developed for PBDEs or PFASs, but information on their occurrence and effects in the environment is lacking.

This report presents a summary of results from monitoring of PBDEs and PFASs in fish tissue collected from the Russian River watershed. The purpose of this study is to provide a preliminary assessment of the occurrence of these CECs and determine whether there are signs of a potential problem. It was designed to provide an initial estimate of fish tissue concentrations in the watershed and a comparison of the results to existing consumption thresholds.

Materials and Methods

Sampling Design

The Russian River watershed receives discharges from municipal wastewater treatment plants (when increased winter flows allow for adequate dilution of effluent) as well as stormwater runoff. Wastewater effluent and stormwater runoff are important delivery pathways for CECs to surface waters. This study is part of the first regional pilot evaluation of the Pilot Study design for CECs, providing data that are both useful for the region and for implementation of the monitoring framework. Fish tissue collection was part of a larger effort to monitor fish in the Russian River watershed for a variety of contaminants, including mercury and PCBs. The study targeted major sport fish species at six popular fishing sites (**Figure 2-1**). **Table 2-1** provides information on the fish samples collected for CEC analysis.

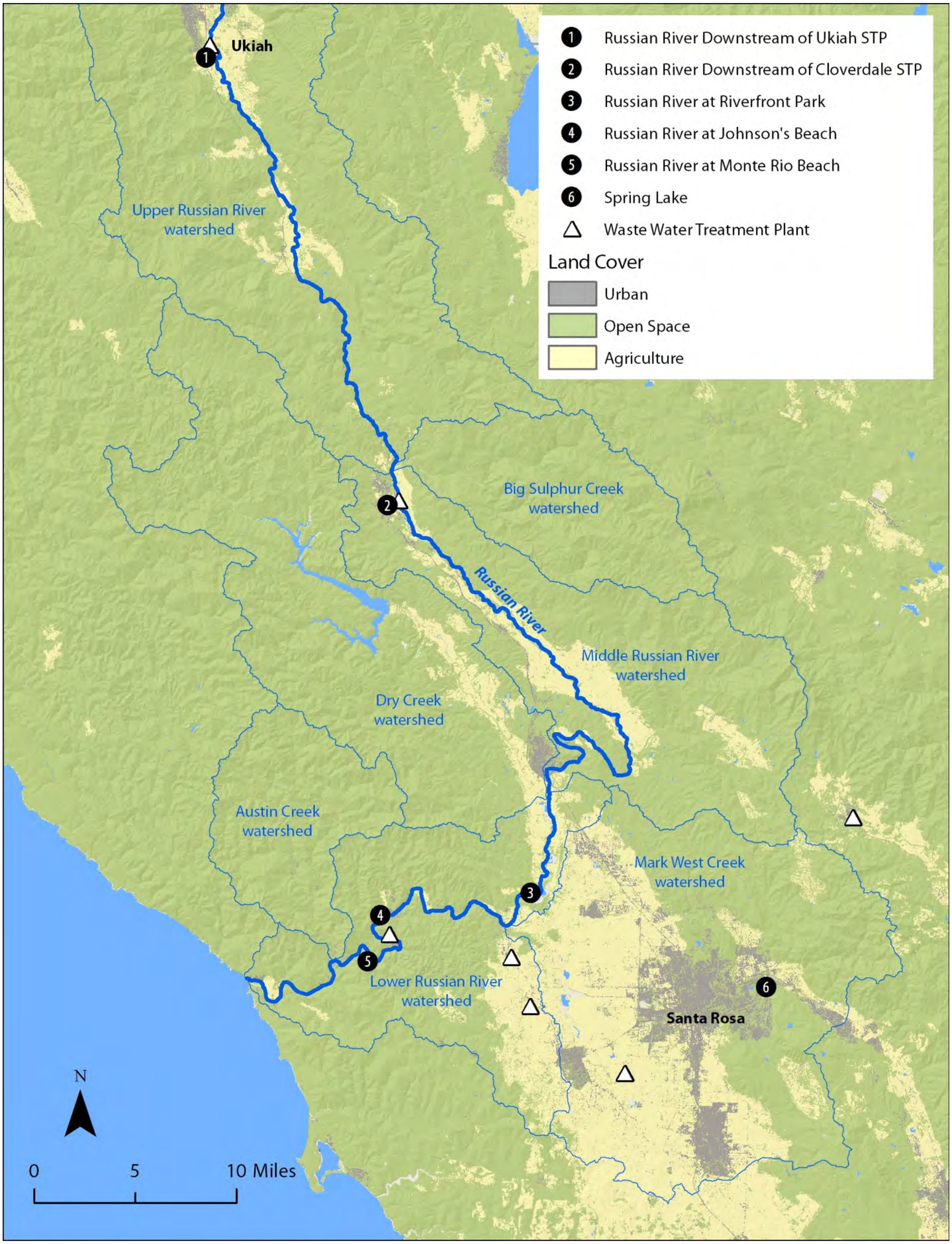

Figure 2-1. Locations sampled in the Russian River Watershed Pilot Monitoring Investigation.

Table 2-1. Scientific and common names of fish species analyzed for CECs, the number of locations sampled, and their minimum, median, and maximum total lengths (mm).

Family	Species Name	Common Name	Number of Fish	Number of Samples	Number of Locations Sampled	Min Length (mm)	Median Length (mm)	Max Length (mm)	Analyzed as Composite	Analyzed as Individual
Cyprinids (Cyprinidae)	*Ptychocheilus grandis*	Sacramento Pikeminnow	21	5	5	355	415	626	X	X
Suckers (Catostomidae)	*Catostomus occidentalis*	Sacramento Sucker	25	5	5	375	430	495	X	
Sunfish (Centrarchidae)	*Lepomis microlophus*	Redear Sunfish	8	1	1	146	173	222	X	
Sunfish (Centrarchidae)	*Micropterus dolomieu*	Smallmouth Bass	3	1	1	300	316	414	X	
Sunfish (Centrarchidae)	*Micropterus salmoides*	Largemouth Bass	5	1	1	306	336	354	X	

Sample Processing

Dissection and compositing of fish tissue samples were performed following USEPA guidance (USEPA 2000). Fish were dissected skin-off and only the fillet muscle tissue was used for analysis. Fish tissue samples were shipped overnight and stored frozen in the dark in clean amber glass jars with screw caps at -20°C prior to analysis. Time between collection and analysis ranged from 159-162 days for PFASs, and from 162-177 days for PBDEs.

The default sample size for PFAS sample analysis was 2 g (wet weight). Surrogate standards were added and the samples were extracted by shaking with methanolic potassium hydroxide solution. After centrifugation, a suitable aliquot of the supernatant was diluted with water and cleaned up by solid phase extraction (SPE) using disposable cartridges containing a weak anion exchange sorbent. The eluate was spiked with recovery standards prior to analysis (AXYS 2015). Fish tissue samples for PBDE analysis were freeze dried and aliquots extracted using accelerated solvent extraction. All samples were analyzed within 6 days of extraction.

Analysis

Perfluorinated alkyl substances (PFASs) in muscle tissue were measured by SGS AXYS (Sidney, British Columbia, Canada) using MLA-043 Revision 07 on a high-performance liquid chromatograph coupled to a triple quadrupole mass spectrometer. PBDEs were measured by the Southern California Coastal Water Research Project (SCCWRP) using gas chromatography–negative chemical ionization (GC-NCI)/MS with an Agilent 7890 GC/5975 quadrupole mass selective detector (Lao et al. 2010).

Analytes included in the study are listed in **Table 2-2**. Four of thirteen analyzed PFASs were detected, and nine of thirteen analyzed PBDEs were detected.

Quality Assurance

Samples were processed as a single batch, following the performance based quality assurance/quality control (QA/QC) guidelines established by the SCCWRP Pilot Study Design. Data that meet the basic measurement quality objectives (MQOs) delineated in these guidelines are considered acceptable and usable for the intended purpose (AXYS 2015, Dodder et al. 2015, SCCWRP 2016).

In compliance with the performance based quality assurance/quality control (QA/QC) guidelines established by the SCCWRP Pilot Study Design (Dodder et al. 2015), NIST SRM 1947 – Lake Michigan Fish Tissue was used as a standard reference material by each laboratory to ensure method accuracy as per the n=20 guidelines.

Results were reported for the thirteen PFASs and thirteen PBDE congeners listed in Table 2-2. Of these:

- 100% were acceptable; no results were rejected
- No qualifiers were needed
- 58% of all PBDE results were non-detects (143 of 247, including field and lab replicates), and 84% of all PFAS results were non-detects (198 of 234).

In summary, all data were considered usable for the intended purpose.

The sample collection effort generally yielded smaller fish, resulting in fewer composite samples than anticipated (A. Bonnema, personal communication). Extended drought conditions may have impacted fish populations along the Russian River. While samples are sufficient for the pilot study, more robust conclusions would require a greater number of samples.

Assessment Thresholds

Tissue concentrations of PBDEs and PFOS were compared to thresholds for concern based on human health risk assessments of a) PBDEs by the State of California's Office of Environmental Health Hazard Assessment (OEHHA), and b) PFOS by the Minnesota Department of Health (MDH 2008, **Table 2-3**). OEHHA published Advisory Tissue Levels (ATLs) for PBDEs in 2011 (Klasing and Brodberg 2011) but has not yet established goals or advisory levels for PFOS or other PFASs. Therefore, levels of PFOS were compared to advisory levels developed by MDH. Minnesota was one of the first states to release advisory levels for PFOS.

Table 2-2. Analytes included in the study, method detection limits (MDLs), frequencies of detection and reporting, and average, median, and range of concentrations (n = 13). Frequency of detection includes all results above detection limits. Frequency of reporting includes all results that were reportable (above the detection limit and passing all QA review). ND = not detected. All concentrations in ppb wet weight.

Analyte	Method Detection Limit (ppb)	Frequency of Detection (%)	Frequency of Reporting (%)	Range, min/max (ppb)	Average (ppb)	Median (ppb)
Perfluorobutanoate (PFBA)	0.50	0%	0%	ND	ND	ND
Perfluorobutanesulfonate (PFBS)	0.99	0%	0%	ND	ND	ND
Perfluoropentanoate (PFPA)	0.50	0%	0%	ND	ND	ND
Perfluorohexanoate (PFHx)	0.50	0%	0%	ND	ND	ND
Perfluorohexanesulfonate (PFHxS)	0.99	0%	0%	ND	ND	ND
Perfluoroheptanoate (PFHpA)	0.50	0%	0%	ND	ND	ND
Perfluorooctanoate (PFOA)	0.50	0%	0%	ND	ND	ND
Perfluorooctanesulfonate (PFOS)	0.99	100%	100%	1.0/10.5	4.68	3.8
Perfluorooctanesulfonamide (PFOSA)	0.60	0%	0%	ND	ND	ND
Perfluorononanoate (PFNA)	0.50	0%	0%	ND	ND	ND
Perfluorodecanoate (PFDA)	0.50	54%	54%	ND/ 1.14	<MDL	<MDL
Perfluoroundecanoate (PFUA)	0.50	31%	31%	ND/ 0.63	<MDL	<MDL
Perfluorododecanoate (PFDoA)	0.50	31%	31%	ND/ 0.76	<MDL	<MDL
PBDE 015	0.80	0%	0%	ND	ND	ND
PBDE 028	0.07	77%	77%	ND/ 0.59	0.13	0.12
PBDE 033	0.05	0%	0%	ND	ND	ND
PBDE 047	0.06	100%	100%	0.08/ 24.6	4.08	2.3
PBDE 049	0.05	77%	77%	ND/ 0.77	0.14	0.06
PBDE 066	0.10	0%	0%	ND	ND	ND
PBDE 075	0.04	0%	0%	ND	ND	ND
PBDE 099	0.05	23%	23%	ND/ 0.271	<MDL	<MDL

Analyte	Method Detection Limit (ppb)	Frequency of Detection (%)	Frequency of Reporting (%)	Range, min/max (ppb)	Average (ppb)	Median (ppb)
PBDE 100	0.04	92%	92%	ND/ 3.60	0.70	0.37
PBDE 153	0.02	85%	85%	ND/ 0.07	0.03	0.03
PBDE 154	0.02	92%	92%	ND/ 1.10	0.26	0.11
PBDE 155	0.02	31%	31%	ND/ 0.09	<MDL	<MDL
PBDE 183	0.03	0%	0%	ND	ND	ND

Table 2-3. Thresholds for concern based on human health risk assessments of a) PBDEs by OEHHA (Klasing and Brodberg 2011) and b) PFOS by the Minnesota Department of Health (MDH 2008) and the Michigan Department of Community Health (MDCH, State of Michigan 2014). All values given in ng/g (ppb) wet weight. OEHHA defines one serving as 8 ounces (227 g) prior to cooking. MDH and MCDH define the size of one meal according to body weight

	OEHHA Advisory Tissue Levels			
Pollutant	**Advisory Tissue Level (3 servings/week)**	**Advisory Tissue Level (2 servings/week)**	**Advisory Tissue Level (1 serving/week)**	**Advisory Tissue Level (No Consumption)**
PBDEs	< 100 ppb	100-210 ppb	210-630 ppb	> 630 ppb
	MDH Meal Advice Categories			
	Unrestricted	**1 meal/week**	**1 meal/month**	**DO NOT EAT**
PFOS	≤ 40 ppb	> 40-200 ppb	> 200-800 ppb	> 800 ppb
	MCDH 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

Data on ecotoxicity are extremely limited; results were compared to available studies or draft agency guidelines, where available.

Results and Discussion

PBDEs

Contributions of Different Congeners

The four most frequently detected PBDE congeners were PBDE 47 (a tetrabromodiphenyl ether, detected in all thirteen analyzed samples, range: 0.08 – 25 ppb); PBDE congeners 100 (a pentabromodiphenyl ether, range: <0.04 – 4 ppb) and 154 (a hexabromodiphenyl ether, range: <0.02 – 1 ppb), both detected in twelve samples; and PBDE 153 (a hexabromodiphenyl ether, range: <0.02 – 0.07 ppb), detected in eleven samples. PBDE 28 (a tribromodiphenyl ether, range: <0.07 – 0.6 ppb) and PBDE 49 (a tetrabromodiphenyl ether, range <0.05 – 0.8 ppb) were both detected in ten samples (Table 2-2).

The contribution of PBDE 47 to the sum of PBDEs in the analyzed fish tissue samples ranged from 57% (in a smallmouth bass sample) to 100% percent (in a redear sunfish sample). However, the sum of PBDEs in the sample containing 100% PBDE 47 was 0.079 ppb, which is near or below the MDL for the analyzed congeners, and therefore this ratio is likely skewed (i.e., other congeners are present but not at detectable levels). PBDE 99 (a pentabromodiphenyl ether) contributed 23% of the sum of PBDEs in one sample (smallmouth bass sample) but was only detected in a total of three samples. The sample with the high proportion of PBDE 99 also had a low sum of PBDE concentration of 1.19 ppb and this result may also be somewhat skewed (other congeners with higher MDLs than PBDE 99 were probably present but not detected). Contributions of the remaining detected PBDE congeners to the sum of PBDEs ranged from 0% to 18% (congener 100, in a Sacramento pikeminnow sample).

Overall, these PBDE fingerprints are consistent with typical PBDE compositions in the tissue of aquatic organisms reported in the literature for a range of aquatic ecosystems and trophic levels (e.g., Carson 2001, Rice et al. 2002, Sutton et al. 2014). Biological samples are typically composed predominantly of PBDE 47 with lower levels of PBDEs 99 and 100. PBDE 47 typically provides over 50% of the sum of PBDEs.

Variation Among Species

The highest concentration measured was 30 ppb in an individual Sacramento pikeminnow sample. This concentration was considered an outlier, i.e., about twice the standard deviation distant from the mean of all samples combined. The sample represents the only individual fish analyzed; all the other samples were composites. This individual was by far the largest fish collected for the study (626 mm, Table 2-1) with the highest lipid content (2.8%). This individual was collected downstream of the Ukiah WWTP.

In general, average PBDE concentrations were highest in Sacramento pikeminnow (average of 7 ppb for composites only, average of 12 ppb including the individual sample with 30 ppb), followed by Sacramento sucker (3 ppb), smallmouth bass (1 ppb), and redear sunfish (0.1 ppb) (**Figure 2-2**). Sacramento pikeminnow and Sacramento sucker were the largest species collected with the highest average lipid content (**Table 2-4**). PBDEs are hydrophobic compounds and tend to associate with lipid tissues. The Sacramento sucker were on average slightly larger than the collected Sacramento pikeminnow (431 mm compared to 410 mm average total length) and had higher lipid content (2.1% compared to 1.6%).

In addition to body size and lipid content, trophic position and biomagnification up the food web may contribute to the relatively high concentrations in Sacramento pikeminnow. Sacramento pikeminnow are characterized as "voracious opportunistic predators" whose prey may include other fish, frogs, and even small rodents (UC Davis 2016). Sacramento sucker, on the other hand, consume mostly diatoms and detritus, and thus feed on a lower trophic level than Sacramento pikeminnow. Differences in the age of caught fish from different species may also contribute to observed differences in concentrations.

Table 2-4. Summary statistics by species. Concentrations in ppb wet weight.

Common Name (Sample Type)		Average Number of Fish in Composites	Average Total Length (mm)	Average Percent Lipid	Average Sum of PBDEs (ppb)	Average PFOS (ppb)
Largemouth Bass - fillet (Composite)	average	5	334	0.47	0.8	10.1
	count		1	1	1	1
Redear Sunfish - fillet (Composite)	average	8	177	0.42	0.1	2.1
	count		1	1	1	1
Sacramento Pikeminnow - fillet (Composite)	average	5	410	1.59	7.1	5.2
	count		4	4	4	4
Sacramento Pikeminnow - fillet (Individual)	average	1	626	2.81	30.1	3.8
	count		1	1	1	1
Sacramento Sucker - fillet (Composite)	average	5	431	2.06	2.9	4.0
	count		5	5	5	5
Smallmouth Bass - fillet (Composite)	average	3	343	0.67	1.2	7.1
	count		1	1	1	1

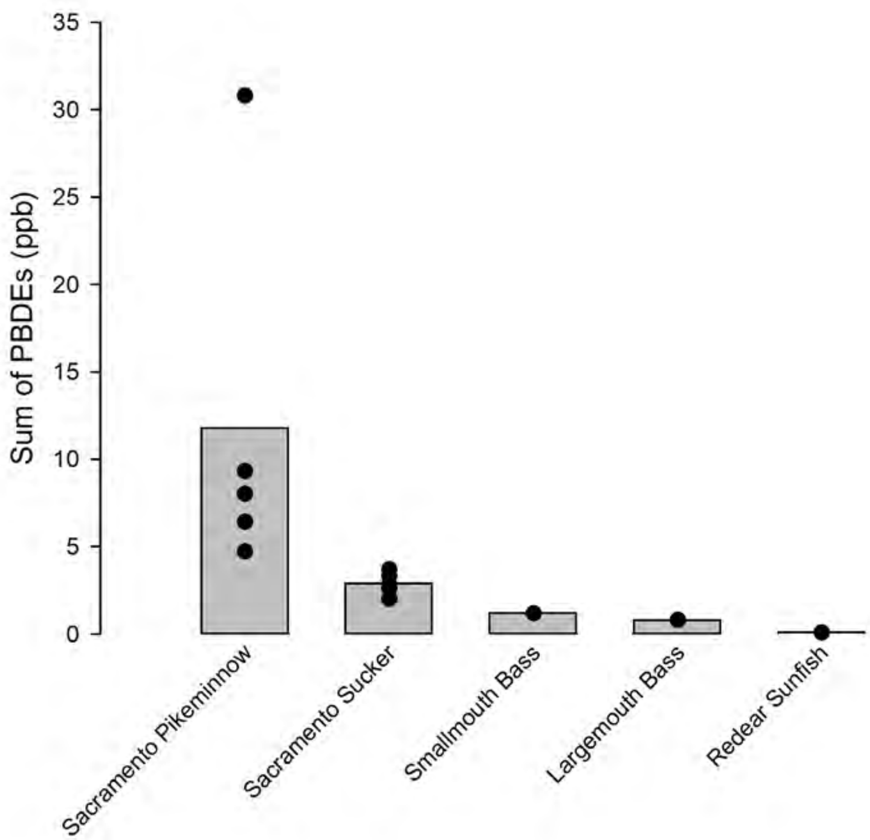

Figure 2-2. Sums of PBDE concentrations (ppb wet weight) in sport fish species in the Russian River watershed, 2015. Bars indicate average concentrations. Points represent composite samples of fillets without skin. All samples were well below the lowest OEHHA threshold (the 100 ppb 2-serving ATL).

Variation Among Stations

In Sacramento pikeminnow, the highest concentrations were observed at the two sites located downstream of the points of discharge of the Ukiah WWTP and the Cloverdale WWTP (**Figure 2-3**). This is consistent with the expectation to find higher concentrations near wastewater discharges. The sum of PBDEs was lower in samples collected at a site located upstream of the Santa Rosa urban area (Russian River at Riverfront Park) than in those collected at sites further downstream and closer to the coast. The lower reach of the Russian River receives flows from tributaries that are heavily impacted by human activities, which may act as pathways for PBDE pollution. These potential pathways are discussed in more detail in Section 4.2. Concentrations in Sacramento pikeminnow composites (excluding outlier individual sample) spanned a 2-fold range, and concentrations in Sacramento sucker spanned a 1.7-fold range.

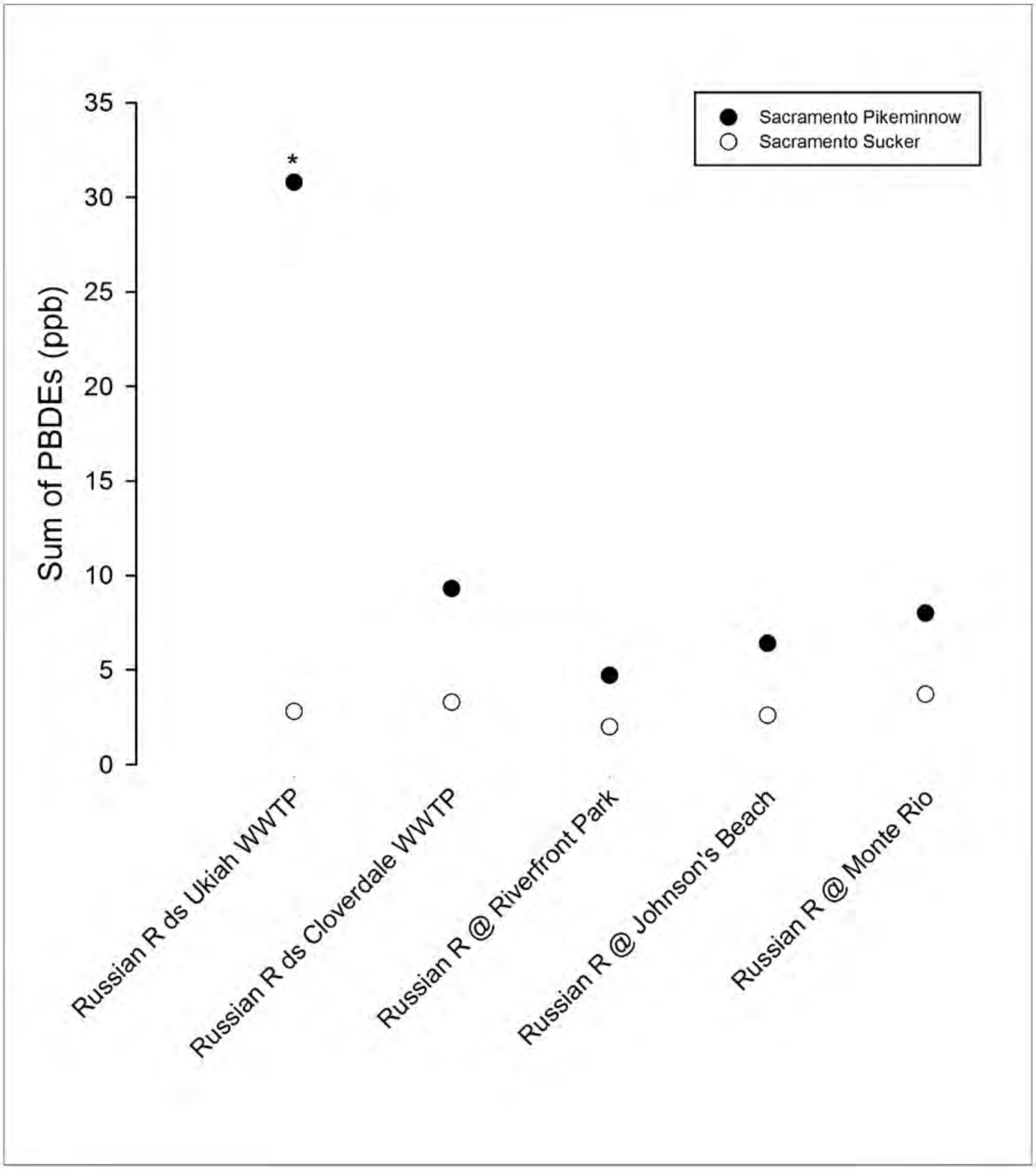

Figure 2-3. Sums of PBDE concentrations (ppb wet weight) in sport fish collected at different locations along the Russian River watershed, 2015. All points represent composites, except for one of the Sacramento Pikeminnow samples that was an individual fish (marked with an asterisk).

Comparison to Thresholds and Fish from Other Regions

Sums of PBDEs were well below established consumption thresholds of concern. The highest sample concentration (which was an outlier) was 30 ppb, compared to 100 ppb as OEHHA's lowest advisory tissue level. OEHHA guidance would therefore suggest that, in terms of PBDEs, it would be safe to eat three meals per week of sport fish species found in the Russian River watershed.

Data gaps prevent a robust assessment of the potential impacts of PBDE contamination to the fish themselves. Increased susceptibility to pathogenic microorganisms (Arkoosh et al. 2010) has been observed in sub-yearling Chinook salmon (*Oncorhynchus tshawytscha*) with PBDE concentrations more than ten times higher than observed in the Russian River watershed. While this suggests that Russian River fish would not experience impaired immune function due to PBDE contamination, no specific tissue-based ecotoxicity thresholds are available.

The ranges of summed PBDE congener concentrations (range: 0.1 – 30 ppb, median: 3 ppb) were somewhat lower than ranges observed in fish from San Francisco Bay (range: 3 – 54 ppb, median: 5 ppb, Sun et al. 2017) and in Southern California coastal urban watersheds, where maximum tissue concentrations varied widely (370 ppb and 7.0 ppb for the Santa Clara River and coastal embayments, respectively). The range of sums of PBDEs in Sacramento pikeminnow composite samples at the Russian River sites was 5 to 9 ppb, compared to a range of 3 to 13 ppb in shiner surfperch, the most contaminated open water species from San Francisco Bay (Davis et al. 2011). The highest concentrations in San Francisco Bay shiner surfperch (13 ppb) were measured near Oakland, the most industrialized area sampled. Other shiner surfperch samples from San Francisco Bay were in a nearly identical range (3 – 9 ppb) to that measured in Sacramento pikeminnow composites from the Russian River. The highest measured Sacramento pikeminnow concentration measured in the Russian River (30 ppb) was lower than the highest measured concentrations in a 2014 study of San Francisco Bay (Sun et al. 2017), which observed 48 ppb in a composite sample of largemouth bass and 54 ppb in a composite sample of carp (average of 37 ppb) from the Artesian Slough, an effluent-dominated slough at the outlet of the San Jose WWTP.

Though this pilot study examined a relatively small number of samples, fish tissue levels of PBDEs appear to be of limited concern. Periodic monitoring (for example, every five to ten years) is recommended to confirm that levels do not rise unexpectedly in the future.

PFASs

Occurrence of Different PFASs

PFOS was detected in all thirteen samples analyzed (range: 1 – 11 ppb). Three other PFASs were detected in some samples: perfluorodecanoate (PFDA, in seven samples, range: < 0.5 – 1.1 ppb), and perfluoroundecanoate and perfluorododecanoate (PFUA and PFDoA, each detected in four of the thirteen samples, range: <0.5 – 0.6 and < 0.5 – 0.8, respectively).

Consistent with studies elsewhere, PFOS was the dominant PFAS detected in samples from the Russian River. Studies of concentrations in Minnesota fish fillet samples determined that: 1) PFOS was the predominate PFAS present, 2) C10, C11, and C12 acids were found above the reporting limit in some samples, and 3) additional congeners occur in very low concentrations or are below the reporting limit (Delinsky et al. 2010).

There were no detections of PFOA, which has been found in the tissues of higher trophic organisms of other aquatic ecosystems. Human and wildlife exposure to PFOA is of concern, because studies have found it to have adverse effects in laboratory animals and their offspring (Lau et el. 2007, Fenton et al. 2009). However, PFOA has low bioaccumulation potential (Martin et al. 2003) and has not been detected in smallmouth bass tissue at sites in the Great Lakes region, even though it was present in the water in detectable amounts (Kannan et al. 2005). PFOA was detected in cormorant eggs but not in fish from the San Francisco Estuary (Sedlak and Greig 2012). Likewise, there was no detection of PFPA in Russian River tissues, though this contaminant was detected at trace levels (~ 1 ppb) in fish from Southern California (SCCWRP 2015).

Variation Among Species
The highest PFOS concentrations were observed in largemouth bass (11 ppb), followed by smallmouth bass (7 ppb), Sacramento pikeminnow (5 ppb), Sacramento sucker (4 ppb), and redear sunfish (2 ppb) (**Figure 2-4**). The observation that largemouth bass and smallmouth bass samples had the highest concentrations would be consistent with their trophic position compared to the other fish. Of note, while these compounds bioaccumulate, they are not lipophilic, so the lack of clear association with tissue lipid content is to be expected. The redear sunfish with the lowest observed concentrations was collected from an urban lake, whereas all the other fish were collected from the Russian River. Therefore, the low concentration may be due to factors specific to that site (such as proximity to pathways, ambient concentrations, and food web structure).

Variation Among Stations
Regional patterns in PFOS accumulation should be interpreted with caution due to the lack of replication at each location, but do suggest spatial variation. PFOS concentrations in Sacramento sucker fillets suggest a progressive increase from the location farthest upstream (Ukiah) towards the coast. PFOS concentrations in Sacramento pikeminnow decreased along the Russian River from Ukiah to Riverfront Park, but then increased again towards the coast in the lower reach. Notably, the highest concentrations observed for both species were from the stations closest to the coast and farthest from upstream locations that are closer to expected stormwater and wastewater discharge points (**Figure 2-5**).

Additional potential pathways for pollution may include discharges from tributaries entering the lower reach of the Russian River below the Riverfront Park and upstream of the Johnson Beach and Monte Rio Beach sampling sites. These include Mark West Creek, Dutch Bill Creek, Austin Creek, and Green Valley Creek. Of these, Mark West Creek and Dutch Bill Creek are the most impacted by human activities and the most likely contributors of PFAS (and PBDE) loads to the lower reach of the Russian River. Mark West Creek collects stormwater discharge from watersheds heavily impacted by human activities, such as residential, commercial, and industrial areas in the Santa Rosa Plain, including parts of Santa Rosa, Rohnert Park, and Sebastopol.

An additional pollution pathway not specifically discussed previously is land application of WWTP biosolids. The City of Santa Rosa Laguna Treatment Plant has a Biosolids Beneficial Use Program, under which 95% of the biosolids generated in the Plant are used as an alternative land cover in these areas (City of Santa Rosa 2016). PFOS can build up in areas where sludge is applied to land (Sepulvado et al. 2011). Unlike PBDEs, PFOS is soluble in water, and may be more readily transported via stormwater runoff.

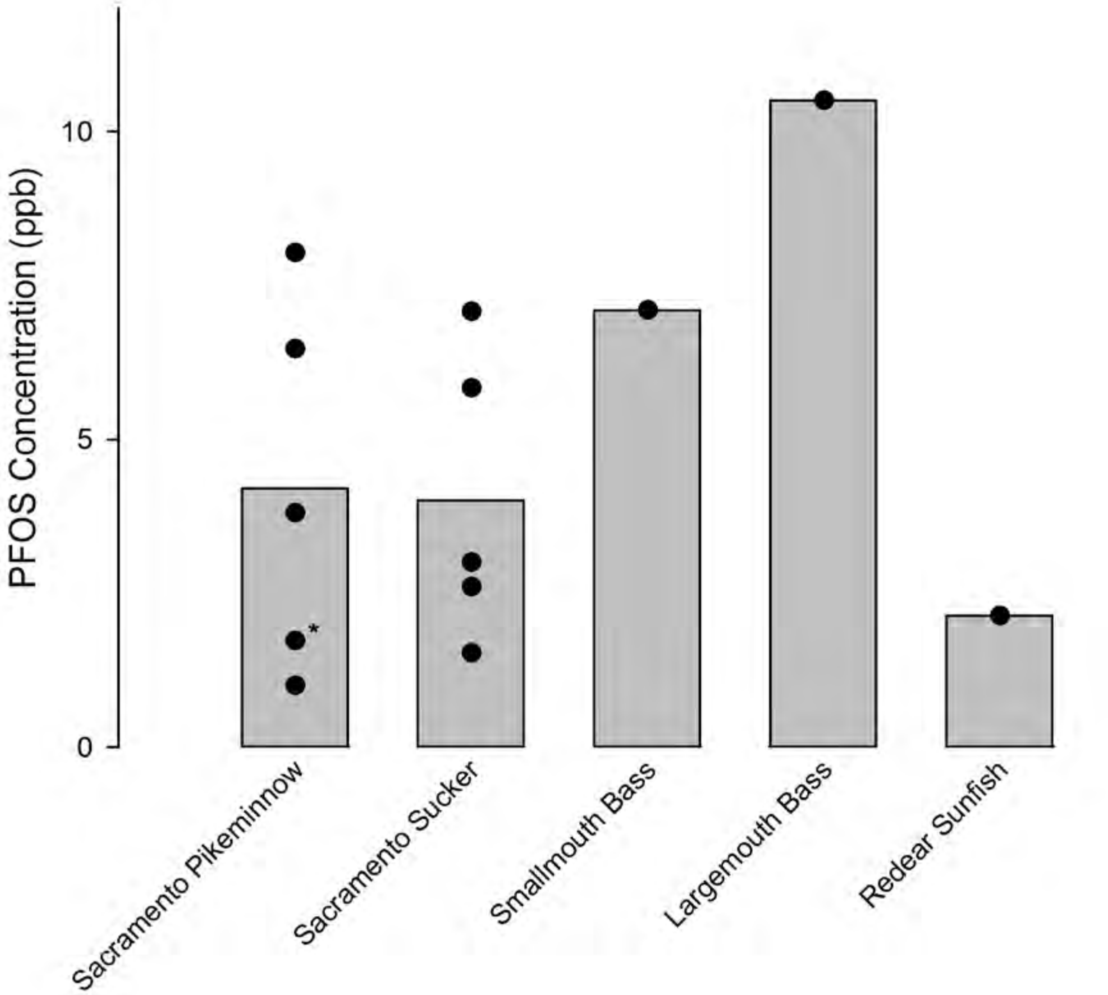

Figure 2-4. PFOS concentrations (ppb wet weight) in sport fish species in the Russian River Watershed, 2015. Bars indicate average concentrations. Points represent composites, except for one of the pikeminnow samples (an individual fish marked with an asterisk). All samples were well below the lowest MDH meal advice category (no more than one meal per week if PFOS > 40 – 200 ppb).

Comparison to Thresholds and Fish from Other Regions

Most observed PFOS concentrations in fish tissue samples from the Russian River watershed were below established consumption thresholds of concern. The highest sample concentration was 11 ppb, compared to 40 ppb as the one serving per week advisory level issued by MDH (Table 2-2). MDH guidance would therefore suggest that, in terms of PFOS, it would be safe to eat at least one meal per week of sport fish species found in the Russian River watershed. However, it exceeds an advisory level issued by the State of Michigan (no greater than 9 ppb for 16 or more meals per month), suggesting potential concern for human health at high consumption rates.

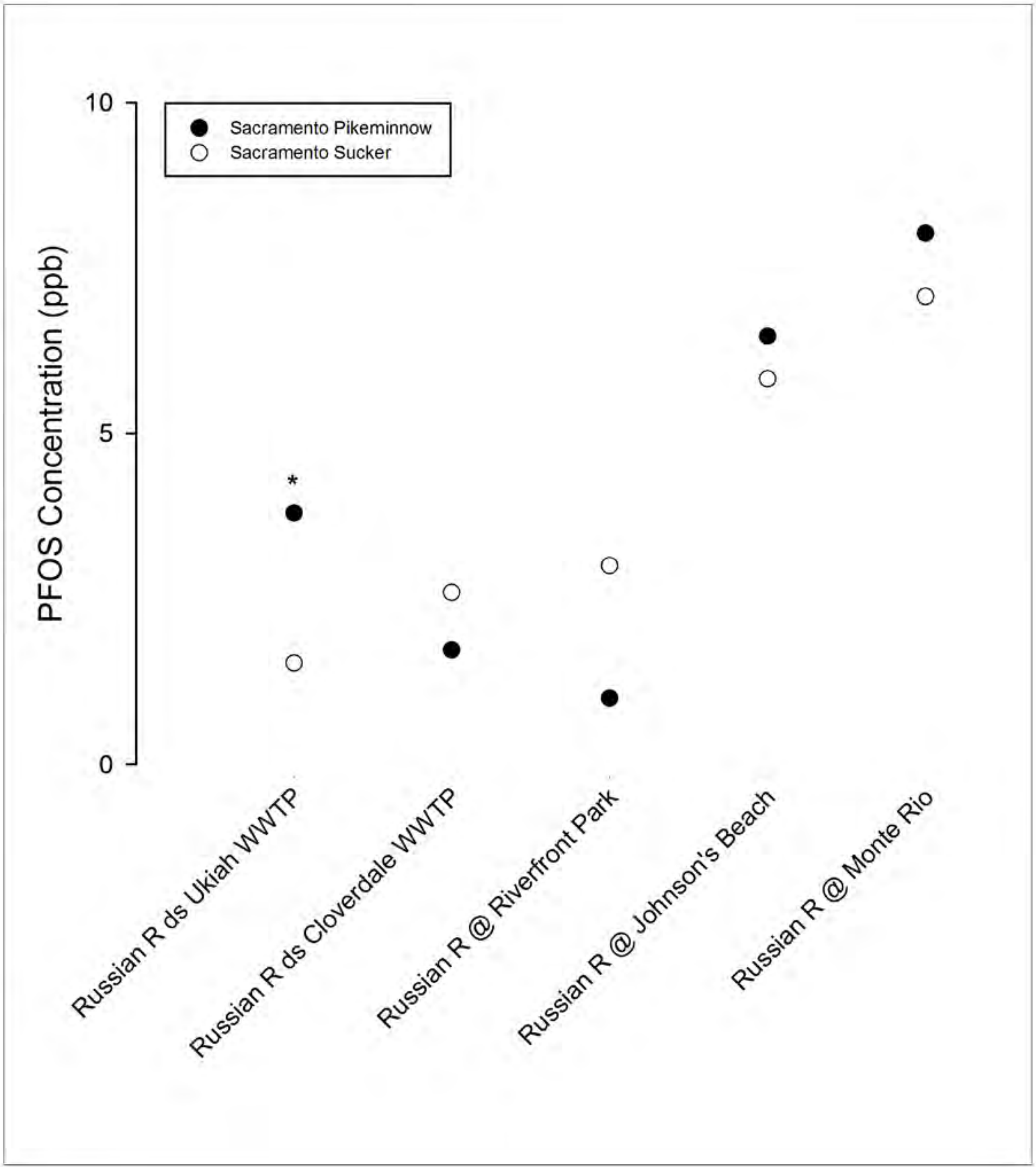

Figure 2-5. PFOS concentrations (ppb) in sport fish species collected at different locations along the Russian River watershed, 2015. Points represent results for composite samples, except for one of the Sacramento Pikeminnow samples (an individual marked with an asterisk).

Data gaps prevent a robust assessment of the potential impacts of PFOS contamination to wildlife. Environment and Climate Change Canada has developed draft Federal Environmental Quality Guidelines (FEQGs) to help assess the significance of PFOS levels in wildlife based on laboratory studies of adverse effects (ECCC 2013). FEQCs include a margin of safety to account for data scarcity. The draft FEQC for fish tissue is 8,300 ppb wet weight; as this level is far higher than levels found in Russian River fish, this suggests that the fish themselves are unlikely to experience adverse effects due to contamination.

Environment and Climate Change Canada also evaluates the potential for impacts among mammals and birds that feed on contaminated fish and wildlife. The “wildlife diet” FEQCs are 4.6 ppb for mammalian predators, and 8.2 ppb for avian predators. Some Russian River samples exceed these guidelines, suggesting the potential for low-level impacts further up the food chain. Dietary diversity expected for many predatory species may serve to reduce the level of risk posed by PFOS in some Russian River fish.

The observed range of reported PFOS concentrations in sport fish from the Russian River watershed (range: 1 – 11 ppb, median: 4 ppb) was narrower than that observed in San Francisco Bay and with a similar but slightly higher median (range: 0 – 17 ppb, median: 3 ppb, Davis et al. 2011, Sun et al. 2017). The highest observed concentration in Russian River sport fish was 10 ppb, compared to 18 ppb in a leopard shark sample from Lower South San Francisco Bay collected in 2009 (Davis et al. 2011) and 17 ppm in a striped bass sample from the Artesian Slough in 2014 (Sun et al. 2017). Average concentrations in small fish collected from the margins of San Francisco Bay ranged from 7 ppb in Central Bay to 43 ppb in the South Bay (Sedlak and Greig 2012). Maximum concentrations in fish samples from the Russian River were near the low end of concentrations observed in fish tissue collected in the Santa Clara River and Santa Clara River Estuary in Southern California (10 to 26 ppb, SCCWRP 2015).

Despite the low number of samples, fish tissue levels of PFOS/PFASs appear to be of limited concern, particularly for human consumption. Monitoring results suggest the potential for low-level impacts to piscivorous species. Periodic monitoring (for example, every five to ten years) is recommended to evaluate contaminant levels.

References

Anderson, P.D., Denslow, N.D., Drewes, J.E., Olivieri, A.W., Schlenk, D., Scott, G.I., and S.A. Snyder. 2012. Monitoring Strategies for Chemicals of Emerging Concern (CECs) in California's Aquatic Ecosystems - Recommendations of a Science Advisory Panel. SCCWRP Technical Report 692. Southern California Coastal Water Research Project, Cosa Mesa, CA.

Arkoosh, M.R., Boylen, D., Dietrich, J., Anulacion, B.F., et al. 2010. Disease susceptibility of salmon exposed to polybrominated diphenyl ethers (PBDEs). Aquat. Toxicol. 98: 51-59.

AXYS. 2015. Summary of AXYS Method MLA-043 Rev 08 Ver 06: Analytical Procedure for the Analysis of Perfluorinated Organic Compounds in Tissue Samples by LC-MS/MS. MSU-043 Rev 10, 09-Nov-2015. AXYS Analytical Services Ltd., Sydney, BC, Canada.

Carson, B.L. 2001. Technical Pentabromodiphenyl Ether (32534-81-9), Technical Octabromodiphenyl Ether (32536-52-0), 2,2«,4,4«-Tetrabromodiphenyl Ether (5436-43-1), 2,2«,4,4«,5-Pentabromodiphenyl Ether (60348-60-9), 2,2«,4,4«,5,5«-Hexabromodiphenyl Ether (68631-49-2) – Review of Toxicological Literature. Submitted by Bonnie L. Carson, M.S.

Integrated Laboratory Systems, Research Triangle Park, NC. Prepared for S. Masten, National Institute of Environmental Health Sciences, Research Triangle Park, NC.

City of Santa Rosa. 2016. Biosolids Management System. Laguna Compost Facility, Santa Rosa, CA. http://ci.santa-rosa.ca.us/departments/utilities/Projects/BMS/Pages/default.aspx [accessed December 7, 2016].

Davis, J.A., K. Schiff, A.R. Melwani, S.N. Bezalel, J.A. Hunt, R.M. Allen, G. Ichikawa, A. Bonnema, W.A. Heim, D. Crane, S. Swenson, C. Lamerdin, and M. Stephenson. 2011. Contaminants in Fish from the California Coast, 2009: Summary Report on Year One of a Two-Year Screening Survey. A Report of the Surface Water Ambient Monitoring Program (SWAMP). California State Water Resources Control Board, Sacramento, CA.

Delinsky, A.D., M.J. Strynar, P.J. McCann, J.L. Varns, L. McMillan, S.F. Nakayama, and A.B. Lindstrom. 2010. Geographical distribution of perfluorinated compounds in fish from Minnesota lakes and rivers. Environ. Sci. Technol. 44: 2549-2554.

Dodder, N.G., Mehinto, A.C., Maruya, K.A. 2015. Monitoring of Constituents of Emerging Concern (CECs) in California's Aquatic Ecosystems – Pilot Study Design and QA/QC Guidance. SCCWRP Technical Report 854. Southern California Coastal Water Research Project, Cosa Mesa, CA.

Environment and Climate Change Canada. 2013. Perfluorooctane Sulfonate in the Canadian Environment: Federal Environmental Quality Guidelines for PFOS. https://www.ec.gc.ca/toxiques-toxics/default.asp?lang=En&n=7331A46C-1&offset=3&toc=hide Accessed December 2016.

Fenton, S. E., J.L. Reiner, S.F. Nakayama, A.D. Delinsky, J.P. Stanko, E.P. Hines, S.S. White, A.B. Lindstrom, M.J. Strynar, S-S.E. Petropoulou, S-S.E. 2009. Analysis of PFOA in dosed CD-1 mice. Part 2: Disposition of PFOA in tissues and fluids from pregnant and lactating mice and their pups. Reprod. Toxicol. 27 (3-4): 365-372.

Fisher, M., Arbuckle, T.E., Liang, C.L., LeBlanc, A., Gaudreau, E., Foster, W.G., Haines, D., Davis, K., Fraser, W.D. 2016. Concentrations of persistent organic pollutants in maternal and cord blood from the maternal-infant research on environmental chemicals (MIREC) cohort study. Environ. Health 15:59

Giesy, J.P., Kannan, K. 2001. Global distribution of perfluorooctane sulfonate in wildlife. Environ. Sci. Technol. 35:1339-1342.

Kannan, K., L. Tao, E. Sinclair, J.S.D. Pastva, D.J. Jude, and J.P. Giesy. 2005. Perfluorinated compounds in aquatic organisms at various trophic levels in a Great Lakes food chain. Arch. Environ. Contam. Toxicol 48(4):559–566.

Klasing, S. and R. Brodberg. 2011. Development of Fish Contaminant Goals and Advisory Tissue Levels for Common Contaminants in California Sport Fish: Polybrominated Diphenyl Ethers (PBDEs). California Office of Environmental Health Hazard Assessment, Sacramento, CA.

Lau, C., K. Anitole, C. Hodes, D. Lai, A. Pfahles-Hutchens, and J. Seed, J. 2007. Perfluoroalkyl acids: a review of monitoring and toxicological findings. Toxicol. Sci. 99(2):366-394.

Lao, W., D. Tsukada, D.J. Greenstein, S.M. Bay, and K.A. Maruya. 2010. Analysis, occurrence and toxic potential of pyrethroids and fipronil in sediments from an urban estuary. Environ. Toxicol. Chem. 29:834–851

Martin, J.W. S.A. Mabury, K.R. Solomon, and D.C.G. Muir. 2003. Dietary accumulation of perfluorinated acids in juvenile rainbow trout (Oncorhynchus mykiss), Environ. Toxicol. Chem. 22(1):189–195.

MDH. 2008. Minnesota Department of Health Fish Consumption Advisory Program Meal Advice Categories. http://www.health.state.mn.us/divs/eh/fish/eating/mealadvicetables.pdf.

Rice, C.P., Chernyak, S.M., Begnoche, L., Quintal, R., Hickey, J. 2002. Comparisons of PBDE composition and concentration in fish collected from the Detroit River, MI and Des Plaines River, IL. Chemosphere 49:731–737

SCCWRP. 2015. Screening Study for Constituents of Emerging Concern (CECs) in Selected Freshwater Rivers in the Los Angeles Region – Phase 2. Final Report, California State Water Quality Control Board Contract Agreement 12-105-140. Southern California Coastal Water Research Project, Cosa Mesa, CA.

SCCWRP. 2016. Standard Operation Procedure for Extraction and Instrumental Analysis of Polybrominated Diphenyl Ethers (PBDE) in Tissue Using the Accelerated Solvent Extraction System (ASE) and Gas Chromatograph (GC)/Negative Chemical Ionization-Mass Spectrometry (GC/NCI-MS). Southern California Coastal Water Research Project, Cosa Mesa, CA.

Sedlak, M.D., and D.J. Greig. 2012. Perfluoroalkyl compounds (PFCs) in wildlife from an urban estuary. J. Environ. Monit. 14:146–154.

Sepulvado, J.G., Blaine, A.C., Hundal, L.S., and C.P. Higgins. 2011. Occurrence and Fate of Perfluorochemicals in Soil Following the Land Application of Municipal Biosolids. Environ. Sci. Technol. 45(19):8106–8112

Siddiqi, M.A., Laessig, R.H., Reed, K.D. 2003. Polybrominated diphenyl ethers (PBDEs): new pollutants-old diseases. Clin. Med. Res.;1(4):281–90.

State of Michigan. 2014. Michigan Fish Consumption Advisory Program Guidance Document. http://www.michigan.gov/documents/mdch/MDCH_MFCAP_Guidance_Document_417043_7.pdf

Sun, J., J.A. Davis, S. N. Bezalel, J.R.M.Ross, A.Wong, R. Fairey, A. Bonnema, D.B. Crane, R. Grace, R. Mayfield, and J. Hobbs. 2017. Contaminant Concentrations in Fish from San Francisco Bay, 2014. SFEI Contribution #806. Regional Monitoring Program for Water Quality in San Francisco Bay, Richmond, CA.

Sutton, R., Sedlak, M., and J. Davis. 2014. Polybrominated Diphenyl Ethers (PBDEs) in San Francisco Bay: A Summary of Occurrence and Trends. RMP Contribution No. 713. San Francisco Estuary Institute, Richmond, California. 62pp.

UC Davis. 2016. California Fish Website. http://calfish.ucdavis.edu [accessed November 21, 2016].

Appendix 2-1: Summary of Pilot Study Results – CECs in Sport Fish from the Russian River Watershed, 2015

Waterbody	Station Name	Common Name	Sample Type	Sum of PBDEs (ng/g ww)	PFOS (ng/g ww)
Russian River	Russian R ds Ukiah WWTP	Sacramento Pikeminnow	Individual	30.8	3.8
Russian River	Russian R ds Ukiah WWTP	Sacramento Sucker	Composite	2.8	1.5
Russian River	Russian R ds Cloverdale WWTP	Sacramento Pikeminnow	Composite	9.3	1.7
Russian River	Russian R ds Cloverdale WWTP	Sacramento Sucker	Composite	3.3	2.6
Russian River	Russian R ds Cloverdale WWTP	Smallmouth Bass	Composite	1.2	7.1
Russian River	Russian R @ Riverfront Park	Sacramento Pikeminnow	Composite	4.7	1.0
Russian River	Russian R @ Riverfront Park	Sacramento Sucker	Composite	2.0	3.0
Russian River	Russian R @ Johnson's Beach	Sacramento Pikeminnow	Composite	6.4	6.5
Russian River	Russian R @ Johnson's Beach	Sacramento Sucker	Composite	2.6	5.8
Russian River	Russian R @ Monte Rio	Largemouth Bass	Composite	0.8	10.5
Russian River	Russian R @ Monte Rio	Sacramento Pikeminnow	Composite	8.0	8.0
Russian River	Russian R @ Monte Rio	Sacramento Sucker	Composite	3.7	7.1
Spring Lake	Spring Lake	Redear Sunfish	Composite	0.1	2.1

Appendix 2-2: Results for polybrominated diphenyl ethers

Station Code	Station	Common Name	Number InComp	TissueName	Prep Preservation Name	Analyte Name	Result	Unit Name	Result Qual Code	Lipid Pct	Avg Total Length
114RR8070	Russian River Downstream of Ukiah STP	Sacramento Sucker	5	fillet	Skin Off	PBDE 015		ng/g ww	ND	1.92	406
114RR8070	Russian River Downstream of Ukiah STP	Sacramento Pikeminnow	1	fillet	Skin Off	PBDE 015		ng/g ww	ND	2.81	368
114RR8070	Russian River Downstream of Ukiah STP	Sacramento Sucker	5	fillet	Skin Off	PBDE 028	0.114	ng/g ww	=	1.92	406
114RR8070	Russian River Downstream of Ukiah STP	Sacramento Pikeminnow	1	fillet	Skin Off	PBDE 028	0.594	ng/g ww	=	2.81	368
114RR8070	Russian River Downstream of Ukiah STP	Sacramento Sucker	5	fillet	Skin Off	PBDE 033		ng/g ww	ND	1.92	406
114RR8070	Russian River Downstream of Ukiah STP	Sacramento Pikeminnow	1	fillet	Skin Off	PBDE 033		ng/g ww	ND	2.81	368
114RR8070	Russian River Downstream of Ukiah STP	Sacramento Sucker	5	fillet	Skin Off	PBDE 047	2.65	ng/g ww	=	1.92	406
114RR8070	Russian River Downstream of Ukiah STP	Sacramento Pikeminnow	1	fillet	Skin Off	PBDE 047	24.6	ng/g ww	=	2.81	368
114RR8070	Russian River Downstream of Ukiah STP	Sacramento Sucker	5	fillet	Skin Off	PBDE 049	0.056	ng/g ww	=	1.92	406
114RR8070	Russian River Downstream of Ukiah STP	Sacramento Pikeminnow	1	fillet	Skin Off	PBDE 049	0.766	ng/g ww	=	2.81	368
114RR8070	Russian River Downstream of Ukiah STP	Sacramento Sucker	5	fillet	Skin Off	PBDE 066		ng/g ww	ND	1.92	406
114RR8070	Russian River Downstream of Ukiah STP	Sacramento Pikeminnow	1	fillet	Skin Off	PBDE 066		ng/g ww	ND	2.81	368

Station Code	Station	Common Name	Number InComp	TissueName	Prep Preservation Name	Analyte Name	Result	Unit Name	Result Qual Code	Lipid Pct	Avg Total Length
114RR8070	Russian River Downstream of Ukiah STP	Sacramento Sucker	5	fillet	Skin Off	PBDE 075		ng/g ww	ND	1.92	406
114RR8070	Russian River Downstream of Ukiah STP	Sacramento Pikeminnow	1	fillet	Skin Off	PBDE 075		ng/g ww	ND	2.81	368
114RR8070	Russian River Downstream of Ukiah STP	Sacramento Sucker	5	fillet	Skin Off	PBDE 099		ng/g ww	ND	1.92	406
114RR8070	Russian River Downstream of Ukiah STP	Sacramento Pikeminnow	1	fillet	Skin Off	PBDE 099		ng/g ww	ND	2.81	368
114RR8070	Russian River Downstream of Ukiah STP	Sacramento Sucker	5	fillet	Skin Off	PBDE 100	0.336	ng/g ww	=	1.92	406
114RR8070	Russian River Downstream of Ukiah STP	Sacramento Pikeminnow	1	fillet	Skin Off	PBDE 100	3.597	ng/g ww	=	2.81	368
114RR8070	Russian River Downstream of Ukiah STP	Sacramento Sucker	5	fillet	Skin Off	PBDE 153	0.037	ng/g ww	=	1.92	406
114RR8070	Russian River Downstream of Ukiah STP	Sacramento Pikeminnow	1	fillet	Skin Off	PBDE 153	0.034	ng/g ww	=	2.81	368
114RR8070	Russian River Downstream of Ukiah STP	Sacramento Sucker	5	fillet	Skin Off	PBDE 154	0.101	ng/g ww	=	1.92	406
114RR8070	Russian River Downstream of Ukiah STP	Sacramento Pikeminnow	1	fillet	Skin Off	PBDE 154	1.103	ng/g ww	=	2.81	368
114RR8070	Russian River Downstream of Ukiah STP	Sacramento Sucker	5	fillet	Skin Off	PBDE 155		ng/g ww	ND	1.92	406
114RR8070	Russian River Downstream of Ukiah STP	Sacramento Pikeminnow	1	fillet	Skin Off	PBDE 155	0.085	ng/g ww	=	2.81	368
114RR8070	Russian River Downstream of	Sacramento Sucker	5	fillet	Skin Off	PBDE 183		ng/g ww	ND	1.92	406

Station Code	Station	Common Name	Number InComp	TissueName	Prep Preservation Name	Analyte Name	Result	Unit Name	Result Qual Code	Lipid Pct	Avg Total Length
	Ukiah STP										
114RR8070	Russian River Downstream of Ukiah STP	Sacramento Pikeminnow	1	fillet	Skin Off	PBDE 183		ng/g ww	ND	2.81	368
114RR5568	Russian River Downstream of Cloverdale STP	Sacramento Sucker	5	fillet	Skin Off	PBDE 015		ng/g ww	ND	1.82	430
114RR5568	Russian River Downstream of Cloverdale STP	Sacramento Pikeminnow	5	fillet	Skin Off	PBDE 015		ng/g ww	ND	1.14	425
114RR5568	Russian River Downstream of Cloverdale STP	Sacramento Sucker	5	fillet	Skin Off	PBDE 028	0.122	ng/g ww	=	1.82	430
114RR5568	Russian River Downstream of Cloverdale STP	Sacramento Pikeminnow	5	fillet	Skin Off	PBDE 028		ng/g ww	ND	1.14	425
114RR5568	Russian River Downstream of Cloverdale STP	Sacramento Sucker	5	fillet	Skin Off	PBDE 033		ng/g ww	ND	1.82	430
114RR5568	Russian River Downstream of Cloverdale STP	Sacramento Pikeminnow	5	fillet	Skin Off	PBDE 033		ng/g ww	ND	1.14	425
114RR5568	Russian River Downstream of Cloverdale STP	Sacramento Sucker	5	fillet	Skin Off	PBDE 047	2.88	ng/g ww	=	1.82	430
114RR5568	Russian River Downstream of Cloverdale STP	Sacramento Pikeminnow	5	fillet	Skin Off	PBDE 047	0.662	ng/g ww	=	1.14	425
114RR5568	Russian River Downstream of Cloverdale STP	Sacramento Sucker	5	fillet	Skin Off	PBDE 049	0.067	ng/g ww	=	1.82	430
114RR5568	Russian River Downstream of	Sacramento	5	fillet	Skin Off	PBDE 049		ng/g ww	ND	1.14	425

Station Code	Station	Common Name	Number InComp	TissueName	Prep Preservation Name	Analyte Name	Result	Unit Name	Result Qual Code	Lipid Pct	Avg Total Length
	Cloverdale STP	Pikeminnow									
114RR5568	Russian River Downstream of Cloverdale STP	Sacramento Sucker	5	fillet	Skin Off	PBDE 066		ng/g ww	ND	1.82	430
114RR5568	Russian River Downstream of Cloverdale STP	Sacramento Pikeminnow	5	fillet	Skin Off	PBDE 066		ng/g ww	ND	1.14	425
114RR5568	Russian River Downstream of Cloverdale STP	Sacramento Sucker	5	fillet	Skin Off	PBDE 075		ng/g ww	ND	1.82	430
114RR5568	Russian River Downstream of Cloverdale STP	Sacramento Pikeminnow	5	fillet	Skin Off	PBDE 075		ng/g ww	ND	1.14	425
114RR5568	Russian River Downstream of Cloverdale STP	Sacramento Sucker	5	fillet	Skin Off	PBDE 099		ng/g ww	ND	1.82	430
114RR5568	Russian River Downstream of Cloverdale STP	Sacramento Pikeminnow	5	fillet	Skin Off	PBDE 099	0.271	ng/g ww	=	1.14	425
114RR5568	Russian River Downstream of Cloverdale STP	Sacramento Sucker	5	fillet	Skin Off	PBDE 100	0.443	ng/g ww	=	1.82	430
114RR5568	Russian River Downstream of Cloverdale STP	Sacramento Pikeminnow	5	fillet	Skin Off	PBDE 100	0.121	ng/g ww	=	1.14	425
114RR5568	Russian River Downstream of Cloverdale STP	Sacramento Sucker	5	fillet	Skin Off	PBDE 153	0.065	ng/g ww	=	1.82	430
114RR5568	Russian River Downstream of Cloverdale STP	Sacramento Pikeminnow	5	fillet	Skin Off	PBDE 153	0.062	ng/g ww	=	1.14	425
114RR5568	Russian River Downstream of Cloverdale	Sacramento Sucker	5	fillet	Skin Off	PBDE 154	0.171	ng/g ww	=	1.82	430

Station Code	Station	Common Name	Number InComp	TissueName	Prep Preservation Name	Analyte Name	Result	Unit Name	Result Qual Code	Lipid Pct	Avg Total Length
	STP										
114RR5568	Russian River Downstream of Cloverdale STP	Sacramento Pikeminnow	5	fillet	Skin Off	PBDE 154	0.054	ng/g ww	=	1.14	425
114RR5568	Russian River Downstream of Cloverdale STP	Sacramento Sucker	5	fillet	Skin Off	PBDE 155		ng/g ww	ND	1.82	430
114RR5568	Russian River Downstream of Cloverdale STP	Sacramento Pikeminnow	5	fillet	Skin Off	PBDE 155		ng/g ww	ND	1.14	425
114RR5568	Russian River Downstream of Cloverdale STP	Sacramento Sucker	5	fillet	Skin Off	PBDE 183		ng/g ww	ND	1.82	430
114RR5568	Russian River Downstream of Cloverdale STP	Sacramento Pikeminnow	5	fillet	Skin Off	PBDE 183		ng/g ww	ND	1.14	425
114RR2370	Russian River at Riverfront Park	Sacramento Sucker	5	fillet	Skin Off	PBDE 015		ng/g ww	ND	2.54	469
114RR2370	Russian River at Riverfront Park	Sacramento Pikeminnow	5	fillet	Skin Off	PBDE 015		ng/g ww	ND	0.67	343
114RR2370	Russian River at Riverfront Park	Sacramento Sucker	5	fillet	Skin Off	PBDE 028	0.12	ng/g ww	=	2.54	469
114RR2370	Russian River at Riverfront Park	Sacramento Pikeminnow	5	fillet	Skin Off	PBDE 028		ng/g ww	ND	0.67	343
114RR2370	Russian River at Riverfront Park	Sacramento Sucker	5	fillet	Skin Off	PBDE 033		ng/g ww	ND	2.54	469
114RR2370	Russian River at Riverfront Park	Sacramento Pikeminnow	5	fillet	Skin Off	PBDE 033		ng/g ww	ND	0.67	343

Station Code	Station	Common Name	Number InComp	TissueName	Prep Preservation Name	Analyte Name	Result	Unit Name	Result Qual Code	Lipid Pct	Avg Total Length
114RR2370	Russian River at Riverfront Park	Sacramento Sucker	5	fillet	Skin Off	PBDE 047	1.97	ng/g ww	=	2.54	469
114RR2370	Russian River at Riverfront Park	Sacramento Pikeminnow	5	fillet	Skin Off	PBDE 047	1.05	ng/g ww	=	0.67	343
114RR2370	Russian River at Riverfront Park	Sacramento Sucker	5	fillet	Skin Off	PBDE 049	0.058	ng/g ww	=	2.54	469
114RR2370	Russian River at Riverfront Park	Sacramento Pikeminnow	5	fillet	Skin Off	PBDE 049	0.054	ng/g ww	=	0.67	343
114RR2370	Russian River at Riverfront Park	Sacramento Sucker	5	fillet	Skin Off	PBDE 066		ng/g ww	ND	2.54	469
114RR2370	Russian River at Riverfront Park	Sacramento Pikeminnow	5	fillet	Skin Off	PBDE 066		ng/g ww	ND	0.67	343
114RR2370	Russian River at Riverfront Park	Sacramento Sucker	5	fillet	Skin Off	PBDE 075		ng/g ww	ND	2.54	469
114RR2370	Russian River at Riverfront Park	Sacramento Pikeminnow	5	fillet	Skin Off	PBDE 075		ng/g ww	ND	0.67	343
114RR2370	Russian River at Riverfront Park	Sacramento Sucker	5	fillet	Skin Off	PBDE 099		ng/g ww	ND	2.54	469
114RR2370	Russian River at Riverfront Park	Sacramento Pikeminnow	5	fillet	Skin Off	PBDE 099		ng/g ww	ND	0.67	343
114RR2370	Russian River at Riverfront Park	Sacramento Sucker	5	fillet	Skin Off	PBDE 100	0.35	ng/g ww	=	2.54	469
114RR2370	Russian River at Riverfront Park	Sacramento Pikeminnow	5	fillet	Skin Off	PBDE 100	0.319	ng/g ww	=	0.67	343
114RR2370	Russian River at Riverfront	Sacramento Sucker	5	fillet	Skin Off	PBDE 153	0.031	ng/g ww	=	2.54	469

Station Code	Station	Common Name	Number InComp	TissueName	Prep Preservation Name	Analyte Name	Result	Unit Name	Result Qual Code	Lipid Pct	Avg Total Length
	Park										
114RR2370	Russian River at Riverfront Park	Sacramento Pikeminnow	5	fillet	Skin Off	PBDE 153		ng/g ww	ND	0.67	343
114RR2370	Russian River at Riverfront Park	Sacramento Sucker	5	fillet	Skin Off	PBDE 154	0.103	ng/g ww	=	2.54	469
114RR2370	Russian River at Riverfront Park	Sacramento Pikeminnow	5	fillet	Skin Off	PBDE 154	0.115	ng/g ww	=	0.67	343
114RR2370	Russian River at Riverfront Park	Sacramento Sucker	5	fillet	Skin Off	PBDE 155		ng/g ww	ND	2.54	469
114RR2370	Russian River at Riverfront Park	Sacramento Pikeminnow	5	fillet	Skin Off	PBDE 155		ng/g ww	ND	0.67	343
114RR2370	Russian River at Riverfront Park	Sacramento Sucker	5	fillet	Skin Off	PBDE 183		ng/g ww	ND	2.54	469
114RR2370	Russian River at Riverfront Park	Sacramento Pikeminnow	5	fillet	Skin Off	PBDE 183		ng/g ww	ND	0.67	343
114RR1325	Russian River at Johnson's Beach	Sacramento Sucker	5	fillet	Skin Off	PBDE 015		ng/g ww	ND	2.03	422
114RR1325	Russian River at Johnson's Beach	Sacramento Pikeminnow	5	fillet	Skin Off	PBDE 015		ng/g ww	ND	1.56	379
114RR1325	Russian River at Johnson's Beach	Sacramento Sucker	5	fillet	Skin Off	PBDE 028	0.145	ng/g ww	=	2.03	422
114RR1325	Russian River at Johnson's Beach	Sacramento Pikeminnow	5	fillet	Skin Off	PBDE 028	0.165	ng/g ww	=	1.56	379
114RR1325	Russian River at Johnson's Beach	Sacramento Sucker	5	fillet	Skin Off	PBDE 033		ng/g ww	ND	2.03	422

Station Code	Station	Common Name	Number InComp	TissueName	Prep Preservation Name	Analyte Name	Result	Unit Name	Result Qual Code	Lipid Pct	Avg Total Length
114RR1325	Russian River at Johnson's Beach	Sacramento Pikeminnow	5	fillet	Skin Off	PBDE 033		ng/g ww	ND	1.56	379
114RR1325	Russian River at Johnson's Beach	Sacramento Sucker	5	fillet	Skin Off	PBDE 047	2.03	ng/g ww	=	2.03	422
114RR1325	Russian River at Johnson's Beach	Sacramento Pikeminnow	5	fillet	Skin Off	PBDE 047	4.89	ng/g ww	=	1.56	379
114RR1325	Russian River at Johnson's Beach	Sacramento Sucker	5	fillet	Skin Off	PBDE 049	0.076	ng/g ww	=	2.03	422
114RR1325	Russian River at Johnson's Beach	Sacramento Pikeminnow	5	fillet	Skin Off	PBDE 049	0.227	ng/g ww	=	1.56	379
114RR1325	Russian River at Johnson's Beach	Sacramento Sucker	5	fillet	Skin Off	PBDE 066		ng/g ww	ND	2.03	422
114RR1325	Russian River at Johnson's Beach	Sacramento Pikeminnow	5	fillet	Skin Off	PBDE 066		ng/g ww	ND	1.56	379
114RR1325	Russian River at Johnson's Beach	Sacramento Sucker	5	fillet	Skin Off	PBDE 075		ng/g ww	ND	2.03	422
114RR1325	Russian River at Johnson's Beach	Sacramento Pikeminnow	5	fillet	Skin Off	PBDE 075		ng/g ww	ND	1.56	379
114RR1325	Russian River at Johnson's Beach	Sacramento Sucker	5	fillet	Skin Off	PBDE 099		ng/g ww	ND	2.03	422
114RR1325	Russian River at Johnson's Beach	Sacramento Pikeminnow	5	fillet	Skin Off	PBDE 099		ng/g ww	ND	1.56	379
114RR1325	Russian River at Johnson's Beach	Sacramento Sucker	5	fillet	Skin Off	PBDE 100	0.393	ng/g ww	=	2.03	422
114RR1325	Russian River at Johnson's	Sacramento	5	fillet	Skin Off	PBDE 100	0.79	ng/g ww	=	1.56	379

Station Code	Station	Common Name	Number InComp	TissueName	Prep Preservation Name	Analyte Name	Result	Unit Name	Result Qual Code	Lipid Pct	Avg Total Length
	Beach	Pikeminnow									
114RR1325	Russian River at Johnson's Beach	Sacramento Sucker	5	fillet	Skin Off	PBDE 153	0.03	ng/g ww	=	2.03	422
114RR1325	Russian River at Johnson's Beach	Sacramento Pikeminnow	5	fillet	Skin Off	PBDE 153	0.018	ng/g ww	=	1.56	379
114RR1325	Russian River at Johnson's Beach	Sacramento Sucker	5	fillet	Skin Off	PBDE 154	0.118	ng/g ww	=	2.03	422
114RR1325	Russian River at Johnson's Beach	Sacramento Pikeminnow	5	fillet	Skin Off	PBDE 154	0.273	ng/g ww	=	1.56	379
114RR1325	Russian River at Johnson's Beach	Sacramento Sucker	5	fillet	Skin Off	PBDE 155		ng/g ww	ND	2.03	422
114RR1325	Russian River at Johnson's Beach	Sacramento Pikeminnow	5	fillet	Skin Off	PBDE 155	0.023	ng/g ww	=	1.56	379
114RR1325	Russian River at Johnson's Beach	Sacramento Sucker	5	fillet	Skin Off	PBDE 183		ng/g ww	ND	2.03	422
114RR1325	Russian River at Johnson's Beach	Sacramento Pikeminnow	5	fillet	Skin Off	PBDE 183		ng/g ww	ND	1.56	379
114RR0898	Russian River at Monte Rio Beach	Largemouth Bass	5	fillet	Skin Off	PBDE 015		ng/g ww	ND	0.47	334
114RR0898	Russian River at Monte Rio Beach	Sacramento Sucker	5	fillet	Skin Off	PBDE 015		ng/g ww	ND	2.01	430
114RR0898	Russian River at Monte Rio Beach	Sacramento Pikeminnow	5	fillet	Skin Off	PBDE 015		ng/g ww	ND	2.57	398
114RR0898	Russian River at Monte Rio Beach	Largemouth Bass	5	fillet	Skin Off	PBDE 028		ng/g ww	ND	0.47	334

Station Code	Station	Common Name	Number InComp	TissueName	Prep Preservation Name	Analyte Name	Result	Unit Name	Result Qual Code	Lipid Pct	Avg Total Length
114RR0898	Russian River at Monte Rio Beach	Sacramento Sucker	5	fillet	Skin Off	PBDE 028	0.244	ng/g ww	=	2.01	430
114RR0898	Russian River at Monte Rio Beach	Sacramento Pikeminnow	5	fillet	Skin Off	PBDE 028	0.205	ng/g ww	=	2.57	398
114RR0898	Russian River at Monte Rio Beach	Largemouth Bass	5	fillet	Skin Off	PBDE 033		ng/g ww	ND	0.47	334
114RR0898	Russian River at Monte Rio Beach	Sacramento Sucker	5	fillet	Skin Off	PBDE 033		ng/g ww	ND	2.01	430
114RR0898	Russian River at Monte Rio Beach	Sacramento Pikeminnow	5	fillet	Skin Off	PBDE 033		ng/g ww	ND	2.57	398
114RR0898	Russian River at Monte Rio Beach	Largemouth Bass	5	fillet	Skin Off	PBDE 047	0.535	ng/g ww	=	0.47	334
114RR0898	Russian River at Monte Rio Beach	Sacramento Sucker	5	fillet	Skin Off	PBDE 047	3.32	ng/g ww	=	2.01	430
114RR0898	Russian River at Monte Rio Beach	Sacramento Pikeminnow	5	fillet	Skin Off	PBDE 047	6.18	ng/g ww	=	2.57	398
114RR0898	Russian River at Monte Rio Beach	Largemouth Bass	5	fillet	Skin Off	PBDE 049		ng/g ww	ND	0.47	334
114RR0898	Russian River at Monte Rio Beach	Sacramento Sucker	5	fillet	Skin Off	PBDE 049	0.143	ng/g ww	=	2.01	430
114RR0898	Russian River at Monte Rio Beach	Sacramento Pikeminnow	5	fillet	Skin Off	PBDE 049	0.319	ng/g ww	=	2.57	398
114RR0898	Russian River at Monte Rio Beach	Largemouth Bass	5	fillet	Skin Off	PBDE 066		ng/g ww	ND	0.47	334
114RR0898	Russian River at Monte Rio Beach	Sacramento Sucker	5	fillet	Skin Off	PBDE 066		ng/g ww	ND	2.01	430

Station Code	Station	Common Name	Number InComp	TissueName	Prep Preservation Name	Analyte Name	Result	Unit Name	Result Qual Code	Lipid Pct	Avg Total Length
114RR0898	Russian River at Monte Rio Beach	Sacramento Pikeminnow	5	fillet	Skin Off	PBDE 066		ng/g ww	ND	2.57	398
114RR0898	Russian River at Monte Rio Beach	Largemouth Bass	5	fillet	Skin Off	PBDE 075		ng/g ww	ND	0.47	334
114RR0898	Russian River at Monte Rio Beach	Sacramento Sucker	5	fillet	Skin Off	PBDE 075		ng/g ww	ND	2.01	430
114RR0898	Russian River at Monte Rio Beach	Sacramento Pikeminnow	5	fillet	Skin Off	PBDE 075		ng/g ww	ND	2.57	398
114RR0898	Russian River at Monte Rio Beach	Largemouth Bass	5	fillet	Skin Off	PBDE 099	0.122	ng/g ww	=	0.47	334
114RR0898	Russian River at Monte Rio Beach	Sacramento Sucker	5	fillet	Skin Off	PBDE 099	0.05	ng/g ww	=	2.01	430
114RR0898	Russian River at Monte Rio Beach	Sacramento Pikeminnow	5	fillet	Skin Off	PBDE 099		ng/g ww	ND	2.57	398
114RR0898	Russian River at Monte Rio Beach	Largemouth Bass	5	fillet	Skin Off	PBDE 100	0.102	ng/g ww	=	0.47	334
114RR0898	Russian River at Monte Rio Beach	Sacramento Sucker	5	fillet	Skin Off	PBDE 100	0.694	ng/g ww	=	2.01	430
114RR0898	Russian River at Monte Rio Beach	Sacramento Pikeminnow	5	fillet	Skin Off	PBDE 100	0.961	ng/g ww	=	2.57	398
114RR0898	Russian River at Monte Rio Beach	Largemouth Bass	5	fillet	Skin Off	PBDE 153	0.035	ng/g ww	=	0.47	334
114RR0898	Russian River at Monte Rio Beach	Sacramento Sucker	5	fillet	Skin Off	PBDE 153	0.047	ng/g ww	=	2.01	430
114RR0898	Russian River at Monte Rio Beach	Sacramento Pikeminnow	5	fillet	Skin Off	PBDE 153	0.034	ng/g ww	=	2.57	398

Station Code	Station	Common Name	Number InComp	TissueName	Prep Preservation Name	Analyte Name	Result	Unit Name	Result Qual Code	Lipid Pct	Avg Total Length
114RR0898	Russian River at Monte Rio Beach	Largemouth Bass	5	fillet	Skin Off	PBDE 154	0.031	ng/g ww	=	0.47	334
114RR0898	Russian River at Monte Rio Beach	Sacramento Sucker	5	fillet	Skin Off	PBDE 154	0.186	ng/g ww	=	2.01	430
114RR0898	Russian River at Monte Rio Beach	Sacramento Pikeminnow	5	fillet	Skin Off	PBDE 154	0.294	ng/g ww	=	2.57	398
114RR0898	Russian River at Monte Rio Beach	Largemouth Bass	5	fillet	Skin Off	PBDE 155		ng/g ww	ND	0.47	334
114RR0898	Russian River at Monte Rio Beach	Sacramento Sucker	5	fillet	Skin Off	PBDE 155	0.022	ng/g ww	=	2.01	430
114RR0898	Russian River at Monte Rio Beach	Sacramento Pikeminnow	5	fillet	Skin Off	PBDE 155		ng/g ww	ND	2.57	398
114RR0898	Russian River at Monte Rio Beach	Largemouth Bass	5	fillet	Skin Off	PBDE 183		ng/g ww	ND	0.47	334
114RR0898	Russian River at Monte Rio Beach	Sacramento Sucker	5	fillet	Skin Off	PBDE 183		ng/g ww	ND	2.01	430
114RR0898	Russian River at Monte Rio Beach	Sacramento Pikeminnow	5	fillet	Skin Off	PBDE 183		ng/g ww	ND	2.57	398
114PSP009	Spring Lake	Redear Sunfish	8	fillet	Skin Off	PBDE 015		ng/g ww	ND	0.42	177
114PSP009	Spring Lake	Redear Sunfish	8	fillet	Skin Off	PBDE 028		ng/g ww	ND	0.42	177
114PSP009	Spring Lake	Redear Sunfish	8	fillet	Skin Off	PBDE 033		ng/g ww	ND	0.42	177
114PSP009	Spring Lake	Redear Sunfish	8	fillet	Skin Off	PBDE 047	0.079	ng/g ww	=	0.42	177
114PSP009	Spring Lake	Redear Sunfish	8	fillet	Skin Off	PBDE 049		ng/g ww	ND	0.42	177
114PSP009	Spring Lake	Redear Sunfish	8	fillet	Skin Off	PBDE 066		ng/g ww	ND	0.42	177

Station Code	Station	Common Name	Number InComp	TissueName	Prep Preservation Name	Analyte Name	Result	Unit Name	Result Qual Code	Lipid Pct	Avg Total Length
114PSP009	Spring Lake	Redear Sunfish	8	fillet	Skin Off	PBDE 075		ng/g ww	ND	0.42	177
114PSP009	Spring Lake	Redear Sunfish	8	fillet	Skin Off	PBDE 099		ng/g ww	ND	0.42	177
114PSP009	Spring Lake	Redear Sunfish	8	fillet	Skin Off	PBDE 100		ng/g ww	ND	0.42	177
114PSP009	Spring Lake	Redear Sunfish	8	fillet	Skin Off	PBDE 153		ng/g ww	ND	0.42	177
114PSP009	Spring Lake	Redear Sunfish	8	fillet	Skin Off	PBDE 154		ng/g ww	ND	0.42	177
114PSP009	Spring Lake	Redear Sunfish	8	fillet	Skin Off	PBDE 155		ng/g ww	ND	0.42	177
114PSP009	Spring Lake	Redear Sunfish	8	fillet	Skin Off	PBDE 183		ng/g ww	ND	0.42	177

Station Code	Station	Common Name	Number InComp	TissueName	Prep Preservation Name	Analyte Name	Result	Unit Name	Result Qual Code	Lipid Pct	Avg Total Length
114RR8070	Russian River Downstream of Ukiah STP	Sacramento Sucker	5	fillet	Skin Off	Perfluorobutanesulfonate	0.00	ng/g ww	ND	1.92	406
114RR8070	Russian River Downstream of Ukiah STP	Sacramento Pikeminnow	1	fillet	Skin Off	Perfluorobutanesulfonate	0.00	ng/g ww	ND	2.81	368
114RR8070	Russian River Downstream of Ukiah STP	Sacramento Sucker	5	fillet	Skin Off	Perfluorobutanoate	0.00	ng/g ww	ND	1.92	406
114RR8070	Russian River Downstream of Ukiah STP	Sacramento Pikeminnow	1	fillet	Skin Off	Perfluorobutanoate	0.00	ng/g ww	ND	2.81	368
114RR8070	Russian River Downstream of Ukiah STP	Sacramento Sucker	5	fillet	Skin Off	Perfluorodecanoate	0.00	ng/g ww	ND	1.92	406
114RR8070	Russian River Downstream of Ukiah STP	Sacramento Pikeminnow	1	fillet	Skin Off	Perfluorodecanoate	0.78	ng/g ww		2.81	368
114RR8070	Russian River Downstream of Ukiah STP	Sacramento Sucker	5	fillet	Skin Off	Perfluorododecanoate	0.00	ng/g ww	ND	1.92	406
114RR8070	Russian River Downstream of Ukiah STP	Sacramento Pikeminnow	1	fillet	Skin Off	Perfluorododecanoate	0.00	ng/g ww	ND	2.81	368
114RR8070	Russian River Downstream of Ukiah STP	Sacramento Sucker	5	fillet	Skin Off	Perfluoroheptanoate	0.00	ng/g ww	ND	1.92	406
114RR8070	Russian River Downstream of Ukiah STP	Sacramento Pikeminnow	1	fillet	Skin Off	Perfluoroheptanoate	0.00	ng/g ww	ND	2.81	368
114RR8070	Russian River Downstream of Ukiah STP	Sacramento Sucker	5	fillet	Skin Off	Perfluorohexanesulfonate	0.00	ng/g ww	ND	1.92	406
114RR8070	Russian River Downstream of Ukiah STP	Sacramento Pikeminnow	1	fillet	Skin Off	Perfluorohexanesulfonate	0.00	ng/g ww	ND	2.81	368
114RR8070	Russian River Downstream of Ukiah STP	Sacramento Sucker	5	fillet	Skin Off	Perfluorohexanoate	0.00	ng/g ww	ND	1.92	406

Station Code	Station	Common Name	Number InComp	TissueName	Prep Preservation Name	Analyte Name	Result	Unit Name	Result Qual Code	Lipid Pct	Avg Total Length
114RR8070	Russian River Downstream of Ukiah STP	Sacramento Pikeminnow	1	fillet	Skin Off	Perfluorohexanoate	0.00	ng/g ww	ND	2.81	368
114RR8070	Russian River Downstream of Ukiah STP	Sacramento Sucker	5	fillet	Skin Off	Perfluorononanoate	0.00	ng/g ww	ND	1.92	406
114RR8070	Russian River Downstream of Ukiah STP	Sacramento Pikeminnow	1	fillet	Skin Off	Perfluorononanoate	0.00	ng/g ww	ND	2.81	368
114RR8070	Russian River Downstream of Ukiah STP	Sacramento Sucker	5	fillet	Skin Off	Perfluorooctanesulfonamide	0.00	ng/g ww	ND	1.92	406
114RR8070	Russian River Downstream of Ukiah STP	Sacramento Pikeminnow	1	fillet	Skin Off	Perfluorooctanesulfonamide	0.00	ng/g ww	ND	2.81	368
114RR8070	Russian River Downstream of Ukiah STP	Sacramento Sucker	5	fillet	Skin Off	Perfluorooctanesulfonate	1.53	ng/g ww		1.92	406
114RR8070	Russian River Downstream of Ukiah STP	Sacramento Pikeminnow	1	fillet	Skin Off	Perfluorooctanesulfonate	3.80	ng/g ww		2.81	368
114RR8070	Russian River Downstream of Ukiah STP	Sacramento Sucker	5	fillet	Skin Off	Perfluorooctanoate	0.00	ng/g ww	ND	1.92	406
114RR8070	Russian River Downstream of Ukiah STP	Sacramento Pikeminnow	1	fillet	Skin Off	Perfluorooctanoate	0.00	ng/g ww	ND	2.81	368
114RR8070	Russian River Downstream of Ukiah STP	Sacramento Sucker	5	fillet	Skin Off	Perfluoropentanoate	0.00	ng/g ww	ND	1.92	406
114RR8070	Russian River Downstream of Ukiah STP	Sacramento Pikeminnow	1	fillet	Skin Off	Perfluoropentanoate	0.00	ng/g ww	ND	2.81	368
114RR8070	Russian River Downstream of Ukiah STP	Sacramento Sucker	5	fillet	Skin Off	Perfluoroundecanoate	0.00	ng/g ww	ND	1.92	406
114RR8070	Russian River Downstream of Ukiah STP	Sacramento Pikeminnow	1	fillet	Skin Off	Perfluoroundecanoate	0.50	ng/g ww		2.81	368

Station Code	Station	Common Name	Number InComp	TissueName	Prep Preservation Name	Analyte Name	Result	Unit Name	Result Qual Code	Lipid Pct	Avg Total Length
114RR5568	Russian River Downstream of Cloverdale STP	Sacramento Sucker	5	fillet	Skin Off	Perfluorobutanesulfonate	0.00	ng/g ww	ND	1.82	430
114RR5568	Russian River Downstream of Cloverdale STP	Smallmouth Bass	5	fillet	Skin Off	Perfluorobutanesulfonate	0.00	ng/g ww	ND	0.67	343
114RR5568	Russian River Downstream of Cloverdale STP	Sacramento Pikeminnow	5	fillet	Skin Off	Perfluorobutanesulfonate	0.00	ng/g ww	ND	1.14	425
114RR5568	Russian River Downstream of Cloverdale STP	Sacramento Sucker	5	fillet	Skin Off	Perfluorobutanoate	0.00	ng/g ww	ND	1.82	430
114RR5568	Russian River Downstream of Cloverdale STP	Smallmouth Bass	5	fillet	Skin Off	Perfluorobutanoate	0.00	ng/g ww	ND	0.67	343
114RR5568	Russian River Downstream of Cloverdale STP	Sacramento Pikeminnow	5	fillet	Skin Off	Perfluorobutanoate	0.00	ng/g ww	ND	1.14	425
114RR5568	Russian River Downstream of Cloverdale STP	Sacramento Sucker	5	fillet	Skin Off	Perfluorodecanoate	0.00	ng/g ww	ND	1.82	430
114RR5568	Russian River Downstream of Cloverdale STP	Smallmouth Bass	5	fillet	Skin Off	Perfluorodecanoate	0.96	ng/g ww		0.67	343
114RR5568	Russian River Downstream of Cloverdale STP	Sacramento Pikeminnow	5	fillet	Skin Off	Perfluorodecanoate	0.00	ng/g ww	ND	1.14	425
114RR5568	Russian River Downstream of Cloverdale STP	Sacramento Sucker	5	fillet	Skin Off	Perfluorododecanoate	0.00	ng/g ww	ND	1.82	430
114RR5568	Russian River Downstream of Cloverdale STP	Smallmouth Bass	5	fillet	Skin Off	Perfluorododecanoate	0.00	ng/g ww	ND	0.67	343
114RR5568	Russian River Downstream of Cloverdale STP	Sacramento Pikeminnow	5	fillet	Skin Off	Perfluorododecanoate	0.00	ng/g ww	ND	1.14	425
114RR5568	Russian River Downstream of Cloverdale STP	Sacramento Sucker	5	fillet	Skin Off	Perfluoroheptanoate	0.00	ng/g ww	ND	1.82	430
114RR5568	Russian River Downstream of Cloverdale STP	Smallmouth Bass	5	fillet	Skin Off	Perfluoroheptanoate	0.00	ng/g ww	ND	0.67	343

Station Code	Station	Common Name	Number InComp	TissueName	Prep Preservation Name	Analyte Name	Result	Unit Name	Result Qual Code	Lipid Pct	Avg Total Length
114RR5568	Russian River Downstream of Cloverdale STP	Sacramento Pikeminnow	5	fillet	Skin Off	Perfluoroheptanoate	0.00	ng/g ww	ND	1.14	425
114RR5568	Russian River Downstream of Cloverdale STP	Sacramento Sucker	5	fillet	Skin Off	Perfluorohexanesulfonate	0.00	ng/g ww	ND	1.82	430
114RR5568	Russian River Downstream of Cloverdale STP	Smallmouth Bass	5	fillet	Skin Off	Perfluorohexanesulfonate	0.00	ng/g ww	ND	0.67	343
114RR5568	Russian River Downstream of Cloverdale STP	Sacramento Pikeminnow	5	fillet	Skin Off	Perfluorohexanesulfonate	0.00	ng/g ww	ND	1.14	425
114RR5568	Russian River Downstream of Cloverdale STP	Sacramento Sucker	5	fillet	Skin Off	Perfluorohexanoate	0.00	ng/g ww	ND	1.82	430
114RR5568	Russian River Downstream of Cloverdale STP	Smallmouth Bass	5	fillet	Skin Off	Perfluorohexanoate	0.00	ng/g ww	ND	0.67	343
114RR5568	Russian River Downstream of Cloverdale STP	Sacramento Pikeminnow	5	fillet	Skin Off	Perfluorohexanoate	0.00	ng/g ww	ND	1.14	425
114RR5568	Russian River Downstream of Cloverdale STP	Sacramento Sucker	5	fillet	Skin Off	Perfluorononanoate	0.00	ng/g ww	ND	1.82	430
114RR5568	Russian River Downstream of Cloverdale STP	Smallmouth Bass	5	fillet	Skin Off	Perfluorononanoate	0.00	ng/g ww	ND	0.67	343
114RR5568	Russian River Downstream of Cloverdale STP	Sacramento Pikeminnow	5	fillet	Skin Off	Perfluorononanoate	0.00	ng/g ww	ND	1.14	425
114RR5568	Russian River Downstream of Cloverdale STP	Sacramento Sucker	5	fillet	Skin Off	Perfluorooctanesulfonamide	0.00	ng/g ww	ND	1.82	430
114RR5568	Russian River Downstream of Cloverdale STP	Smallmouth Bass	5	fillet	Skin Off	Perfluorooctanesulfonamide	0.00	ng/g ww	ND	0.67	343
114RR5568	Russian River Downstream of Cloverdale STP	Sacramento Pikeminnow	5	fillet	Skin Off	Perfluorooctanesulfonamide	0.00	ng/g ww	ND	1.14	425
114RR5568	Russian River Downstream of	Sacramento Sucker	5	fillet	Skin Off	Perfluorooctanesulfo	2.60	ng/g ww		1.82	430

Station Code	Station	Common Name	Number InComp	TissueName	Prep Preservation Name	Analyte Name	Result	Unit Name	Result Qual Code	Lipid Pct	Avg Total Length
	Cloverdale STP					nate					
114RR5568	Russian River Downstream of Cloverdale STP	Smallmouth Bass	5	fillet	Skin Off	Perfluorooctanesulfonate	7.09	ng/g ww		0.67	343
114RR5568	Russian River Downstream of Cloverdale STP	Sacramento Pikeminnow	5	fillet	Skin Off	Perfluorooctanesulfonate	1.73	ng/g ww		1.14	425
114RR5568	Russian River Downstream of Cloverdale STP	Sacramento Sucker	5	fillet	Skin Off	Perfluorooctanoate	0.00	ng/g ww	ND	1.82	430
114RR5568	Russian River Downstream of Cloverdale STP	Smallmouth Bass	5	fillet	Skin Off	Perfluorooctanoate	0.00	ng/g ww	ND	0.67	343
114RR5568	Russian River Downstream of Cloverdale STP	Sacramento Pikeminnow	5	fillet	Skin Off	Perfluorooctanoate	0.00	ng/g ww	ND	1.14	425
114RR5568	Russian River Downstream of Cloverdale STP	Sacramento Sucker	5	fillet	Skin Off	Perfluoropentanoate	0.00	ng/g ww	ND	1.82	430
114RR5568	Russian River Downstream of Cloverdale STP	Smallmouth Bass	5	fillet	Skin Off	Perfluoropentanoate	0.00	ng/g ww	ND	0.67	343
114RR5568	Russian River Downstream of Cloverdale STP	Sacramento Pikeminnow	5	fillet	Skin Off	Perfluoropentanoate	0.00	ng/g ww	ND	1.14	425
114RR5568	Russian River Downstream of Cloverdale STP	Sacramento Sucker	5	fillet	Skin Off	Perfluoroundecanoate	0.00	ng/g ww	ND	1.82	430
114RR5568	Russian River Downstream of Cloverdale STP	Smallmouth Bass	5	fillet	Skin Off	Perfluoroundecanoate	0.00	ng/g ww	ND	0.67	343
114RR5568	Russian River Downstream of Cloverdale STP	Sacramento Pikeminnow	5	fillet	Skin Off	Perfluoroundecanoate	0.00	ng/g ww	ND	1.14	425
114RR2370	Russian River at Riverfront Park	Sacramento Sucker	5	fillet	Skin Off	Perfluorobutanesulfonate	0.00	ng/g ww	ND	2.54	469
114RR2370	Russian River at Riverfront Park	Sacramento Pikeminnow	5	fillet	Skin Off	Perfluorobutanesulfonate	0.00	ng/g ww	ND	1.09	438

Station Code	Station	Common Name	Number InComp	TissueName	Prep Preservation Name	Analyte Name	Result	Unit Name	Result Qual Code	Lipid Pct	Avg Total Length
114RR2370	Russian River at Riverfront Park	Sacramento Sucker	5	fillet	Skin Off	Perfluorobutanoate	0.00	ng/g ww	ND	2.54	469
114RR2370	Russian River at Riverfront Park	Sacramento Pikeminnow	5	fillet	Skin Off	Perfluorobutanoate	0.00	ng/g ww	ND	1.09	438
114RR2370	Russian River at Riverfront Park	Sacramento Sucker	5	fillet	Skin Off	Perfluorodecanoate	0.00	ng/g ww	ND	2.54	469
114RR2370	Russian River at Riverfront Park	Sacramento Pikeminnow	5	fillet	Skin Off	Perfluorodecanoate	0.00	ng/g ww	ND	1.09	438
114RR2370	Russian River at Riverfront Park	Sacramento Sucker	5	fillet	Skin Off	Perfluorododecanoate	0.00	ng/g ww	ND	2.54	469
114RR2370	Russian River at Riverfront Park	Sacramento Pikeminnow	5	fillet	Skin Off	Perfluorododecanoate	0.00	ng/g ww	ND	1.09	438
114RR2370	Russian River at Riverfront Park	Sacramento Sucker	5	fillet	Skin Off	Perfluoroheptanoate	0.00	ng/g ww	ND	2.54	469
114RR2370	Russian River at Riverfront Park	Sacramento Pikeminnow	5	fillet	Skin Off	Perfluoroheptanoate	0.00	ng/g ww	ND	1.09	438
114RR2370	Russian River at Riverfront Park	Sacramento Sucker	5	fillet	Skin Off	Perfluorohexanesulfonate	0.00	ng/g ww	ND	2.54	469
114RR2370	Russian River at Riverfront Park	Sacramento Pikeminnow	5	fillet	Skin Off	Perfluorohexanesulfonate	0.00	ng/g ww	ND	1.09	438
114RR2370	Russian River at Riverfront Park	Sacramento Sucker	5	fillet	Skin Off	Perfluorohexanoate	0.00	ng/g ww	ND	2.54	469
114RR2370	Russian River at Riverfront Park	Sacramento Pikeminnow	5	fillet	Skin Off	Perfluorohexanoate	0.00	ng/g ww	ND	1.09	438
114RR2370	Russian River at Riverfront Park	Sacramento Sucker	5	fillet	Skin Off	Perfluorooctanesulfonamide	0.00	ng/g ww	ND	2.54	469

Station Code	Station	Common Name	Number InComp	TissueName	Prep Preservation Name	Analyte Name	Result	Unit Name	Result Qual Code	Lipid Pct	Avg Total Length
114RR2370	Russian River at Riverfront Park	Sacramento Pikeminnow	5	fillet	Skin Off	Perfluorooctanesulfonamide	0.00	ng/g ww	ND	1.09	438
114RR2370	Russian River at Riverfront Park	Sacramento Sucker	5	fillet	Skin Off	Perfluorooctanoate	0.00	ng/g ww	ND	2.54	469
114RR2370	Russian River at Riverfront Park	Sacramento Pikeminnow	5	fillet	Skin Off	Perfluorooctanoate	0.00	ng/g ww	ND	1.09	438
114RR2370	Russian River at Riverfront Park	Sacramento Sucker	5	fillet	Skin Off	Perfluoropentanoate	0.00	ng/g ww	ND	2.54	469
114RR2370	Russian River at Riverfront Park	Sacramento Pikeminnow	5	fillet	Skin Off	Perfluoropentanoate	0.00	ng/g ww	ND	1.09	438
114RR1325	Russian River at Johnson's Beach	Sacramento Sucker	5	fillet	Skin Off	Perfluorobutanesulfonate	0.00	ng/g ww	ND	2.03	422
114RR1325	Russian River at Johnson's Beach	Sacramento Pikeminnow	5	fillet	Skin Off	Perfluorobutanesulfonate	0.00	ng/g ww	ND	1.56	379
114RR0898	Russian River at Monte Rio Beach	Largemouth Bass	5	fillet	Skin Off	Perfluorobutanesulfonate	0.00	ng/g ww	ND	0.47	334
114RR0898	Russian River at Monte Rio Beach	Sacramento Sucker	5	fillet	Skin Off	Perfluorobutanesulfonate	0.00	ng/g ww	ND	2.01	430
114RR0898	Russian River at Monte Rio Beach	Sacramento Pikeminnow	5	fillet	Skin Off	Perfluorobutanesulfonate	0.00	ng/g ww	ND	2.57	398
114RR2370	Russian River at Riverfront Park	Sacramento Sucker	5	fillet	Skin Off	Perfluorononanoate	0.00	ng/g ww	ND	2.54	469
114RR2370	Russian River at Riverfront Park	Sacramento Pikeminnow	5	fillet	Skin Off	Perfluorononanoate	0.00	ng/g ww	ND	1.09	438
114RR2370	Russian River at Riverfront Park	Sacramento Sucker	5	fillet	Skin Off	Perfluorooctanesulfonate	3.00	ng/g ww		2.54	469

Station Code	Station	Common Name	Number InComp	TissueName	Prep Preservation Name	Analyte Name	Result	Unit Name	Result Qual Code	Lipid Pct	Avg Total Length
114RR2370	Russian River at Riverfront Park	Sacramento Pikeminnow	5	fillet	Skin Off	Perfluorooctanesulfonate	1.00	ng/g ww		1.09	438
114RR2370	Russian River at Riverfront Park	Sacramento Sucker	5	fillet	Skin Off	Perfluoroundecanoate	0.00	ng/g ww	ND	2.54	469
114RR2370	Russian River at Riverfront Park	Sacramento Pikeminnow	5	fillet	Skin Off	Perfluoroundecanoate	0.00	ng/g ww	ND	1.09	438
114RR1325	Russian River at Johnson's Beach	Sacramento Sucker	5	fillet	Skin Off	Perfluorobutanoate	0.00	ng/g ww	ND	2.03	422
114RR1325	Russian River at Johnson's Beach	Sacramento Pikeminnow	5	fillet	Skin Off	Perfluorobutanoate	0.00	ng/g ww	ND	1.56	379
114RR1325	Russian River at Johnson's Beach	Sacramento Sucker	5	fillet	Skin Off	Perfluorodecanoate	0.79	ng/g ww		2.03	422
114RR1325	Russian River at Johnson's Beach	Sacramento Pikeminnow	5	fillet	Skin Off	Perfluorodecanoate	0.75	ng/g ww		1.56	379
114RR1325	Russian River at Johnson's Beach	Sacramento Sucker	5	fillet	Skin Off	Perfluorododecanoate	0.00	ng/g ww	ND	2.03	422
114RR1325	Russian River at Johnson's Beach	Sacramento Pikeminnow	5	fillet	Skin Off	Perfluorododecanoate	0.65	ng/g ww		1.56	379
114RR1325	Russian River at Johnson's Beach	Sacramento Sucker	5	fillet	Skin Off	Perfluoroheptanoate	0.00	ng/g ww	ND	2.03	422
114RR1325	Russian River at Johnson's Beach	Sacramento Pikeminnow	5	fillet	Skin Off	Perfluoroheptanoate	0.00	ng/g ww	ND	1.56	379
114RR1325	Russian River at Johnson's Beach	Sacramento Sucker	5	fillet	Skin Off	Perfluorohexanesulfonate	0.00	ng/g ww	ND	2.03	422
114RR1325	Russian River at Johnson's Beach	Sacramento Pikeminnow	5	fillet	Skin Off	Perfluorohexanesulfonate	0.00	ng/g ww	ND	1.56	379

Station Code	Station	Common Name	Number InComp	TissueName	Prep Preservation Name	Analyte Name	Result	Unit Name	Result Qual Code	Lipid Pct	Avg Total Length
114RR1325	Russian River at Johnson's Beach	Sacramento Sucker	5	fillet	Skin Off	Perfluorohexanoate	0.00	ng/g ww	ND	2.03	422
114RR1325	Russian River at Johnson's Beach	Sacramento Pikeminnow	5	fillet	Skin Off	Perfluorohexanoate	0.00	ng/g ww	ND	1.56	379
114RR1325	Russian River at Johnson's Beach	Sacramento Sucker	5	fillet	Skin Off	Perfluorononanoate	0.00	ng/g ww	ND	2.03	422
114RR1325	Russian River at Johnson's Beach	Sacramento Pikeminnow	5	fillet	Skin Off	Perfluorononanoate	0.00	ng/g ww	ND	1.56	379
114RR1325	Russian River at Johnson's Beach	Sacramento Sucker	5	fillet	Skin Off	Perfluorooctanesulfonamide	0.00	ng/g ww	ND	2.03	422
114RR1325	Russian River at Johnson's Beach	Sacramento Pikeminnow	5	fillet	Skin Off	Perfluorooctanesulfonamide	0.00	ng/g ww	ND	1.56	379
114RR1325	Russian River at Johnson's Beach	Sacramento Sucker	5	fillet	Skin Off	Perfluorooctanoate	0.00	ng/g ww	ND	2.03	422
114RR1325	Russian River at Johnson's Beach	Sacramento Pikeminnow	5	fillet	Skin Off	Perfluorooctanoate	0.00	ng/g ww	ND	1.56	379
114RR1325	Russian River at Johnson's Beach	Sacramento Sucker	5	fillet	Skin Off	Perfluorooctanesulfonate	5.83	ng/g ww		2.03	422
114RR1325	Russian River at Johnson's Beach	Sacramento Pikeminnow	5	fillet	Skin Off	Perfluorooctanesulfonate	6.47	ng/g ww		1.56	379
114RR1325	Russian River at Johnson's Beach	Sacramento Sucker	5	fillet	Skin Off	Perfluoropentanoate	0.00	ng/g ww	ND	2.03	422
114RR1325	Russian River at Johnson's Beach	Sacramento Pikeminnow	5	fillet	Skin Off	Perfluoropentanoate	0.00	ng/g ww	ND	1.56	379
114RR1325	Russian River at Johnson's Beach	Sacramento Sucker	5	fillet	Skin Off	Perfluoroundecanoate	0.00	ng/g ww	ND	2.03	422

Station Code	Station	Common Name	Number InComp	TissueName	Prep Preservation Name	Analyte Name	Result	Unit Name	Result Qual Code	Lipid Pct	Avg Total Length
114RR1325	Russian River at Johnson's Beach	Sacramento Pikeminnow	5	fillet	Skin Off	Perfluoroundecanoate	0.00	ng/g ww	ND	1.56	379
114RR0898	Russian River at Monte Rio Beach	Largemouth Bass	5	fillet	Skin Off	Perfluorobutanoate	0.00	ng/g ww	ND	0.47	334
114RR0898	Russian River at Monte Rio Beach	Sacramento Sucker	5	fillet	Skin Off	Perfluorobutanoate	0.00	ng/g ww	ND	2.01	430
114RR0898	Russian River at Monte Rio Beach	Sacramento Pikeminnow	5	fillet	Skin Off	Perfluorobutanoate	0.00	ng/g ww	ND	2.57	398
114RR0898	Russian River at Monte Rio Beach	Largemouth Bass	5	fillet	Skin Off	Perfluorodecanoate	1.14	ng/g ww		0.47	334
114RR0898	Russian River at Monte Rio Beach	Sacramento Sucker	5	fillet	Skin Off	Perfluorodecanoate	0.91	ng/g ww		2.01	430
114RR0898	Russian River at Monte Rio Beach	Sacramento Pikeminnow	5	fillet	Skin Off	Perfluorodecanoate	1.14	ng/g ww		2.57	398
114RR0898	Russian River at Monte Rio Beach	Largemouth Bass	5	fillet	Skin Off	Perfluorododecanoate	0.76	ng/g ww		0.47	334
114RR0898	Russian River at Monte Rio Beach	Sacramento Sucker	5	fillet	Skin Off	Perfluorododecanoate	0.58	ng/g ww		2.01	430
114RR0898	Russian River at Monte Rio Beach	Sacramento Pikeminnow	5	fillet	Skin Off	Perfluorododecanoate	0.74	ng/g ww		2.57	398
114RR0898	Russian River at Monte Rio Beach	Largemouth Bass	5	fillet	Skin Off	Perfluoroheptanoate	0.00	ng/g ww	ND	0.47	334
114RR0898	Russian River at Monte Rio Beach	Sacramento Sucker	5	fillet	Skin Off	Perfluoroheptanoate	0.00	ng/g ww	ND	2.01	430
114RR0898	Russian River at Monte Rio Beach	Sacramento Pikeminnow	5	fillet	Skin Off	Perfluoroheptanoate	0.00	ng/g ww	ND	2.57	398
114RR0898	Russian River at Monte Rio	Largemouth Bass	5	fillet	Skin Off	Perfluorohexanesulfo	0.00	ng/g ww	ND	0.47	334

Station Code	Station	Common Name	Number InComp	TissueName	Prep Preservation Name	Analyte Name	Result	Unit Name	Result Qual Code	Lipid Pct	Avg Total Length
	Beach					nate					
114RR0898	Russian River at Monte Rio Beach	Sacramento Sucker	5	fillet	Skin Off	Perfluorohexanesulfonate	0.00	ng/g ww	ND	2.01	430
114RR0898	Russian River at Monte Rio Beach	Sacramento Pikeminnow	5	fillet	Skin Off	Perfluorohexanesulfonate	0.00	ng/g ww	ND	2.57	398
114RR0898	Russian River at Monte Rio Beach	Largemouth Bass	5	fillet	Skin Off	Perfluorohexanoate	0.00	ng/g ww	ND	0.47	334
114RR0898	Russian River at Monte Rio Beach	Sacramento Sucker	5	fillet	Skin Off	Perfluorohexanoate	0.00	ng/g ww	ND	2.01	430
114RR0898	Russian River at Monte Rio Beach	Sacramento Pikeminnow	5	fillet	Skin Off	Perfluorohexanoate	0.00	ng/g ww	ND	2.57	398
114RR0898	Russian River at Monte Rio Beach	Largemouth Bass	5	fillet	Skin Off	Perfluorononanoate	0.00	ng/g ww	ND	0.47	334
114RR0898	Russian River at Monte Rio Beach	Sacramento Sucker	5	fillet	Skin Off	Perfluorononanoate	0.00	ng/g ww	ND	2.01	430
114RR0898	Russian River at Monte Rio Beach	Sacramento Pikeminnow	5	fillet	Skin Off	Perfluorononanoate	0.00	ng/g ww	ND	2.57	398
114RR0898	Russian River at Monte Rio Beach	Largemouth Bass	5	fillet	Skin Off	Perfluorooctanesulfonamide	0.00	ng/g ww	ND	0.47	334
114RR0898	Russian River at Monte Rio Beach	Sacramento Sucker	5	fillet	Skin Off	Perfluorooctanesulfonamide	0.00	ng/g ww	ND	2.01	430
114RR0898	Russian River at Monte Rio Beach	Sacramento Pikeminnow	5	fillet	Skin Off	Perfluorooctanesulfonamide	0.00	ng/g ww	ND	2.57	398
114RR0898	Russian River at Monte Rio Beach	Largemouth Bass	5	fillet	Skin Off	Perfluorooctanesulfonate	10.50	ng/g ww		0.47	334
114RR0898	Russian River at Monte Rio Beach	Sacramento Sucker	5	fillet	Skin Off	Perfluorooctanesulfonate	7.07	ng/g ww		2.01	430

Station Code	Station	Common Name	Number InComp	TissueName	Prep Preservation Name	Analyte Name	Result	Unit Name	Result Qual Code	Lipid Pct	Avg Total Length
114RR0898	Russian River at Monte Rio Beach	Sacramento Pikeminnow	5	fillet	Skin Off	Perfluorooctanesulfonate	8.03	ng/g ww		2.57	398
114RR0898	Russian River at Monte Rio Beach	Largemouth Bass	5	fillet	Skin Off	Perfluorooctanoate	0.00	ng/g ww	ND	0.47	334
114RR0898	Russian River at Monte Rio Beach	Sacramento Sucker	5	fillet	Skin Off	Perfluorooctanoate	0.00	ng/g ww	ND	2.01	430
114RR0898	Russian River at Monte Rio Beach	Sacramento Pikeminnow	5	fillet	Skin Off	Perfluorooctanoate	0.00	ng/g ww	ND	2.57	398
114RR0898	Russian River at Monte Rio Beach	Largemouth Bass	5	fillet	Skin Off	Perfluoropentanoate	0.00	ng/g ww	ND	0.47	334
114RR0898	Russian River at Monte Rio Beach	Sacramento Sucker	5	fillet	Skin Off	Perfluoropentanoate	0.00	ng/g ww	ND	2.01	430
114RR0898	Russian River at Monte Rio Beach	Sacramento Pikeminnow	5	fillet	Skin Off	Perfluoropentanoate	0.00	ng/g ww	ND	2.57	398
114RR0898	Russian River at Monte Rio Beach	Largemouth Bass	5	fillet	Skin Off	Perfluoroundecanoate	0.71	ng/g ww		0.47	334
114RR0898	Russian River at Monte Rio Beach	Sacramento Sucker	5	fillet	Skin Off	Perfluoroundecanoate	0.59	ng/g ww		2.01	430
114RR0898	Russian River at Monte Rio Beach	Sacramento Pikeminnow	5	fillet	Skin Off	Perfluoroundecanoate	0.76	ng/g ww		2.57	398
114PSP009	Spring Lake	Redear Sunfish	8	fillet	Skin Off	Perfluorobutanesulfonate	0.00	ng/g ww	ND	0.42	177
114PSP009	Spring Lake	Redear Sunfish	8	fillet	Skin Off	Perfluorobutanoate	0.00	ng/g ww	ND	0.42	177
114PSP009	Spring Lake	Redear Sunfish	8	fillet	Skin Off	Perfluorodecanoate	0.00	ng/g ww	ND	0.42	177
114PSP009	Spring Lake	Redear Sunfish	8	fillet	Skin Off	Perfluorododecanoate	0.00	ng/g ww	ND	0.42	177

Station Code	Station	Common Name	Number InComp	TissueName	Prep Preservation Name	Analyte Name	Result	Unit Name	Result Qual Code	Lipid Pct	Avg Total Length
114PSP009	Spring Lake	Redear Sunfish	8	fillet	Skin Off	Perfluoroheptanoate	0.00	ng/g ww	ND	0.42	177
114PSP009	Spring Lake	Redear Sunfish	8	fillet	Skin Off	Perfluorohexanesulfonate	0.00	ng/g ww	ND	0.42	177
114PSP009	Spring Lake	Redear Sunfish	8	fillet	Skin Off	Perfluorohexanoate	0.00	ng/g ww	ND	0.42	177
114PSP009	Spring Lake	Redear Sunfish	8	fillet	Skin Off	Perfluorononanoate	0.00	ng/g ww	ND	0.42	177
114PSP009	Spring Lake	Redear Sunfish	8	fillet	Skin Off	Perfluorooctanesulfonamide	0.00	ng/g ww	ND	0.42	177
114PSP009	Spring Lake	Redear Sunfish	8	fillet	Skin Off	Perfluorooctanesulfonate	2.13	ng/g ww		0.42	177
114PSP009	Spring Lake	Redear Sunfish	8	fillet	Skin Off	Perfluorooctanoate	0.00	ng/g ww	ND	0.42	177
114PSP009	Spring Lake	Redear Sunfish	8	fillet	Skin Off	Perfluoropentanoate	0.00	ng/g ww	ND	0.42	177
114PSP009	Spring Lake	Redear Sunfish	8	fillet	Skin Off	Perfluoroundecanoate	0.00	ng/g ww	ND	0.42	177

TASK 3: PESTICIDES IN WATER AND SEDIMENT FROM THE RUSSIAN RIVER WATERSHED

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Summary

Pesticides are used throughout the Russian River watershed in both agricultural and urban regions, but have not been comprehensively monitored in surface water or stream sediment. The purpose of this study was to conduct an initial screening of the potential impact of current use pesticides in the Russian River and its tributaries, with a focus on agricultural pesticide applications. This study supplements the recommended design of a statewide pilot monitoring study for contaminants of emerging concern (CECs) in aquatic ecosystems by conducting a regionally specific prioritization and monitoring of pesticides in water and sediment. This limited screening effort is not intended to provide a definitive characterization, but rather a preliminary assessment of occurrence and potential concerns associated with current use pesticides in the watershed.

Water and sediment samples were collected at five sites along the Russian River and its tributaries in fall 2016. The Russian River watershed is dominated by forests and agricultural land (including crop and animal agriculture), where wine grapes are the main agricultural crop (concentrated south of Cloverdale), followed by apple and pear trees. Approximately 360,000 residents live in the watershed, with about half concentrated in the cities of Windsor and Santa Rosa. Sites were selected to provide broad spatial coverage of the watershed while characterizing subregions with high volumes of reported agricultural pesticide use. The four northernmost sites (Potter Valley, Hopland, Jimtown, Pull-Out/Riverfront) characterize agricultural watersheds, while the southernmost site (Trenton Road) characterizes mixed urban and agricultural areas. The three southernmost sites (Jimtown, Pull-Out/Riverfront, and Trenton Road) also characterize dense wine-growing regions.

Water and sediment samples were analyzed by the U.S. Geological Survey California Water Science Center (USGS-CWSC) laboratory in Sacramento. Separate analyses were conducted for aqueous contaminants in the dissolved phase and in suspended sediment (particulate phase). Twenty-two of the 162 pesticides and degradates analyzed in water (dissolved phase) were detected, while none of the 131 pesticides analyzed in suspended sediment (particulate phase) were detected. Six of 118 pesticides analyzed were detected in bed sediment. Sixteen of the pesticides detected in water (dissolved phase) and one of the pesticides detected in bed sediment were found only at the mixed-use site on the Mark West Creek tributary near Santa Rosa (Trenton Road), including several pesticides that have not been reported as used in agricultural applications in this watershed, but are commonly used in urban settings.

The concentrations of pesticides detected during this study were relatively low compared to aquatic toxicity thresholds, and thus far suggest that pesticide toxicity from fall season agricultural runoff may not be a major concern in the Russian River and the East Fork Russian River. However, the data indicate that some pesticides in urban runoff are at or near toxicity

thresholds. Imidacloprid, which was detected only at the mixed-used Trenton Road site, was measured above a newly lowered U.S. Environmental Protection Agency (USEPA) Office of Pesticide Prevention (OPP) chronic invertebrate benchmark (10 ng/L). Aside from imidacloprid, all other detections in water were below available USEPA OPP aquatic life benchmarks, and all detections in sediment were below sediment benchmarks developed by USGS. However, data from recent aquatic toxicity studies suggest that fipronil and its degradates could be approaching levels of concern near urban areas in the Russian River watershed, based on concentrations measured in water during this study. A third common urban-use pesticide, bifenthrin, was detected in sediment below a USGS-calculated sediment toxicity benchmark, but above a monitoring trigger level included in the statewide CEC monitoring guidance. Bifenthrin use has been increasing in urban areas of California, and has very high aquatic toxicity, although recent restrictions have been placed on outdoor use. These compounds should be considered for further monitoring in both water and sediment.

Concentrations of most compounds were in the lower or average range of concentrations measured in other agricultural or mixed-use regions in California. Only the mixed-use Trenton Road site had concentrations in water that were at the upper end of those previously measured in the Delta or in other agricultural or mixed-use regions (herbicides oxidiazon and prodiamine; fungicides boscalid, iprodione, and carbendazim; fipronil sulfone). The water samples collected at this site characterized the greatest proportion of stormwater runoff compared to other sites, but the higher concentrations observed there may also suggest urban sources for these compounds.

However, concentrations measured at Trenton Road still fell within the range of expected concentrations. Elevated fungicide concentrations are expected in wine-growing regions, but these compounds exhibit low aquatic toxicity and do not present a toxicity concern based on the levels observed in this study. Fipronil and its degradates, which were detected only at the mixed-use site in this study (Trenton Road) and are predominantly urban-use pesticides in this region, were detected at the low end of concentrations measured in highly urbanized areas throughout California. Likewise, imidacloprid and bifenthrin were measured at levels on the lower end of concentrations typically measured in urban areas; however, higher concentrations would be expected at locations closer to sources.

The scope of this initial screening study was relatively limited. Patterns in this initial dataset suggest that additional monitoring is warranted in order to fully characterize potential pesticide concerns in the watershed. In particular, additional monitoring of urban areas and monitoring of spring runoff is recommended to more fully characterize a greater spatial and temporal range than was assessed in this study. Additional fall stormwater monitoring in watersheds north of Cloverdale is also recommended, as the water samples collected during this study characterized limited stormwater runoff. If resources are limited, composite or passive sampling over the duration of a storm period is recommended to ensure a more robust characterization of runoff, particularly in more rural or agricultural regions where stormwater runoff may be more variable.

Periodic monitoring of both water and sediment is recommended to identify any potential new concerns over time, based on changing pesticide use patterns, improved analytical methods, and new toxicity information. As resources are available, non-targeted analyses are also recommended on a less frequent but recurring basis in order to identify any high priority compounds that may not be captured using traditional targeted analyses, including pesticide degradates.

Background

The Russian River watershed (**Figure 3-1**) is a predominantly rural watershed that drains 1,485 mi^2 in Mendocino and Sonoma counties. The main stem of the Russian River runs from headwaters near Redwood Valley and Potter Valley 110 miles south and west to the Pacific Ocean (RRWA 2016). The watershed is dominated by forests and agricultural lands, and features 238 streams and creeks as well as three threatened or endangered fish species. Pesticides are used in both agricultural and urban areas in this watershed, but most current-use pesticides have not yet been monitored in the region. The purpose of this study was to conduct an initial screening of current use pesticides potentially impacting the Russian River and its tributaries, with a focus on agricultural pesticide applications.

Wine grapes make up the main agricultural crop grown in this region, followed by apple and pear trees. Pesticides are used in the cultivation of these crops. Geospatially-specific pesticide application data are collected and made publicly available by California's Department of Pesticide Regulation (DPR).

The Russian River watershed is also home to approximately 360,000 residents, roughly half of which live in the cities of Windsor and Santa Rosa to the south. These main urban areas drain into the Russian River as it turns west in the southern region of the watershed. The main stem of the Russian River and the East Fork Russian River to the north are dotted with small, unincorporated communities, as well as the small cities of Ukiah and Cloverdale. Pesticides are widely used in urban regions of California, though geospatial application information is not available. No wastewater effluent was discharged directly to tributaries during the period of sampling, but outdoor pesticide applications may have contributed to pesticides in stormwater runoff. In this watershed, previous monitoring of urban use pesticides has been conducted as part of the statewide Surface Water Ambient Monitoring Program (SWAMP), but has been limited in scope and focused primarily on organophosphate and pyrethroid pesticides (CDPR 2017b).

In spring 2016, a prioritized list of pesticides recommended for monitoring in the Russian River watershed was developed using the DPR's Pesticide Use Reporting (PUR) database and Surface Water Monitoring Prioritization model (SWMP) (CDPR 2017c; Luo 2015). This model uses pesticide chemical toxicity benchmarks and recent past county pesticide use data (township-range section resolution) for agricultural pesticides to provide a watershed-based pesticide prioritization to inform surface water monitoring (Appendix A). The prioritization list was then used to inform selection of an analytical laboratory (USGS-CWSC, Sacramento, CA) with the most cost-effective and comprehensive target analyte list that best matched those pesticides that were predicted to have the highest potential be present at levels of concern in surface waters. Water and sediment samples were collected at five sites in fall 2016.

This project supplements the recommended design of a statewide pilot monitoring study for CECs in aquatic ecosystems (Dodder et al. 2015), and represents the first regional application of this pilot study design for CECs. This report presents results from one element of a larger project. The other elements are: (1) monitoring of CECs via targeted chemistry and bioanalytical tools in wastewater treatment plant (WWTP) effluent, stormwater, receiving water, and sediment, and (2) monitoring of prioritized CECs in fish tissue. This regionally-specific prioritization and monitoring of pesticides in water and sediment is a limited screening effort that is not intended to provide a definitive characterization of pesticide toxicity concerns in the watershed, but instead provides a preliminary assessment of occurrence and potential concerns associated with current use pesticides. Recommendations for future monitoring are presented based on patterns and data gaps observed in this initial screening effort.

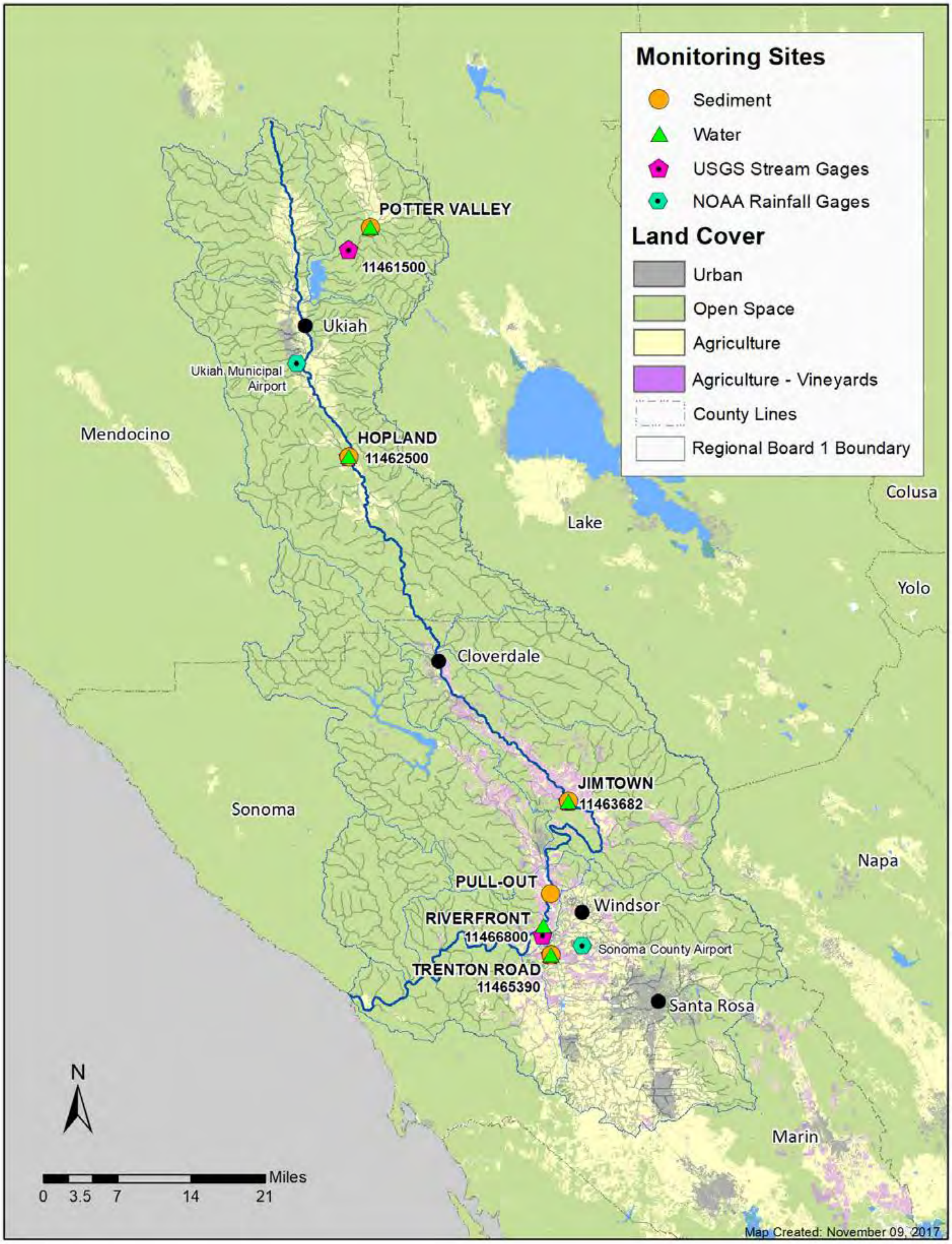


Figure 3-1. Site Map

Materials and Methods

Pesticide Prioritization Exercise as a Guide for Monitoring

The target pesticide analyte list was informed by the Department of Pesticide Regulation's (DPR) Surface Water Monitoring Prioritization (SWMP) model, which utilizes both pesticide use data (DPR's Pesticide Use Reporting [PUR] database) as well as toxicity data (EPA OPP water benchmarks) to prioritize pesticides for monitoring. The resulting prioritized pesticide list was subsequently informed by professional judgment, including additional information about pesticide degradates and recent toxicity studies that were not included in the model. For this study, the model was run using agricultural pesticide application data only, which includes applications in parks, cropland, rangeland, and pastures, but not structural, landscape maintenance, and rights-of-way uses in urban areas. DPR's urban use model can be used to prioritize pesticides for targeted monitoring of urban areas based on professional pesticide application reporting data, but was not used for this study. For this study, the agricultural model was run using year-round application data. The most recent pesticide application data available were used, including data from 2012-2014.

A detailed description of this prioritization exercise is included in Appendix A.

Sampling Locations

In fall 2016, water and sediment samples were collected at five sites along the Russian River and its tributaries: Potter Valley, Hopland, Jimtown, Pull-Out/Riverfront, and Trenton Road (**Table 3-1**). Sites were selected to (1) provide broad spatial coverage of the watershed, including regions with different land use characteristics; (2) target watersheds most likely to be impacted by agricultural pesticide contamination, based on use volumes reported in the PUR database; and (3) integrate upstream watershed pesticide use. Thus, samples were collected at or near the bottom of watersheds – either on the main stem of the Russian River or along major tributaries – downstream of agricultural pesticide application hot spots throughout the watershed. Water and sediment sites were co-located as much as possible, but one site (the Pull-Out sediment site on the Russian River below Kabutts Road) was relocated (to the Riverfront Park site) during water sampling due to private property access restrictions during the storm (Figure 3-1).

The two northernmost sites characterize comparatively smaller pesticide application hot spots downstream of cultivated crop- and pasturelands in the northeast corner of the watershed in Potter Valley (Potter Valley site) and just south of Ukiah (Hopland site). In contrast, the three remaining sites (Jimtown, Pull-Out/Riverfront Park, and Trenton Road) are located in the dense wine-growing regions south of Cloverdale. The Trenton Road site also receives some runoff from pasturelands in the Santa Rosa region. County pesticide use data from 2012-2014 show that agricultural pesticide applications are greatest in spatial extent and volume in this wine-growing region.

While urban-use pesticides were not a focus of this study, the downstream sites also characterize some urban pesticide uses. The Trenton Road site is located on a tributary that receives urban runoff from the City of Santa Rosa, the largest city in the watershed, as well as the City of Sebastopol and parts of the City of Rohnert Park. This site is considered a mixed-use site, and was expected to reflect the greatest influence from urban-use pesticides. The Pull-Out/Riverfront and Jimtown sites are also located near small rural communities, and may receive a small amount of urban-influenced runoff.

Sites were also co-located as much as possible with USGS stream gauges and water quality sampling sites, including sites that were sampled in spring 2017 as part of the USGS National Water Quality Assessment (NAWQA) Stream Quality Assessment Project. The Trenton Road site is co-located with a USGS NAWQA site, and the Pull-Out/Riverfront sites are located just downstream of a second USGS NAWQA site. While the USGS study focused on the southern region of the watershed, sites for this initial screening study were selected to be located near more intense applications of agricultural pesticides, based on recent use patterns for the top 12 agricultural pesticides prioritized for this region (Appendix A, Use Maps).

Table 3-1. Site List

Site Name	Latitude	Longitude	USGS Gauge Number	Water Body Sampled	Upstream Land Use
POTTER VALLEY	39.27026	-123.10091	11461500	East Fork Russian River	Agricultural – crop and pastureland
HOPLAND	39.02629	-123.13036	11462500	Russian River	Agricultural – crop and pastureland; forested
JIMTOWN	38.65873	-122.8296	11463682	Russian River	Agricultural – predominantly vineyards
PULL-OUT RIVERFRONT	38.55993 38.52573	-122.85423 -122.8638	11465390	Russian River	Agricultural – predominantly vineyards
TRENTON ROAD	38.49399	-122.85316	11466800	Mark West Creek	Mixed-use – agricultural (predominantly vineyards) and urban (Santa Rosa, Windsor)

Sample Collection

Sediment samples were collected in late September 2016, prior to the beginning of the wet season. The sediment samples were expected to capture sediment-bound particles that may have been transported from the upper watersheds during the dry season, but would not yet have been diluted or transported downstream by large flow events.

Water samples were collected as instantaneous grab samples in late October 2016 and were targeted for collection during the first significant runoff event of the season. The water samples were designed to capture the “first fall flush,” or the first significant rainstorm that would mobilize pesticides that were applied during the dry season and may have remained sediment-bound in the upper watersheds, in part due to their application using low-flow irrigation methods that are common in vineyards and orchards. Prior to the sampling date, two small rain events in late September and mid-October took place, but were not considered large enough to be sampled. The storm that was sampled occurred in two pulses, and sampling occurred towards the beginning of the second storm pulse (Appendix D). Sampling method details are described in the field sampling report (Appendix A).

Each site was characterized by measurements of water velocity, stream width, and distance of the sampling site from the right stream bank when facing downstream. Ancillary field parameters collected included water temperature, specific conductivity, salinity, dissolved oxygen, pH, and barometric pressure, measured with a YSI 600XL Data Sonde (Appendix A).

Analytical Methods

The prioritized target analyte list was used to inform selection of an analytical laboratory with the most cost-effective and comprehensive target analyte list that best matched the pesticides with the highest potential to be present at levels of concern in surface waters. The USGS-CWSC laboratory in Sacramento best met these parameters, with a comprehensive target analyte list that included about 70% of the pesticides on the prioritized target analyte list.

Water samples were analyzed for 137 compounds in the dissolved phase and 131 compounds in the particulate phase (i.e., suspended sediment) by GC/MS (Hladik et al. 2008). An additional 25 compounds were analyzed in the dissolved phase only by LC/MS/MS (Hladik and Calhoun 2012). 3,4-dichlorobenzenamine (also 3,4-dichloroaniline or 3,4-DCA) was reported in the particulate phase by GC/MS and in the dissolved phase by LC/MS/MS. Sediment (i.e., bed sediment) samples were analyzed for 118 compounds by GC/MS (Hladik and McWayne 2012). Total Organic Carbon (TOC) was also measured in the sediment samples using a modified version of USEPA 440.0 (Appendix B). Complete analyte lists and method detection limits are presented in Appendix C.

Quality Assurance / Quality Control

One field replicate (collected at the Jimtown site), one field blank (collected at the Trenton Road site), a matrix spike and a matrix spike duplicate were analyzed by GC/MS in dissolved-phase water. The same analyses were completed by GC/MS in suspended sediment except for the matrix spike duplicate, which was accidentally processed as a second laboratory replicate (collected at the Hopland site). Only a field blank was analyzed by LC/MS/MS in dissolved-phase water samples.

A matrix spike sample and a laboratory blank sample were analyzed by GC/MS in sediment. No field replicate was analyzed for the sediment samples, but replicate sample data were provided for sediment samples submitted for other projects and analyzed within the same lab batch. These other data were used to estimate precision for the sediment sample analyses.

The measurement quality objectives for the Delta Regional Monitoring Program (Jabusch et al. 2016) were used to evaluate the QA/QC results in water, as this Program monitored a near-identical analyte list in FY15/16. These objectives include: (1) < 25% relative percent difference for field replicates and matrix spike duplicates; (2) < MDL for field blanks; and (3) recoveries of 70-130% for matrix spikes and surrogate spikes. All objectives were met, and no results were censored (i.e., not reported). Similar objectives were also met in sediment samples, with the exception of the matrix spike duplicate and field blank samples, which were not run in sediment. No detections were identified in the sediment laboratory blank sample.

These objectives are consistent with method quality objectives outlined by the Statewide CEC guidance (Dodder et al. 2015), with a few exceptions. The previously described objectives for blanks, duplicates, and matrix spikes either meet or exceed the minimum method quality objectives outlined by the statewide CEC pilot study design and QA/QC guidance (Dodder et al. 2015). The initial calibration and spiked standard recovery objectives (50-150%) were also met. However, the laboratory's continuing calibration verification objective of +/- 25% is slightly greater than the statewide guidance of +/- 20%. Additionally, a laboratory control sample or standard reference material was not run.

No target pesticides were detected in the water field blank. Precision for both water and sediment samples was good based on the field replicate data, with a relative percent difference of < 25%

for both water and sediment field replicates. All analytes detected in the first field replicate were detected in the second field replicate for water. Surrogate and spiked sample recoveries were between 70-130% for all analytes, with the majority of sample recoveries measured below 100%. Samples were not corrected with lab blank or surrogate recovery results. Analytes detected below MDLs were reported as estimated values, and are included in this report as such.

Data Analysis

Three major types of analyses were conducted in this report: (1) descriptive statistics, (2) comparisons of concentrations and MDLs to available aquatic toxicity benchmarks, and (3) comparisons of detection frequencies and concentrations to data collected in other regions in California. Further statistical analyses were not conducted due to the limited number of samples collected.

Statistics

Field and laboratory replicates are reported as averages. Non-detect values were considered to be zero when calculating sums and averages, as well as in figures and tables. However, estimated values (i.e., reported values below the method detection limit) are included in figures, tables, sums, and averages, and are marked as estimated in the figures and tables.

Comparisons with aquatic toxicity benchmarks and other thresholds

Water concentrations and MDLs were compared to aquatic life benchmarks established by the Environmental Protection Agency Office of Pesticide Programs (EPA OPP), aquatic life criteria established by the EPA Office of Water, and aquatic life benchmark equivalents calculated by DPR (Luo et al. 2013; Luo 2015; Luo *personal communication*). Both acute and chronic benchmark equivalent values are used in the DPR pesticide prioritization (SWMP) model and included in this report (Appendix C, Table C1), but the process for calculating chronic benchmark equivalent values has not yet been formalized by DPR.

Sediment concentrations and MDLs were compared to a recently published set of USGS sediment benchmarks for freshwater invertebrates (Nowell et al. 2016). These benchmarks were calculated based on spiked sediment bioassay studies or – when these data are not available – equilibrium partitioning methods, using data compiled by various pesticide working groups or published in the open scientific literature. USGS calculated two organic carbon-normalized benchmark values (µg/g-oc basis): a higher Likely Effect Benchmark (LEB) and a lower Threshold Effect Benchmark (TEB). USGS-conducted case studies comparing the use of these calculated benchmarks with toxicity values found that they correctly predicted toxicity to *Hyalella azteca* but not *Chironomus dilutus* in the majority of samples from two major USGS studies; however, the equilibrium partitioning-based thresholds were less predictive of measured toxicity than the spiked sediment bioassay-based thresholds. Long-term spiked sediment bioassay data were less available to calculate TEBs compared to short-term bioassay data used to calculate LEBs, so in many cases TEBs were estimated by USGS as 1/10 the LEB value, and the case studies found that the estimated TEBs tended to be conservative (i.e., overpredicted toxicity). More long-term spiked sediment bioassay studies and a better understanding of pesticide bioavailability in stream sediment field conditions are needed to refine these USGS benchmarks; however, this set of benchmarks represents the most rigorous and comprehensive standardized set of sediment thresholds available, and are useful as an initial toxicity screening tool.

Water and sediment results were also compared to monitoring trigger levels (MTLs) recommended by the statewide CEC pilot study design guidance (Anderson et al. 2012; Dodder et al. 2015), which are conservative benchmarks developed based on potential ecological and human health risks. MTL exceedances indicate a need for additional monitoring, but do not necessarily indicate a toxicity concern. Monitoring trigger levels have been established for bifenthrin in the aqueous phase and bifenthrin and fipronil in sediment for coastal embayments in California; no MTLs for pesticides detected in this study have been established for effluent-dominated inland waterways, the CEC pilot study design scenario most comparable to that of the Russian River watershed. Coastal embayment MTLs were used to further assess whether additional monitoring of these insecticides is warranted in the region.

Comparisons with other studies

Results were compared to pesticide monitoring data available in the DPR Surface Water Database (SURF) (CDPR 2017b). The SURF database was updated in June 2017 to include all water and sediment data available from DPR studies as well as the California State Water Resources Control Board California Environmental Data Exchange Network (CEDEN) database, the USGS National Water Information System (NWIS) database, and the EPA Storage and Retrieval and Water Quality Exchange (STORET/WQX) database. Samples reported in the SURF database represent a wide range of land use and pesticide use patterns in California. Water results were also compared to previous results measured in the Sacramento-San Joaquin Delta by the Delta RMP in FY 15/16 (CEDEN 2017, Project="Delta RMP 2015 Current Use Pesticides"**)** and in Cache Slough by UC Davis using non-targeted analysis (Moschet et al. 2017). Additional peer reviewed literature was used to supplement these data sources when needed.

Samples collected by the Delta RMP were analyzed by the same USGS laboratory that analyzed samples for this study. Results measured in other studies may have been analyzed by other labs with different analyte lists and method detection limits, which may have biased the number of detections observed in other studies.

Results and Discussion

Pesticides in Water

A total of 22 pesticides and degradates out of the 162 analyzed were detected at one or more sites in water (dissolved phase only) (**Table 3-2**). None of the 131 pesticides analyzed in suspended sediment (particulate phase) were detected. The compounds detected in water (dissolved phase) included seven fungicides, eight herbicides (five parent compounds and three degradates), and seven insecticides (four parent compounds and three degradates) (**Table 3-3**). Four compounds were detected at more than one site: the fungicides carbendazim and boscalid, and the herbicide diuron and its metabolite, 3,4-dichlorophenyl urea (3,4-DCPU). Simazine was detected only at Jimtown, and the remaining 16 pesticides were detected only at the Trenton Road site.

No pesticides were detected at the Potter Valley site. The hydrograph from a USGS gauge just downstream of the Potter Valley site suggests that this sample may have been collected at near-base flow conditions, indicating that the lack of detections at this site may have been more reflective of dry-weather conditions (Appendix D, Figure D1). Between three and four compounds were detected at the Hopland, Jimtown, and Riverfront sites. At the more rural Hopland site, the first storm pulse delivered very limited runoff, while a relatively long lag time was observed before runoff from the second storm pulse reached the stream. The hydrograph from the Hopland site suggests that the sample collected may have included a relatively small amount of stormwater runoff (Appendix D, Figure D2). In contrast, the downstream Jimtown and Riverfront sites appear to have been sampled at the very front end of the rising limb of a second storm pulse as measured by nearby USGS stream gauges (Appendix D, Figures D3-D4)**.** At these sites, samples also appeared to capture some runoff from the receding limb of the first storm pulse.

Twenty-one compounds were detected at the Trenton Road site, which receives both agricultural and urban inputs. With the exception of simazine, which was detected only at Jimtown, the highest concentrations of all pesticides detected were measured at the Trenton Road site. This site was sampled during an initial runoff period during the second storm peak, which may have been substantially influenced by urban runoff that would have been flushed off the landscape more quickly than runoff from agricultural or rural areas. According to the storm hydrographs, the sample collected at the Trenton Road site captured the greatest percentage of stormwater runoff relative to total flow, compared to other sites (Appendix D, Figure D5).

Imidacloprid was detected above the EPA OPP chronic invertebrate aquatic life benchmark at the Trenton Road site. No other compounds measured were present at levels above established EPA Office of Pesticide Programs (OPP) aquatic life benchmarks, EPA Office of Water aquatic life criteria, or OPP benchmark equivalents calculated by DPR when neither EPA threshold was available. Fipronil was measured below the monitoring trigger level recommended by the statewide CEC monitoring guidance for water in coastal embayments (no monitoring trigger level is recommended for fipronil in inland waters or for any other pesticides detected in water in this study; Dodder et al. 2015). However, concentrations of fipronil sulfide and fipronil sulfone at Trenton Road were higher than chronic aquatic invertebrate toxicity thresholds measured in a recent study (Weston and Lydy 2014).

Table 3-2. Summary of compounds analyzed and detected in water samples

	Dissolved Phase				Suspended Sediment	
Pesticide Type[1]	**Compounds Analyzed**	**Compounds Detected**	**Total Number of Detections**	**Number of Sites with Detections**	**Compounds Analyzed**	**Compounds Detected**
Fungicides	51	7	13 (2 estimated below quantification level)	4	44	0
Herbicides	41	8	12	4	34	0
Insecticides	57	7	7 (2 estimated below quantification level)	1	46	0
Synergists	2	0	0	0	2	0

1 - Degradates are included in the compounds counted within each pesticide type

Table 3-3. Water results – detected analytes

Pesticide	Type[1]	Lowest EPA or DPR threshold (ng/L)	Type[2]	Other (ng/L)	Detection Frequency	Max. Conc. (ng/L)	MDL (ng/L)	Results (ng/L)[3]				
								Trenton Road	River front	Jim-town[5]	Hop-land	Potter Valley
Azoxystrobin	F	44000	Invert, C		1 / 5	26.4	3.1	26.4				
Boscalid	F	116000	Fish, C		4 / 5	148.7	2.8	148.7	39	41.9	18.2	
Carbendazim	F	75000	BE, A		4 / 5	196	4.2	196	*3.8*	3.9	8.5	
Chlorantraniliprole	I	4500	Invert, C		1 / 5	2.4	4	*2.4*				
Clothianidin	I	11000	Invert, C		1 / 5	2.4	3.9	*2.4*				
Dichlorobenzenamine, 3,4-	H (D)	--	--		1 / 5	5.7	3.2	5.7				
Dichlorophenyl Urea, 3,4-	H (D)	--	--		3 / 5	8.9	3.4	8.9	6.2		6.9	
Dichlorophenyl-3-methyl Urea, 3,4-	H (D)	--	--		1 / 5	11.2	3.5	11.2				
Dithiopyr	H	20000	NVP, A		1 / 5	23.3	1.6	23.3				
Diuron	H	2400	NVP, A		3 / 5	65.4	3.2	65.4	15.8		10.2	
Fipronil	I	11	Invert, A/C		1 / 5	3.8	2.9	3.8				
Fipronil Desulfinyl	I (D)	590	Fish, C		1 / 5	6.7	1.6	6.7				
Fipronil Sulfide	I (D)	110	Invert, C	9-11[4]	1 / 5	4.9	1.8	4.9				
Fipronil Sulfone	I (D)	37	Invert, C	8[4]	1 / 5	14.7	3.5	14.7				
Fluopyram	F	67500	BE, C		1 / 5	69	3.8	69.0				
Flutolanil	F	233000	Fish, C		1 / 5	42	4.4	42				
Fluxapyroxad	F	18000	BE, C		1 / 5	12.4	4.8	12.4				
Imidacloprid	I	10	Invert, C		1 / 5	11.2	3.8	11.2				
Iprodione	F	120000	Invert, CA		1 / 5	536.3	4.4	536.3				
Oxadiazon	H	5200	NVP, A		1 / 5	50	2.1	50				
Prodiamine	H	1500	Invert, C		1 / 5	10.8	5.2	10.8				
Simazine	H	2240	NVP, A		1 / 5	16.7	5			16.7		

1 - F = fungicide, H = herbicide, I = insecticide, (D) = degradate

2 - Invert = freshwater invertebrate, NVP = nonvascular plant, A = acute, C = chronic, BE = OPP benchmark equivalent (calculated by DPR). The method for calculating chronic toxicity benchmark equivalents has not been formalized by DPR, but these values are used in the SWMP model and thus are included here.

3 - Estimated values, or values quantified below the method detection limit, are italicized and shown in red.

4 – Wofford et al. 2017, Weston and Lydy 2014 – proposed benchmark equivalent based on a chronic freshwater invertebrate EC50 based on paralysis in *Chironomus tentans*

5 - Boscalid and simazine (GC/MS) measured at Jimtown are reported the average of two field replicates. The results for each replicate are as follows (rep 1, rep 2): boscalid (39.4, 44.4); simazine (15.9, 17.5). No replicate was run for carbendazim at Jimtown (LC/MS/MS).

Fungicides

At each site, fungicides were the compounds detected at the highest concentrations (**Figure 3-2**); however, the aquatic toxicities of these compounds are relatively low, and concentrations at all sites remained at least two orders of magnitude below the lowest EPA OPP benchmark or calculated benchmark equivalent (Table 3-3). Carbendazim was detected at four sites, although it was reported at levels below the MDL at both the Riverfront and Jimtown sites. In addition to its direct application as a benzimidazole fungicide, carbendazim is also a degradate of thiophanate-methyl, which is commonly used on tree crops. Direct carbendazim use was not reported within the Russian River watershed in 2012-2014, but it may occur in urban runoff due to its use as a preservative in outdoor building paints. Boscalid, a common systemic fungicide used on food crops, was also measured at four sites; this pesticide is one of the highest-volume agricultural pesticides used in the Russian River watershed, as well as in the San Francisco Estuary watershed (i.e., San Francisco Bay-Delta, San Joaquin River and Sacramento River watersheds) and Central Coast regions (Kuivila and Hladik 2008, Smalling et al. 2013b).

The five remaining fungicides – iprodione, fluopyram, flutolanil, azoxystrobin, and fluxapyroxad – were detected only at the Trenton Road site. The comparatively high concentrations and number of detections at Trenton Road is likely due at least in part to the greater proportion of stormwater runoff characterized at this site compared to other sites similarly located in dense wine-growing areas (based on storm hydrographs, see Appendix D), but could also be attributed in part to urban sources. For example, azoxystrobin is used as an anti-fungal agent in building materials, and fungicides including azoxystrobin, thiophanate-methyl (carbendazim parent compound), iprodione, fluxapyroxad, and flutolanil are approved for use on turfgrass and ornamentals, among other non-agricultural uses (USEPA 2009b; USEPA 2014a; USEPA 2013a; USEPA 2012; USEPA 2014b). Potential sources include several golf courses and a regional park upstream of the Trenton Road site on Mark West Creek. Furthermore, three of these fungicides – fluxapyroxad, iprodione, and flutolanil – have had very low or no agricultural use reported during the 2012-2014 period (39 kgs, 8.9 kgs, no use reported, respectively; CDPR 2017c).

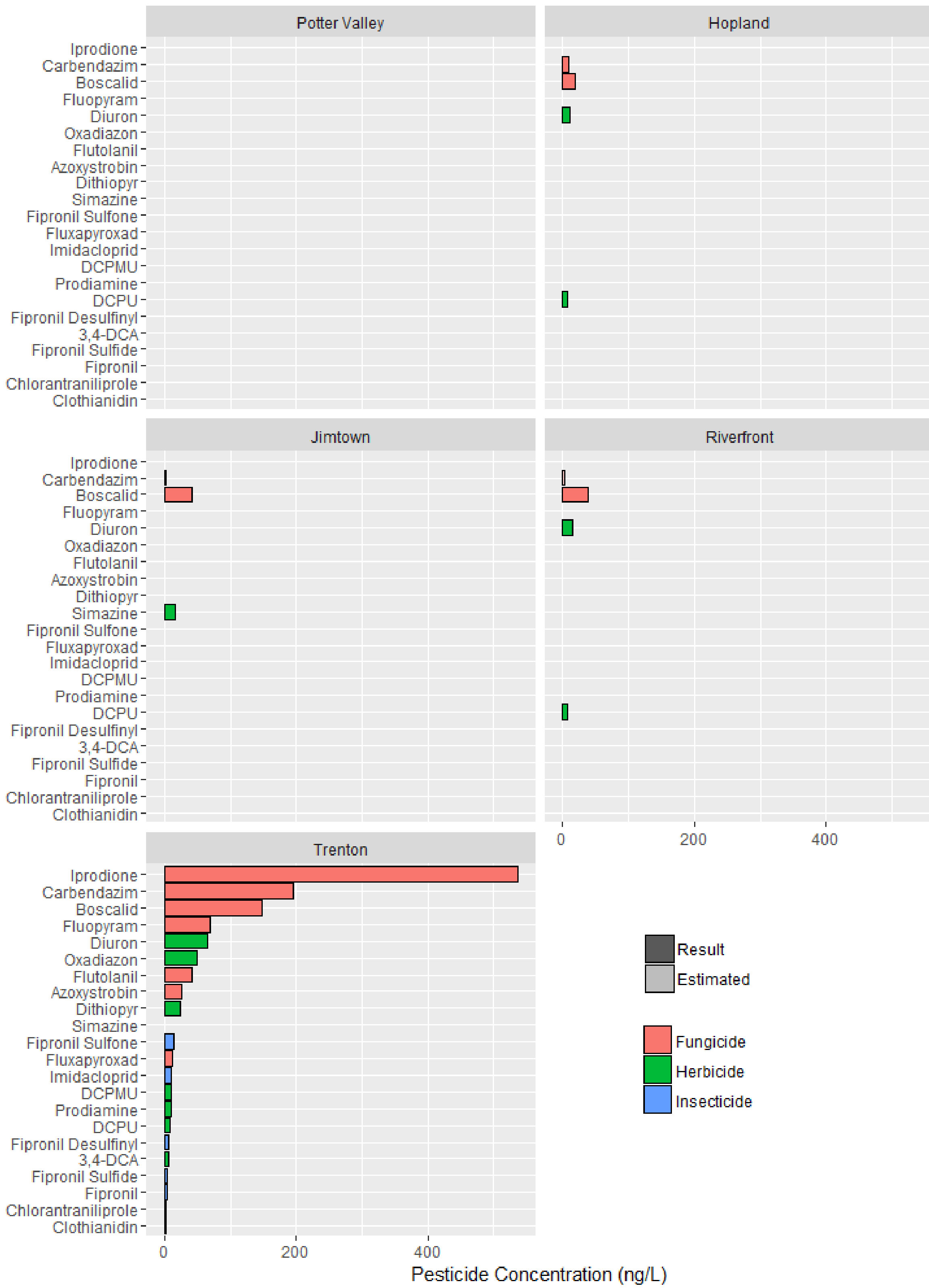


Figure 3-2. Water results by location – detected analytes

Herbicides

Diuron, a systemic substituted phenylurea herbicide, is one of the most commonly detected pesticides in California surface waters (USEPA 2009a). Diuron and one of its metabolites, 3,4-DCPU, were detected at three sites – Hopland, Riverfront, and Trenton Road. Two other diuron metabolites, 3,4-dichlorobenzeneamine (3,4-dichloroaniline or 3,4-DCA) and 3,4-dichlorophenyl-3-methyl-urea (3,4-DCPMU), were also detected at the Trenton Road site. Diuron and its degradates were not given a high priority based on the DPR prioritization exercise, which may be due in part to urban uses not captured within the agricultural application data on which it was based – in addition to its use on grapes and fruit trees, diuron is also commonly used to control weeds in urban rights-of-way (USEPA 2009a). The maximum concentration of diuron itself was two orders of magnitude lower than the lowest EPA OPP benchmark. Benchmarks for the diuron metabolites are not readily available, and studies show mixed results on the relative toxicities of these compounds. One study suggests that the DCPMU may be less toxic than diuron to biofilms (Pesce et al. 2010) and another study suggests that all three may be less toxic than diuron based on various freshwater phytoplankton endpoints (Gatidou and Thomaidis 2007), but both studies show that synergistic effects may occur when diuron and its metabolites are present. Diuron may also cause synergistic estrogenic effects in combination with other contaminants, including bifenthrin (detected in sediment in this study) and alkylphenols or alkylphenol ethoxylates, which have been used in pesticide formulations and in a wide range of other urban applications (Schlenk et al. 2012). However, it is unclear whether the mixtures measured in the Russian River watershed would be associated with toxicity concerns.

Simazine, a triazine herbicide, is used in orchards and vineyards, among other food crops. Although it is one of the most commonly used and detected pesticides in US rivers and streams nationally (USEPA 2013c), in this study it was detected only at Jimtown, which is influenced primarily by agricultural runoff. The remaining three herbicides, oxadiazon, prodiamine, and dithiopyr, were detected only at the Trenton Road site. It is notable that these three herbicides were not used in agricultural applications in the Russian River watershed in 2012-2014 (< 1 lb of oxadiazon applied, 0 lbs of prodiamine and dithiopyr applied; CDPR 2017c), but they are approved for use as turfgrass and ornamental plant treatments (USEPA 2014c; USEPA 2011; USEPA 2013b). Again, all compounds were measured at levels below established EPA OPP benchmarks.

Insecticides

All seven insecticides were detected only at the mixed-use Trenton Road site. As noted above, imidacloprid, a neonicotinoid pesticide, was detected slightly above a recently revised EPA OPP chronic invertebrate aquatic life benchmark, indicating a likely toxicity concern from imidacloprid in urban runoff (**Figure 3-3**). Imidacloprid is a common urban-use pesticide, with applications including lawn and landscape maintenance, outdoor structural pest control, indoor bedbug and insect control, underground termite injections, and pet flea and tick treatments (CDPR 2017a; USEPA 2008). Although imidacloprid as not detected at any of the more agriculturally-influenced sites in this study, substantial agricultural use of imidacloprid was reported in the watershed between 2012-2014 (2397 lbs). Additional monitoring of imidacloprid in both urban and agricultural areas is warranted.

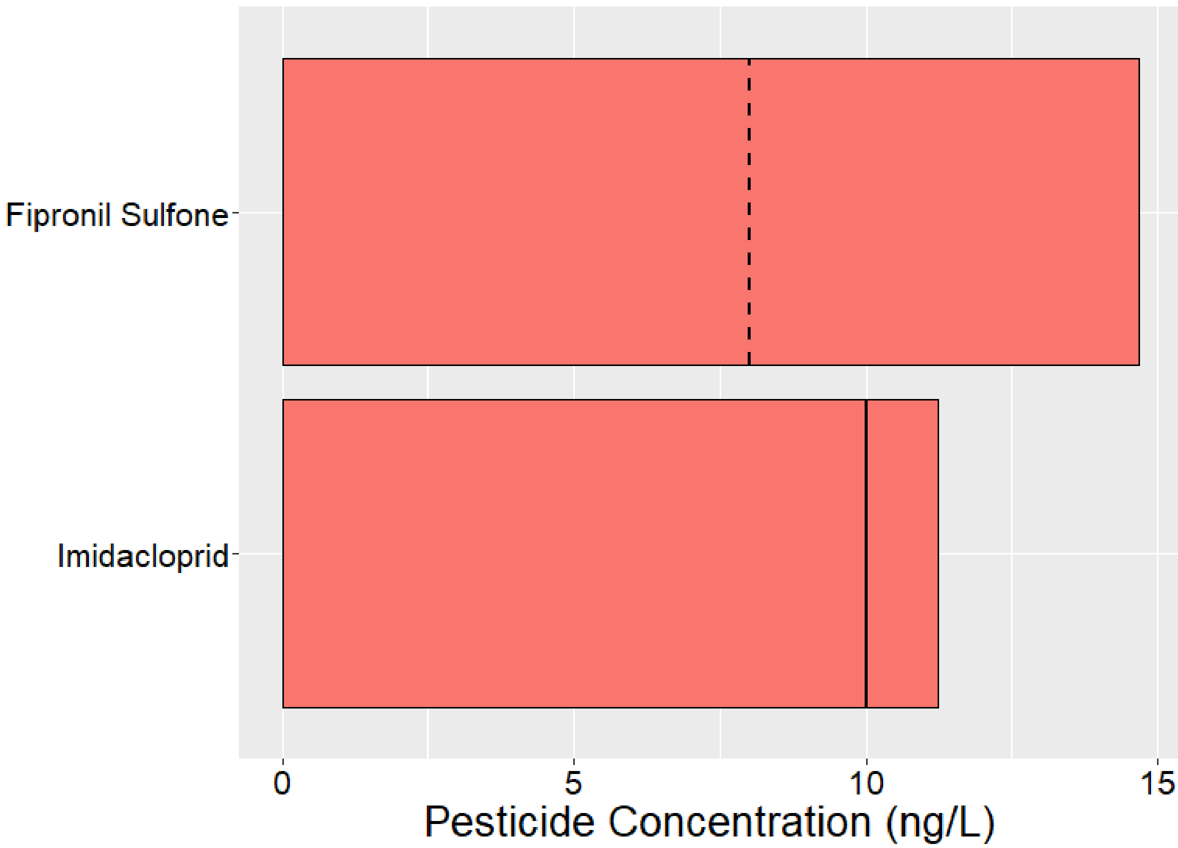


Figure 3-3. Water results that exceed toxicity thresholds. All values shown were measured at the mixed-use Trenton Road site. The solid line represents an Environmental Protection Agency, Office of Pesticide Protection chronic aquatic invertebrate benchmark (imidacloprid=10 ng/L). The dashed line represents chronic aquatic invertebrate toxicity thresholds that have not been formalized into an EPA OPP benchmark. This threshold for fipronil sulfone was established by Weston & Lydy 2014 (Fipronil sulfone=8 ng/L).

Fipronil is approved only for urban uses in California, and is used in a variety of applications including outdoor building sprays, underground termite treatment injections, gels for crack and crevice treatment, insect control baits, and pet flea and tick treatments (CDPR 2017a; Ensminger 2014). Fipronil and the three major fipronil degradates (desulfinyl, sulfide, and sulfone) were detected at levels above MDLs but below established EPA OPP benchmarks and available statewide CEC monitoring trigger levels. However, as noted above, a 2014 study showed higher toxicity of fipronil and its degradates to other freshwater invertebrate species compared to those used to establish the EPA OPP benchmark, especially *Chironomus dilutus* (Weston and Lydy 2014). This study measured a chronic toxicity threshold (EC_{50}) of 9-11 ng/L for fipronil sulfide and 8 ng/L for fipronil sulfone, levels that are substantially lower than EPA benchmarks for invertebrates (110 ng/L for fipronil sulfide and 37 ng/L for fipronil sulfone). The fipronil sulfone concentration measured at Trenton Road (14.7 ng/L) is below the lowest EPA benchmark but slightly above the chronic toxicity threshold reported by Weston and Lydy (2014) (Figure 3-3).

Chlorantraniliprole and clothianidin results were low, with all concentrations measured below MDLs and therefore reported as estimated concentrations.

Comparisons with Other Studies

Pesticide concentrations were compared to recently measured levels in the Sacramento-San Joaquin Delta, a nearby region with similarly high agricultural uses as well as mixed land-uses (CEDEN 2017, Project="Delta RMP 2015 Current Use Pesticides"; Moschet et al. 2017; **Table 3-4**). Overall, fewer pesticides were detected in the Russian River watershed compared to recent monitoring in the Delta, which has been conducted by the same laboratory with a nearly-identical target analyte list. Sites sampled in the Delta represent large upstream watersheds rather than local sources, and thus likely include substantially more diverse pesticide use but may not represent the highest concentrations observed in the region. Across a year of monthly sampling, between 30 and 40 pesticides were detected at each site monitored in the Delta, with the highest number of detections occurring during winter storm periods (CEDEN 2017, Project="Delta RMP 2015 Current Use Pesticides"). Compared to concentrations measured in the Delta, herbicides and insecticides were detected at relatively low to moderate levels in the Russian River, mostly within the range of the minimum or average concentrations recently measured in the Delta. In contrast, concentrations of the herbicides oxadiazon and prodiamine, measured at Trenton Road, were closer to the maximum concentrations measured in the Delta. Urban weed control may explain the higher concentrations measured at this mixed-use site.

Concentrations of the widely used urban insecticides fipronil and imidacloprid were also compared to urban-influenced regions in California. Fipronil and degradates measured at Trenton Road was mostly within the average to upper end of the range of previously measured values in several studies of agricultural and mixed-used regions of California (Weston et al. 2015; Gan et al. 2012; Weston and Lydy 2014), but on the lower end of the range of concentrations measured in the dominantly urban areas (Budd et al. 2015). In a California statewide survey conducted by DPR, median concentrations measured in urban areas of Northern California were lower than those measured in Southern California, but still well above concentrations measured at Trenton Road (fipronil: 33 ng/L; fipronil sulfone: 26 ng/L; fipronil desulfinyl: 15 ng/L; fipronil sulfide: 4 ng/L), with the exception of fipronil sulfide (measured in only 2 samples). Fipronil sulfide measured at Trenton Road was still below the median concentration measured in Southern California. Based on this study, fipronil use in urban areas is estimated to peak during the dry season (between April and November), and concentrations of fipronil are significantly higher during the first storms of the season (i.e., "first flush"). This suggests that fipronil concentrations measured during this study represent the high end of concentrations that can be expected at this site, although concentrations are likely to be greater farther upstream and closer to sources within the urban area. Indeed, during the first task of this pilot study, slightly higher concentrations of fipronil were measured further upstream from Trenton Road in the Santa Rosa area in March 2016, when expected use is lower. In contrast, degradate concentrations typically are not significantly different between the wet and dry season, and fipronil sulfone and desulfinyl represent a greater proportion of fipronils measured during the dry season, given the opportunities for degradation to occur during transport under low-flow conditions (Budd et al. 2015). This suggests that fipronil sulfone, which exceeded a recently identified chronic toxicity threshold (Weston and Lydy 2014) in this study, could represent an even greater toxicity concern during the dry season. The single imidacloprid detection at the Trenton Road site was on the lower end of the range of concentrations measured previously in both urban and mixed use areas (Weston et al. 2015).

Concentrations of fungicides were present at comparatively higher levels in this study: the maximum concentrations of boscalid, carbendazim (both a registered pesticide and a thiophanate-methyl degradate) and iprodione were greater than the maximum concentrations measured recently in the Delta (CEDEN 2017, Project="Delta RMP 2015 Current Use Pesticides"; Moschet et al. 2017; Table 3-4). Iprodione in particular was measured at Trenton Road at a level that was over two times the concentrations measured in the Delta by the Delta RMP in 2015-2016, and over ten times the concentrations measured in Cache Slough by scientists at UC Davis in winter 2016. Compared to other regions in the state, fungicides are expected to be applied in greater volume in the wine-growing regions of the Russian River; however, it is important to note that the highest fungicide concentrations measured at Trenton Road were much higher than those measured at other sites dominated by agricultural influences. These higher levels may have been due in part to the comparatively greater proportion of stormwater runoff captured in the sample collected at this site, based on the storm hydrographs measured downstream of each site (Appendix D). However, these results also suggest potential contributions from urban sources as well. Still, these relatively high-concentration compounds exhibit low aquatic toxicity, and are not considered compounds of concern based on levels measured in this study and available toxicity data.

Pesticides in Sediment

A total of six pesticides out of the 118 analyzed were detected in sediment, including two fungicides – boscalid and iprodione – and four insecticides – bifenthrin, and the legacy pesticide DDT and two of its degradates, DDD and DDE (**Table 3-5**). No herbicides were detected. Pesticide concentrations and total organic carbon measured at each site are presented in **Table 3-6**.

Concentrations on a dry weight and organic carbon basis for the six detected pesticides at each of the study sites are shown in **Figures 3-4A and 3-4B**, respectively. No pesticides or degradates were measured in bed sediment at Jimtown, where TOC concentrations were particularly low (0.4% dw; Table 3-6). Hydrophobic pesticides are largely sorbed to the organic fraction of sediment, so low organic carbon content may limit partitioning of these contaminants to sediment. Similar to the water samples, the greatest number of compounds – six – was detected at the Trenton Road site. The highest concentrations of the three current use pesticides detected were also found at the Trenton Road site. Concentrations of the legacy pesticide DDT and related compounds were similar across sites, and the location of the highest concentrations of these compounds varied. The majority of compounds were detected at more than one site.

Toxicity benchmarks are rarely available for sediment, but a comprehensive set of benchmarks was recently calculated by USGS including a lower threshold effects benchmark (TEB) and an upper Likely Effects Benchmark (LEB; Nowell et al. 2016). Below the TEB, toxic effects are not expected, between the TEB and LEB effects are indeterminate, and above the LEB effects are expected. None of the pesticide concentrations quantified or estimated were above the lowest benchmark calculated by USGS.

Monitoring trigger levels (MTLs) have been developed for fipronil in sediments of effluent dominated inland waterways, as well as bifenthrin, permethrin, and fipronil in coastal embayments. Fipronil was not detected in sediments. The method detection limits for bifenthrin and permethrin were above their respective MTLs, which are conservative benchmarks calculated with safety factors of 100, based on freshwater toxicity thresholds. While permethrin was not detected in this study, bifenthrin concentrations were measured at an order of magnitude or more above the MTL at two sites. Together, these results indicate a need for continued monitoring of bifenthrin, and pyrethroids in general.

Table 3-4. Comparison of water results with other studies (ng/L)

Pesticide	Type[1]	Region 1 Screening Study		DPR Surface Water database[2] (2012-2017)			Delta RMP, FY15/16 (Jabusch et al. *in prep)*				Delta Cache Slough (Moschet et al. 2016)	
		Max	% Detects	Max	Avg	% Detects	Min	Avg	Max	% Detects	Max	% Detects
Azoxystrobin	F	26.4	20%	3270	37	44%	3.7	43.9	347.8	75	25	98%
Boscalid	F	148.7	80%	11200	85	45%	3.0	26.1	118.0	93	368	100%
Carbendazim	F	196	80%	4870	37	46%	4.2	33.2	155.9	50		
Chlorantraniliprole	I	2.4	20%	3550	60	35%	4.0	28.7	260.0	55	110	78%
Clothianidin	I	2.4	20%	1340	8	5%						
Dichlorobenzenamine, 3,4-[3]	H (D)	5.7	20%	145	15	51	3.2	13.3	144.9	50		
Dichlorophenyl Urea, 3,4-	H (D)	8.9	60%				3.4	7.7	15.9	32		
Dichlorophenyl-3-methyl Urea, 3,4-	H (D)	11.2	20%				3.5	15.6	54.6	57		
Dithiopyr	H	23.3	20%	3990	15	24%	1.9	24.3	202.8	58	NQ	100%
Diuron	H	65.4	60%	44000	209	42%	3.3	55.1	450.8	73		
Fipronil	I	3.8	20%	752	13	24%	3.1	7.8	25.0	30	14	100%
Fipronil Desulfinyl	I (D)	6.7	20%	220	6	21%	2.1	4.6	13.1	20	4.5	100%
Fipronil Sulfide	I (D)	4.9	20%	102	1	9%	3.0	6.1	10.8	5	0.7	82%
Fipronil Sulfone	I (D)	14.7	20%	265	16	30%	3.9	6.0	12.2	8	9	100%
Fluopyram	F	69.0	20%								101	57%
Flutolanil	F	42.0	20%	58	0	1%						
Fluxapyroxad	F	12.4	20%	214	4	19%	4.8	18.7	71.4	55	76	100%
Imidacloprid	I	11.2	20%	12700	206	49%	3.9	13.4	60.1	52	50	57%
Iprodione	F	536.3	20%	1240	7	4%	6.0	65.2	201.4	15	50	47%
Oxadiazon	H	50	20%	1530	6	9%	7.7	18.1	50.4	8	87	8%
Prodiamine	H	10.8	20%	423	2	3%	8.5	8.5	8.5	3	19	16%
Simazine	H	15.9	20%	6400	20	25%	5.3	56.6	386.8	63	86	31%

1 - F = fungicide, H = herbicide, I = insecticide, (D) = degradate

2 - Data extracted from the California Department of Pesticide Regulation's Surface Water Database (CDPR 2017a). This database includes results from a wide range of sites throughout California, including agricultural, urban, and mixed-use sites. Data for 3,4-dichlorobenzenamine was not reported in the SURF database under this analyte name or 3,4-dichloroaniline; this data was instead extracted from CEDEN. Detected values

3 – 3,4-Dichlorobenzenamine is reported as 3,4-dichloroaniline in other studies

Table 3-5. Summary of compounds analyzed and detected in sediment samples

Pesticide Type[1]	Compounds Analyzed	Compounds Detected	Total Number of Detections[2]	Number of Sites with Detections
Fungicides	36	2	4	3
Herbicides	34	0	0	0
Insecticides	44	4	4 Q; 7 E	4
Synergists	2	0	0	0

1 – Degradates are included in the compounds counted within each pesticide type.
2 - Values split out between Q and E are detections that were either fully quantified or estimated at a level below the MDL. Those without a Q or E designation in the box indicate that all detections were quantified above the MDL.

Table 3-6. Sediment results - detected analytes. Results are reported both as raw concentrations (ug/g dw) and normalized by the total organic content measured at each site (ug/g-oc)

Pesticide	**Type[1]**	**TEB Threshold (µg/g-oc)[2]**	**LEB Threshold (µg/g-oc)[2]**	**USGS Threshold Type[3]**	**Detection Frequency**	**Maximum Conc.**	**MDL**	**Trenton Road[4]**	**Pull-Out[4]**	**Jimtown**	**Hopland[4]**	**Potter Valley[4]**
Total Organic Carbon (% dw)								2.89	1.54	0.4	2.22	1
Results (µg/kg dw)												
Bifenthrin	I					1.36	0.61	1.36	*0.4*			
Boscalid	F					3.00	1.19	2.54	1.81		3.00	
Iprodione	F					1.44	0.87	1.44				
p,p'-DDD	I (D)					0.76	0.98	*0.41*	*0.65*		*0.76*	*0.41*
p,p'-DDE	I (D)					1.51	0.97	*0.96*	*0.77*		*0.86*	1.51
p,p'-DDT	I					1.02	0.84	*0.51*			1.02	*0.40*
TOC-normalized Results (µg/g-OC)												
Bifenthrin	I	0.17	0.6	SSB	2 / 5	0.05		0.05	0.03	< 0.15	< 0.03	< 0.06
Boscalid	F	240	860	EqP	3 / 5	0.14		0.09	0.12	< 0.30	0.14	< 0.12
Iprodione	F	16	160	EqP	2 / 5	0.05		0.05	< 0.06	< 0.22	< 0.04	< 0.09
p,p'-DDD	I (D)	66	240	SSB	4 / 5	0.04		0.01	0.04	< 0.24	0.03	0.04
p,p'-DDE	I (D)	55	550	SSB	4 / 5	0.15		0.03	0.05	< 0.24	0.04	0.15
p,p'-DDT	I	33	200	SSB	3 / 5	0.05		0.02	< 0.05	< 0.21	0.05	0.04

1 – F = fungicide, H = herbicide, I = insecticide, (D) = degradate

2 – Threshold Effects Benchmark and Likely Effects Benchmark values were developed by USGS in Nowell et al. 2016.

3 – USGS thresholds were calculated using spiked sediment bioassay data (SSB) or using an equilibrium partitioning approach (EqP). Further discussion of these methods and their assumptions is described in Nowell et al. 2016.

4 – Estimated values, or values quantified below the method detection limit, are italicized and shown in red.

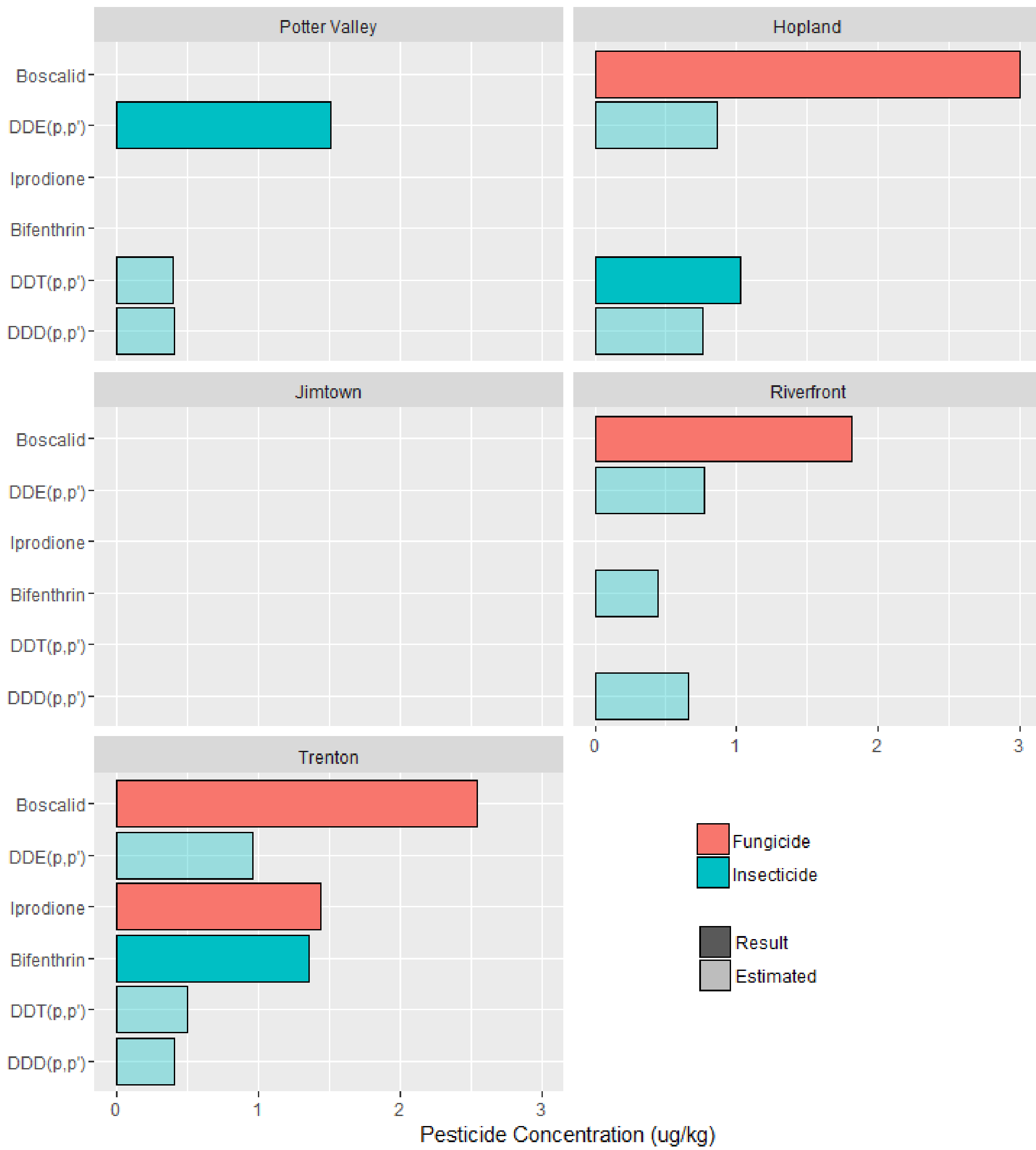


Figure 3-4A. Sediment results (µg/kg) by location – detected analytes

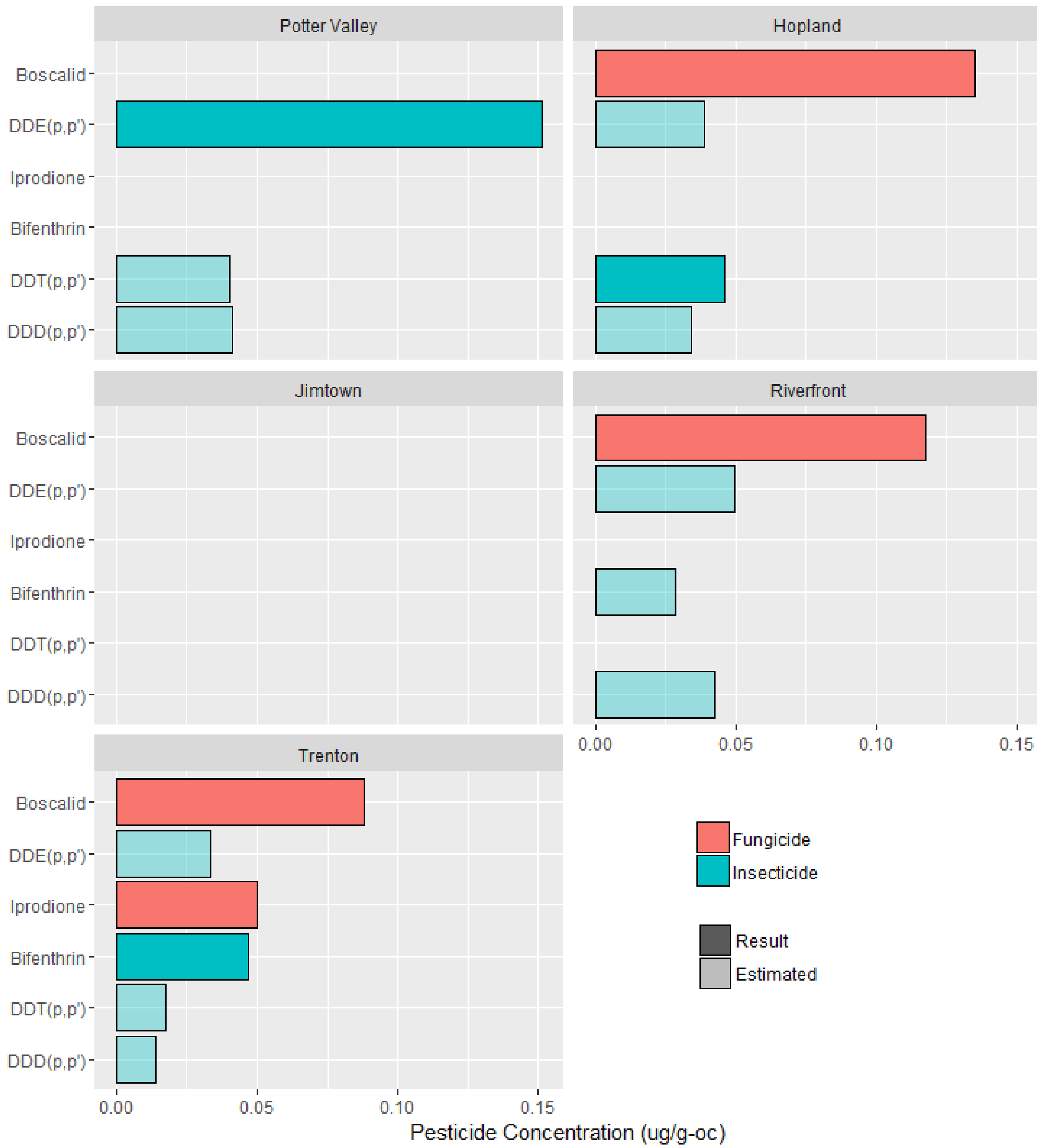


Figure 3-4B. Sediment results (μg/g-oc) by location – detected analytes

Fungicides
Detections of the two moderately hydrophobic fungicides found in sediment, boscalid and iprodione, corresponded with relatively high concentrations of these compounds in water. Agricultural pesticide use data from the PUR database shows a high volume of use for boscalid (7265 kgs total use from 2012-2014) in the watershed. Compared to detections in water, boscalid was detected in sediment at only three rather than four sites, but may not have been detected at the Jimtown site in part due to low TOC at that site.

In contrast, a relatively low overall agricultural use volume was reported for iprodione (39 kgs total use from 2012-2014), but an uncommonly high concentration in water was detected at Trenton Road, suggesting an urban runoff source for this fungicide. Iprodione was the highest concentration pesticide detected in water at the Trenton Road site, and was detected in sediment only at Trenton Road. The relatively low persistence of iprodione in water and sediment suggests that urban applications are common in the late summer and fall, during the period of sampling.

All concentrations of boscalid and iprodione measured in sediment were at least three orders of magnitude below the lowest USGS benchmark (TEBs calculated from water toxicity data using equilibrium partitioning; Nowell et al. 2016).

Herbicides
No herbicides were detected in sediment samples.

Insecticides
Bifenthrin, a highly toxic pyrethroid pesticide, was detected at the two farthest downstream sites in the watershed (Trenton Road and Pull-Out) at concentrations below the lowest USGS benchmark (TEB based on a spiked sediment bioassay with *H. azteca*). The TOC-normalized MDLs at the other three sites were below the TEB, indicating that trace levels of bifenthrin present at levels below the MDL are unlikely to cause toxic effects. However, the MDL at the low-TOC Jimtown site was within the analytical margin of error of this threshold (TEB=0.17 µg/g-oc; MDL=0.15 µg/g-oc), suggesting that lack of detection at this site may not necessarily indicate a lack of toxicity concern.

Agricultural use of bifenthrin in 2012-2014 in the watershed was very low (6 lbs applied total), suggesting primarily urban sources for this compound. Indeed, both sites where bifenthrin was detected (Trenton Road and Pull-Out) receive at least some urban runoff. In recent years, bifenthrin use has increased in urban areas of California, and due to its high toxicity and persistence in soils, is considered the dominant cause of pyrethroid toxicity in urban areas (Luo et al. 2017).

Bifenthrin was also found to be the single best predictor of *Hyalella azteca* toxicity measured during a USGS study of contaminants in 98 streams in seven metropolitan areas, with a target analyte list including 108 pesticides, metals, PAHs, and PCBs (Moran et al. 2012). Pyrethroids are known to be more toxic at lower temperatures: a 10-day spiked sediment study conducted in 2009 measured an LC_{50} at 18 °C that was less than half the LC_{50} measured at 23 °C, and suggested a relatively linear relationship between temperature and toxicity between 13 and 23 °C (Weston et al. 2009). Water temperatures measured at Trenton and Pull-Out sites (17-18 °C) as well as the other three sites (17-21 °C) were lower than the standard temperature used in the studies used by USGS to calculate the sediment benchmarks (23 °C).

Although the detected bifenthrin concentrations are considered low compared to those measured in previous studies focused on urban streams in California (see "Comparisons with Other Studies" below), the high toxicity and recent increases in urban use of this compound in California suggests that continued monitoring of this compound is needed, although recent restrictions have also been placed on outdoor use of this compound (Luo 2017, CDPR 2012). The bifenthrin concentration measured at the Trenton Road site was also two orders of magnitude above the statewide monitoring trigger level of bifenthrin in coastal embayment sediments (0.052 ng/g dw, Anderson et al. 2012); the method detection limit, 0.61 ng/g, is also an order of magnitude greater than this trigger level. These results further support the need to continue monitoring bifenthrin in sediments, particularly in urban areas, as analytical methods continue to improve.

The only other insecticides detected were the legacy pesticide DDT and its degradates DDD and DDE. In contrast with current use pesticides, these compounds were the most commonly detected pesticides in sediment and were found at similar concentrations at all sites, likely reflecting residual presence of these persistent legacy contaminants in soils. Many of the detected values were estimated, or measured at levels below MDLs. DDD and DDE were detected at all sites except Jimtown, but all DDD values were measured below the MDL. The DDE value measured at Hopland was also below the MDL. DDT was detected above the MDL at one site and below the MDL at two sites. These concentrations are considered very low values, several orders of magnitude below the calculated USGS benchmarks (Nowell et al. 2016).

Comparisons with Other Studies

Total pesticide detections in sediment in this study were low, including only three current use pesticides in addition to DDT and DDT degradates. In comparison, 17 of the 40 compounds that have been tested in agricultural areas of California as part of the Irrigated Lands Regulatory Program have been detected, including eight pyrethroids and frequent detections of chlorpyrifos, which is more commonly used on crops grown in the Central Valley compared to the Russian River watershed. It is notable that no other pyrethroids were detected during this study, although it is likely that targeted monitoring of urban areas would find additional compounds. Previous SWAMP urban pyrethroid monitoring between 2008 and 2012 detected permethrin, cyfluthrin, delamethrin, s-cypermethrin, and lambda cyhalothrin in addition to bifenthrin within urban creeks in Santa Rosa. Permethrin has also been detected downstream of this region on the Russian River (CDPR 2017b). Monitoring further upstream in urban creeks in the Santa Rosa region was conducted as part of the first element of this pilot study during September 2016; analysis of these samples resulted in several detections of other pyrethroids, including permethrin, lambda-cyhalothrin, cyfluthrin, cypermethrin, esfenvalerate, and deltamethrin.

Bifenthrin has been measured throughout the state, predominantly in studies of urban regions, and has been identified by multiple studies to be the dominant pyrethroid of aquatic toxicity concern (Moran et al. 2012). The highest concentrations of bifenthrin have been found in urban drainages or creeks; various studies of urban regions regularly find concentrations above 100 µg/kg dw (Kuivila et al. 2012; Weston et al. 2005; Holmes et al. 2008; Haldik and Kuivila 2012). Previous studies also suggest that concentrations of highly hydrophobic urban pesticides such as pyrethroids may be higher in urban creeks during the dry season, when dry-season runoff is not diluted by stormwater flow (Weston et al. 2005). Urban application and water use patterns should be taken carefully into consideration when designing future studies.

Similar to the present study, previous studies in the Russian River watershed did not detect bifenthrin at sites on the Russian River itself (at Alexander RV Park and downstream of Duncan Mills), but did detect it in urban areas, as measured in creeks within Santa Rosa (0.68-46.9 µg/L). Concentrations measured in this study at Trenton Road and Pull-Out are on the lower end of concentrations previously measured in Santa Rosa, which may be due to greater dilution of these samples compared to those that were collected within the City itself (CDPR 2017b, SWAMP SPoT program 2008-2014 data and SWAMP Statewide Project Urban Pyrethroid Status Monitoring [Study Codes 620, 639-641, 643, 645, 647], data also available in CEDEN). In 2012, DPR took actions to restrict the use of this high toxicity class of insecticides in urban areas (CDPR 2012).

Sediment detections of boscalid and iprodione, two moderately hydrophobic fungicides (log K_{ow} = 2.96 and 3.0, respectively), likely reflect the high use volumes of these compounds in the Russian River watershed. In studies of agriculturally influenced regions, boscalid has been regularly detected within the range of concentrations found in the Russian River watershed. One study of bed sediment in a California Central Coast watershed found boscalid in a creek sample and seven of eight estuary samples (5.0-9.4 µg/kg) (Smalling et al. 2013b). In a second study of agricultural streams in Maine, Wisconsin, and Idaho, boscalid was detected in 50% of samples (median = 2.1 µg/kg, max = 22.5 µg/kg; Smalling et al. 2013a). Iprodione was measured but not detected in these studies (Smalling et al. 2013a; Smalling et al. 2013b). In comparison, a study of pesticides in urban streams in northwest Washington showed water concentrations of iprodione that were well below the concentration measured in this study, but sediment concentrations that were well above (Carpenter et al. 2016). As explained above, concentrations of these compounds in Russian River sediment are not likely to be a toxicity concern.

Once a widely used insecticide prior to the 1980s, DDT and its degradates are currently still widely detected, although typically at low concentrations. Nine of the eleven detects in this study were estimated at values below MDLs at µg/kg levels. For comparison, in the SWAMP 2013 Statewide Stream Pollution Trends Study, a significant proportion of DDT and DDT degradates were non-detect, including over 50% of DDT measurements, but measured concentrations ranged up to 81, 220, and 33 µg/kg dw for DDT, DDD, and DDE, respectively (SFEI 2017, Project = Statewide Stream Pollution Trends Study 2013). Concentrations detected in the present study are low, likely reflecting residual soil contamination from historical use.

Non-Detects

The majority of compounds analyzed were not detected. However, for a subset of these compounds, MDLs were found to be above the lowest available benchmarks, indicating that the lack of detection may not necessarily mean that these compounds are not present at potentially concerning levels (Appendix C, Table C2). Additional method development, collection of larger sample volumes, and passive sampling techniques should be considered for future monitoring efforts in order to detect whether these compounds are present at levels of concern.

For dissolved-phase water samples, the majority of MDLs were well below available benchmarks. However, the MDL for DDT (4 ng/L) was higher than the EPA nationally recommended aquatic life criteria of 1 ng/L. Chronic toxicity thresholds are particularly low for pyrethroids, but improvements in the analytical method have lowered the MDLs for these compounds below these thresholds. However, for two pyrethroids measured, allethrin and tetramethrin, none of the benchmark sources used in this paper have chronic toxicity benchmarks. Although the MDLs for these two compounds are below acute toxicity benchmarks, it is possible that chronic toxicity impacts occur at lower contaminant levels.

For sediment samples, maximum and minimum TOC-normalized sediment MDLs were calculated based on the lowest and highest TOC values measured at any site in this study, and both MDLs were compared to the TEB and LEB thresholds established by USGS. For the most part the calculated sediment MDLs were below both thresholds. Of the cases in which one or both of the thresholds was exceeded by one or both of the MDLs, about half were instances of the maximum MDL exceeding an estimated TEB value, which tend to be particularly conservative. In only three cases was the upper benchmark (LEB) exceeded, and only by the maximum MDL calculated (deltamethrin, fipronil, and tebupirimfos).

The MDLs for bifenthrin and permethrin were also above the monitoring trigger level (MTL) recommended by the state CEC monitoring guidance for these compounds in coastal and estuarine sediments (no MTLs were calculated for freshwater). Although MTLs are conservative thresholds that do not necessarily indicate toxicity, this finding indicates that either (1) additional method development to lower available MDLs and/or (2) additional toxicity studies to reduce uncertainties about toxicity effects particularly in estuarine environments, is warranted for these compounds, as well as other highly toxic pyrethroids.

Comparison Between Prioritized Pesticides and Pesticides Detected

The purpose of the SWMP model is to identify priority pesticides of potential toxicity concern that should be monitored, rather than to identify all pesticides that are likely to be detected. Comparing the actual monitoring results to the model prioritization provides a useful method for evaluating the effectiveness of using this prioritization approach for future studies. While the modeling tool provides valuable information about pesticide use and toxicity, this list may not always overlap with those compounds that are detected at the highest frequencies or concentrations. In many cases, compounds that are detected at high levels but not highly prioritized may be of relatively low toxicity for the aquatic environment. In other cases, differences between the priority pesticide list and the monitoring results may point towards potential modifications that can be made to future development of both priority pesticide lists and monitoring study designs, to help make both as comprehensive as possible.

Sixty-one compounds were prioritized for monitoring due to potential concern based on both application levels and toxicity information (Appendix A). Nine of the 22 pesticides detected in water were initially prioritized for monitoring. These compounds generally had low log K_{ow} values (< 3), and thus would be expected to be rapidly flushed from the upper watersheds and transported downstream during an early fall storm. While several of the detected compounds were not applied in the late summer or early fall in 2012-2014, it is possible that use patterns may be slightly different in more recent years. In addition, the contribution from urban uses is not captured by the application dataset used in the agricultural version of the prioritization model used for this study.

In contrast, 52 compounds prioritized for monitoring were not detected. There are a number of possible explanations for compounds that were highly prioritized but not detected. First, as previously discussed, compounds applied predominantly during the winter and spring are expected to be flushed into surface waters during spring rains, rather than in the fall when monitoring for this study was conducted (see "Seasonal Timing" under the "Recommendations for Future Monitoring" section below). For this reason, the initial prioritization report recommended a second spring sampling effort (Appendix A). Second, 24 of these compounds were not detected because analytical methods were not available, particularly for several key degradates (see "Target Analyte List" under "Recommendations for Future Monitoring"). Third, the SWMP model was developed to inform surface water rather than sediment monitoring, and was not expected to be fully predictive of compounds that might be of highest concern in sediment. Fourth, use volumes vary year to year, so a prioritization based on 2012-2014 data may not fully represent 2016.

Additionally, smaller-scale spatial and temporal mismatches between pesticide application and sampling may have contributed to the relatively low number and concentrations of compounds sampled. In some cases, compounds are prioritized based on their high toxicity despite low use volumes, and may be diluted by the time they reach the Russian River or its major tributaries. In the present study, samples were also collected relatively early within the storm period, and samples collected at the northernmost sites may have characterized limited runoff from the storm. Furthermore, pesticides span a large range of physicochemical properties, and may be transported or degraded at different rates that make a wide range of compounds difficult to detect within a single grab sample. Alternative sampling methods could be considered to better capture the range of pesticides used in the watersheds (see "Sampling Methods" under "Recommendations for Future Monitoring").

On the other hand, because this prioritization exercise did not specifically address many urban applications by professionals or residents, it was unlikely to fully capture concerns relating more specifically to urban-use pesticides. 13 of the detected compounds were either considered low priorities for monitoring or were not identified by the modeling tool at all. For example, dithiopyr, fipronil (and three fipronil degradates), flutolanil, and prodiamine were detected at the most urban-influenced site in this study, Trenton Road, but were not identified by the monitoring prioritization tool. Dithiopyr and prodiamine are used as lawn weed killers, flutolanil is used as a turfgrass and ornamental plant fungal treatment, and fipronil is a commonly used urban professional and pet pest control product. Similarly, compounds like iprodione, fluxapyroxad, and diuron (and three diuron degradates) were not prioritized for monitoring due to their low volume of agricultural use, but are used in many urban applications: iprodione and fluxapyroxad are used as turfgrass fungal treatments, while diuron is commonly used as a weed-killer on urban rights-of-way and a paint additive.

Additionally, compounds of greatest concern identified in this monitoring study – imidacloprid and fipronil (and fipronil degradates) – are commonly or predominantly used in urban areas. While imidacloprid was prioritized for monitoring due to its uses in agricultural applications, the potential level of concern about this compound may have been underestimated due to the exclusion of urban residential uses. Results from this initial monitoring effort suggest that pesticide monitoring priorities for urban areas, as well as agricultural areas, should be included in future study designs for this watershed.

Lastly, it is notable that several diuron degradates detected were also not examined during the prioritization exercise because they are not addressed in the DPR prioritization model. Target analyte lists based on the DPR prioritization model should also take into consideration information about degradates or toxicity that may not yet be included in the model.

Recommendations for Future Monitoring

Urban Sources

This initial screening study design focused on pesticides in agricultural runoff, since the land uses in the Russian River watershed are primarily agricultural. However, the results clearly showed a higher number of pesticides detected and, in general, higher concentrations detected at the site most influenced by urban runoff (Trenton Road). All but one of the pesticides detected in this study were found at this site, including compounds that were not identified or not highly prioritized by the SWMP model using agricultural pesticide use data. Additionally, imidacloprid, fipronil sulfide and fipronil sulfone, common urban insecticides or insecticide degradates, were detected above chronic thresholds developed in recent toxicity studies (Roessink et al. 2013, Weston and Lydy 2014). Bifenthrin, another common urban pyrethroid insecticide, was detected at two orders of magnitude above a monitoring trigger level established for estuarine sediments in the statewide CEC monitoring guidance (Anderson et al. 2012). Fipronil and bifenthrin use reported within agricultural regions of the watershed are negligible (CDPR 2017c), clearly indicating urban sources for these insecticides of potential concern.

<u>Based on these results, additional monitoring of more urban-influenced surface waters and urban pesticides is recommended.</u> In particular, imidacloprid, fipronil, and fipronil degradates, which may be approaching levels of aquatic toxicity concern, are target analytes of interest. Further monitoring of bifenthrin should also be considered, given its high aquatic toxicity, detection at an urban-influenced site in the Russian River watershed, and high level of detection and relationship with amphipod toxicity in other studies (Moran et al. 2012). The DPR SWMP modeling tool can also be run on urban use mode to identify other urban pesticides that may be of interest using professional pesticide application data (Luo et al. 2013; Luo et al. 2017). This model does not include non-professional urban pesticide use, but DPR and other organizations have used market surveys and door-to-door residential surveys to supplement prioritizations developed with the SWMP model (CDPR 2017d; Osienski et al. 2010; Budd 2015; and others). Pesticides registered for urban uses can also be identified with DPR's pesticide registration database (CDPR 2017a).

The statewide framework for urban pesticide monitoring and reduction currently being developed by the State Water Resources Control Board, DPR, and the California Stormwater Quality Association presents an important opportunity to coordinate with and leverage statewide resources to conduct further urban pesticide monitoring (SWRCB 2017). Because similar pesticide use and trends tend to occur across urban watersheds, information generated through this statewide working group can and should be utilized to ensure monitoring data generated within the Russian River watershed is as valuable and cost-effective as possible.

Sampling Locations
Due to the limited number of samples available and the difficulty of accessing remote upper watershed sites, samples were collected at or near the bottom of watersheds, either on the main stem of the Russian River or along major tributaries (East Fork Russian River to the north and Mark West Creek to the south). In concept, initial screening at the bottom of watersheds can help to identify which regions should be targeted for further monitoring. A finding of low pesticide levels in the main stem would support the conclusion that aquatic toxicity from agricultural pesticide runoff is not an extremely high concern, at least during the time period of sampling.

However, the low concentrations and number of detections found at these sites do not necessarily exclude the potential for pesticide toxicity to occur higher in these watersheds, at locations that are closer to sources and potentially less diluted by runoff from nearby uncontaminated regions. Monitoring conducted further upstream in creeks in the Santa Rosa region as part of the first element of this pilot study, for example, found higher concentrations of fipronil compared to this study, as well as detectable levels of a number of pyrethroids not detected during this study. Significant concentrations of fipronil and pyrethroids detected in wastewater treatment plant effluent, particularly the Ukiah wastewater treatment plant, also suggest that monitoring of urban use pesticides in the less-populated regions of the Russian River watershed downstream of point source discharges may be needed, particularly during periods of discharge. <u>A larger screening study might consider additional site reconnaissance in order to monitor key agricultural and urban watersheds closer to source areas.</u>

Seasonal Timing
Another significant data gap remains in the timing of sample collection (Appendix D). It is expected that higher pesticide concentrations will be found in streams during periods when high use overlaps with high rainfall, leading to runoff. At the same time, stormwater runoff that occurs immediately following the dry season can be expected to deliver significant pesticide loads that have accumulated on land during the dry season, when many prioritized pesticides are applied at higher quantities.

The current study targeted pesticides that fall in this latter category, with sampling occurring during a storm event at the beginning of the fall wet season following summer dry season pesticide applications. However, some of the highest use pesticides in the Russian River watershed are predominantly applied in the spring. Mancozeb (which is not recommended for monitoring, although the degradate ethylene thiourea is recommended) and glyphosate (which is considered to have low aquatic toxicity but has recently been identified as a probable human carcinogen), the two highest-use pesticides, are predominantly applied between February and April. Other pesticides in the recommended list that are predominantly applied during early spring months include flumioxazin, oxyfluorfen, pendimethalin, oxytetracycline, thiophanate-methyl, chlorpyrifos, oryazlin, and simazine. Although simazine and the thiophanate-methyl degradate carbendazim were detected in this study, in general these chemicals and their degradates would be best monitored during the spring, during concurrent periods of high use and high rainfall.

Additional monitoring in spring 2017 has occurred as part of the USGS National Water Quality Assessment Pesticide National Synthesis Project. However, the USGS study targeted ambient concentrations rather than periods of high runoff, and the target analyte list did not include many pesticides prioritized for monitoring in the Russian River watershed. Further monitoring of spring runoff with an expanded pesticide target analyte list is recommended.

Composite or Passive Sampling

Grab samples collected during a single time point, as done in this initial screening study, provide valuable quantitative information about contaminants present at a single snapshot in time, but alone provide limited information about the presence and concentrations of contaminants over time. Particularly in agricultural areas, pesticide applications occur in pulses, and resulting environmental contamination may not be captured within any one particular grab sample. Similarly, transport via stormwater runoff can be variable and often difficult to predict, depending on watershed-specific land use, hydrology, irrigation methods, and previous storm patterns.

For example, the water samples collected during this study, particularly at the more rural sites to the north (i.e., Potter Valley and Hopland), may have missed a stronger pulse of pesticides delivered later in the storm (Appendix D). Additionally, the size of this storm may not have been substantial enough to mobilize more sediment-bound pesticides from upper watersheds into the main stem of the Russian River. Several of the more highly prioritized pesticides that were not detected – cyprodinil, pyraclostrobin, trifloxystrobin, difenoconazole, quinoxyfen, etoxazole, methoxyfenozide, fenhexamid – have $\log K_{ow}$ values in the range of 3.5-8, indicating they are likely to partition to sediment; it is possible that they were not transported downstream during this storm.

While the timing of single grab samples can be optimized based on known historical patterns of pesticide application and stormwater runoff, it is also recommended that multiple samples be taken over time. If resources are limited, passive or composite sampling over the course of a storm or longer time period could be considered during future monitoring efforts, to ensure pulses of contaminants are not missed. Although passive sampling may not yield strong quantitative results, it may have the benefit of more comprehensively characterizing which compounds are present, including relatively low-concentration compounds of concern such as imidacloprid, fipronil and fipronil degradates (Lao et al. 2012, Alvarez et al. 2013, Scoy-DaSilva et al. 2014, Lao et al. 2016, Ensminger et al. 2017). Some passive samplers may also have the added benefit of being able to detect low levels of highly toxic pesticides, such as pyrethroids (Moschet et al. 2014b).

Expanding the Target Analyte List

The USGS-CWSC pesticide target analyte list is one of the most comprehensive currently available. However, pesticide use data and new information from novel screening methods suggest that still other potential pesticides and degradates of concern that were not analyzed could be present. Several pesticides and degradates not included in the USGS method but identified during the prioritization process are listed below (see Appendix A for further description of the prioritization process). Compounds are listed in approximate order of priority based on the prioritization score and best professional judgment.

- Ethylene thiourea (mancozeb degradate; mancozeb is the highest used pesticide in the Russian River watershed)

- 1,2,4-triazole; triazole alanine; triazole acetic acid (myclobutanil and other triazole degradate)
- THPA; 482-HA; APF (flumioxazin degradates)
- Etoxazole
- Diflubenzuron (high toxicity but very low use)
- Oxytetracycline, calcium complex
- Chlorantraniliprole degradates
- Endosulfan (currently being phased out)
- Pyridaben degradates
- Buprofezin
- Glufosinate-ammonium
- Bifenazate degradates
- Metrafenone
- Abamectin
- Paraquat dichloride
- Sulfometuron-methyl
- Dimethoate
- Fenbutatin-oxide
- Spinosad
- Diquat Dibromide
- Spimetoram
- Phosmet
- Acequinocyl
- Glyphosate

<u>Out of this long list, ethylene thiourea, a degradate of the highest priority pesticide in the Russian River watershed (mancozeb), is a key compound for which analytical method development should be prioritized.</u>

Other studies have used non-targeted screening methods to identify potential compounds that traditional targeted analytical methods may be missing (Moschet et al. 2017, Moschet et al. 2014a). In addition to detecting a number of pesticide compounds not currently included on the USGS-CWSC list, one study used a LC-HRMS non-targeted screening method that included an extended screening for over 130 transformation products, including the high-priority mancozeb degradate ethylene thiourea and several triazole degradates (Moschet et al. 2014a). A second study used non-targeted LC-QTOF-MS and GC-QTOF-MS methods in the Delta Cache Slough complex to screen for over 5,000 target and suspect compounds; in this study, the insecticide dimethoate was detected, a pesticide that is used in the Russian River watershed but was not analyzed in this study (Moschet et al. 2017; Appendix A, Table 3-1). While many compounds may not yet be quantifiable using currently available methods, non-targeted screening methods are valuable tools for periodic monitoring to screen for the presence of compounds that might otherwise be missed.

Conclusions

Water and sediment samples were collected from five sites on the Russian River and its tributaries in fall 2016 and analyzed for an extensive list of current use pesticides. A total of 22 pesticides and degradates out of a list of 162 analytes (13%) were detected at one or more sites in dissolved water, none of the 131 pesticides analyzed in suspended sediment were detected, and six of the 118 pesticides analyzed in bed sediment (5%) were detected at one or more sites.

Relative to EPA or USGS benchmarks, only a single exceedance was noted: Imidacloprid was detected above the EPA OPP chronic invertebrate aquatic life benchmark at the mixed-use, Trenton Road site, likely reflecting urban runoff sources. A recent toxicity study also suggests that the urban insecticide fipronil and its degradates could be approaching levels of concern at this site. These compounds should be considered high priorities for continued monitoring. A third common urban-use pesticide, bifenthrin, was detected above a monitoring trigger level established by the statewide CEC monitoring guidance for estuarine sediments at two sites with the greatest influence from urban runoff sources, and is minimally applied in agricultural regions in the watershed. This highlights the need for additional monitoring of this compound, and pyrethroids more generally, in urban areas.

Concentrations of most compounds were below or within the range of concentrations measured in other agricultural or mixed-use regions in California, including recently measured values in the more highly agricultural Sacramento-San Joaquin Delta region. However, concentrations of some fungicides and fipronil degradates were found to be in the upper range of those previously measured in agricultural and mixed-use regions. Fipronil degradates could potentially be present at levels of concern, while fungicide concentrations are likely of low concern.

These preliminary results suggest that pesticide toxicity from agricultural runoff is not likely to be a major concern in the Russian River watershed in the fall season. However, additional monitoring in the northern region of the watershed above Cloverdale may be warranted due to the limited amount of stormwater runoff that was captured in this sampling effort. Additionally, a number of agricultural pesticides are predominantly applied in the winter and spring, indicating the importance of additional monitoring during the spring wet season. Finally, results of this study suggest urban areas may be significant sources of pesticides and should be targeted in future monitoring efforts.

Future monitoring is recommended both in the short- and long-term. Additional monitoring targeted at characterizing urban areas and spring runoff is needed to provide a more robust initial characterization of pesticide levels in the watershed. Grab samples collected during a single time point are not fully representative of the variability and range of pesticide compounds and concentrations that may occur at any one location, so further monitoring of additional time points during the fall season may also be desirable. If resources are limited, composite or passive sampling over longer time periods is recommended to ensure a more robust characterization of runoff, particularly in more rural or agricultural regions where stormwater runoff may be more variable.

Periodic monitoring of both water and sediment is recommended to identify any potential new concerns over time, based on changing pesticide use patterns, improved analytical methods, and new toxicity studies. Agricultural pesticide monitoring prioritization with the DPR prioritization model provided valuable information about regional pesticide use and toxicity, but should be amended to take into consideration urban-use pesticides using the urban pesticide model and supplementary information on residential urban use, as well as new toxicity information and newly identified degradates that are not included in the modeling tool. As resources are available, non-targeted analyses are recommended on a less frequent but recurring basis in order to identify any high priority compounds that may not be captured using traditional targeted analyses, including pesticide degradates.

References

Anderson, P.D., Denslow, N.D., Drewes, J.E., Olivieri, A.W., Schlenk, D., Scott, G.I., Snyder, S.A. 2012. Monitoring Strategies for Chemicals of Emerging Concern (CECs) in California's Aquatic Ecosystems – Recommendations of a Science Advisory Panel. Southern California Coastal Water Research Project, Costa Mesa, CA.

Alvarez, D.A., Maruya, K.A., Dodder, NG., Lao, W, Furlong, E.T., Smalling, K.L. 2013. Occurrence of contaminants of emerging concern along the California coast (2009-2010) using passive sampling devicies. Marine Pollution Bulletin. 81(2): 347-354. doi: 10.1016/j.marpolbul.2013.04.022

Budd, R. 2015. Survey of Pesticide Use by Homeowners in Two California Residential Neighborhoods. California Department of Pesticide Regulation, Sacramento, CA. http://www.cdpr.ca.gov/docs/emon/pubs/ehapreps/analysis_memos/res_pest_use_survey_budd.pdf

Budd, R., Ensminger, M., Wang, D., and Goh, K.S. 2015. Monitoring Fipronil and Degradates in California Surface Waters, 2008-2013. J. Environ. Qual. Doi: 10.2134/jeq2015.01.0018

California Environmental Data Exchange Network (CEDEN). Sacramento, CA. 2010 [cited 20170801]. Available from: http://www.ceden.org

California Department of Pesticide Regulation (CDPR). 2012. Department of Pesticide Regulation Announces New Restrictions to Protect Water Quality in Urban Areas (press release). http://www.cdpr.ca.gov/docs/pressrls/2012/120718.htm

California Department of Pesticide Regulation (CDPR). 2017a. California Product / Label Database Queries and Lists.

California Department of Pesticide Regulation (CDPR). 2017b. Surface Water Monitoring Database (SURF). Updated through June 10, 2017. http://www.cdpr.ca.gov/docs/emon/surfwtr/surfdata.htm

California Department of Pesticide Regulation (CDPR). 2017c. Pesticide Use Reporting (PUR). Pesticide Use Report Data. Updated through 2015. http://www.cdpr.ca.gov/docs/pur/purmain.htm

California Department of Pesticide Regulation (CDPR). 2017d. Reports of Pesticide Sold in California. http://www.cdpr.ca.gov/docs/mill/nopdsold.htm

Carpenter, K.D., Kuivila, K.M., Hladik, M.L, Haluska, T., and Cole, M.B. 2016. Storm-event-transport of urban-use pesticides to streams likely impairs invertebrate assemblages. Environmental Monitoring and Management 188: 345. doi: 10.1007/s10661-016-5215-5

Dodder, N.G., Mehinto, A.C., Maruya, K.A. 2015. Monitoring of Constituents of Emerging Concern (CECs) in California's Aquatic Ecosystem - Pilot Study Design and QA/QC Guidance (No. 854). Southern California Coastal Water Research Project Authority, Costa Mesa, CA.

Ensminger M. 2014. Review of Representative Currently Registered Fipronil Product Labels in California, Department of Pesticide Regulation.

Ensminger, M.P., Vasquez, M., Tsai, H.-J., Mohammed, S., Van Scoy, A., Goodell, K., Cho, G., Goh, K.S. 2017. Continuous low-level aquatic monitoring (CLAM) samplers for pesticide contaminant screening in urban runoff: Analytical approach and a field test case. Chemosphere 184, 1028–1035. doi:10.1016/j.chemosphere.2017.06.085

Gan, J., Bondarenko, S., Oki, L., Haver, D., Li, J.X. 2012. Occurrence of Fipronil and Its Biologically Active Derivatives in Urban Residential Runoff. Environ. Sci. Technol. 46, 1489–1495. doi:10.1021/es202904x

Gatidou, G., Thomaidis, N.S. 2007. Evaluation of single and joint toxic effects of two antifouling biocides, their main metabolites and copper using phytoplankton bioassays. Aquat. Toxicol. 85, 184–191. doi:10.1016/j.aquatox.2007.09.002

Hladik, M., Calhoun, D.L. 2012. Analysis of the herbicide diuron, three diuron degradates, and six neonicotinoid insecticides in water-Method details and application to two Georgia streams (Report No. 2012–5206), Scientific Investigations Report. Reston, VA.

Hladik, M., McWayne, M.M. 2012. Methods of analysis-Determination of pesticides in sediment using gas chromatography/mass spectrometry (Report No. 5-C3), Techniques and Methods. Reston, VA.

Hladik, M.L., Kuivila, K.M. 2012. Pyrethroid insecticides in bed sediments from urban and agricultural streams across the United States. J. Environ. Monit. 14, 1838–1845.

Hladik, M.L., Smalling, K.L., Kuivila, K.M. 2008. A Multi-residue Method for the Analysis of Pesticides and Pesticide Degradates in Water Using HLB Solid-phase Extraction and Gas Chromatography–Ion Trap Mass Spectrometry. Bull. Environ. Contam. Toxicol. 80, 139–144. doi:10.1007/s00128-007-9332-2

Jabusch, T., Yee, D., Franz, A. 2016. Quality Assurance Program Plan for the Delta Regional Monitoring Program. San Francisco Estuary Institute. Richmond, CA.

Kuivila, K., Hladik, M. 2008. Understanding the Occurrence and Transport of Current-use Pesticides in the San Francisco Estuary Watershed. San Francisco Estuary and Watershed Science 6.

Kuivila, K.M., Hladik, M.L., Ingersoll, C.G., Kemble, N.E., Moran, P.W., Calhoun, D.L., Nowell, L.H., Gilliom, R.J. 2012. Occurrence and Potential Sources of Pyrethroid Insecticides in Stream Sediments from Seven U.S. Metropolitan Areas. Environ. Sci. Technol. 46, 4297–4303. doi:10.1021/es2044882

Lao, W., Tiefenthaler, L., Greenstein, D.J., Maruya, K.A., Bay, S.M., Ritter, K., Schiff, K. 2012. Pyrethroids in Southern California coastal sediments. Environmental Toxicology and Chemistry, 31: 1649-1656. doi: 10.1002/etc.1867

Luo, Y., Deng, X., Budd, R., Starner, K., Ensminger, M.P. 2013. Methodology for Prioritizing Pesticides for Surface Water Monitoring in Agricultural and Urban Areas. California Department of Pesticide Regulation, Sacramento, CA.

Luo, Y. 2015. Surface Water Monitoring Prioritization Model (SWMP). California Department of Pesticide Regulation. California Department of Pesticide Regulation, Sacramento, CA. http://www.cdpr.ca.gov/docs/emon/surfwtr/sw_models.htm

Luo, Y. 2017. Modeling bifenthrin outdoor uses in residential areas of California. California Department of Pesticide Regulation, Sacramento, CA.

Luo, Y., Ensminger, M.P., Budd, R., Wang, D., Deng, X. 2017. Methodology for prioritizing areas of interest for surface water monitoring of pesticides in urban receiving waters of California. California Department of Pesticide Regulation, Sacramento, CA.

Luo, Y. *personal communication*. Updated Benchmark Equivalent values. California Departmetn of Pesticide Regulation, Sacramento, CA. August 9-11, 2017.

Moran, P.W., Calhoun, D.L., Nowell, L.H., Kemble, N.E., Ingersoll, C.G., Hladik, M., Kuivila, K., Falcone, J.A., Gilliom, R.J. 2012. Contaminants in stream sediments from seven U.S. metropolitan areas: Data summary of a National Pilot Study (Report No. 2011–5092), Scientific Investigations Report. Reston, VA.

Moschet, C., Lew, B.M., Hasenbein, S., Anumol, T., Young, T.M. 2017. LC- and GC-QTOF-MS as Complementary Tools for a Comprehensive Micropollutant Analysis in Aquatic Systems. Environ. Sci. Technol. 51, 1553–1561. doi:10.1021/acs.est.6b05352

Moschet, C., Vermeirssen, E.L.M., Seiz, R., Pfefferli, H., Hollender, J. 2014a. Picogram per liter detections of pyrethroids and organophosphates in surface waters using passive sampling. Water Res. 66, 411–422. doi:10.1016/j.watres.2014.08.032

Moschet, C., Wittmer, I., Simovic, J., Junghans, M., Piazzoli, A., Singer, H., Stamm, C., Leu, C., Hollender, J. 2014b. How a Complete Pesticide Screening Changes the Assessment of Surface Water Quality. Environ. Sci. Technol. 48, 5423–5432. doi:10.1021/es500371t

Nowell, L.H., Norman, J.E., Ingersoll, C.G., Moran, P.W. 2016. Development and application of freshwater sediment-toxicity benchmarks for currently used pesticides. Sci. Total Environ. 550, 835–850. doi:10.1016/j.scitotenv.2016.01.081

Osienski, K., Lisker, E., and Budd, R. 2010. Survey of Pesticide Products Sold in Retail Stores in Northern and Southern California, 2010. California Department of Pesticide Regulation, Sacramento, CA. http://www.cdpr.ca.gov/docs/emon/surfwtr/swanalysismemo/retail_memo_final.pdf

Pesce, S., Lissalde, S., Lavieille, D., Margoum, C., Mazzella, N., Roubeix, V., Montuelle, B. 2010. Evaluation of single and joint toxic effects of diuron and its main metabolites on natural phototrophic biofilms using a pollution-induced community tolerance (PICT) approach. Aquat. Toxicol. 99, 492–499. doi:10.1016/j.aquatox.2010.06.006

Roessink, I., Merga, L.B., Zweers, H.J., Van den Brink, P.J. 2013. The neonicotinoid imidacloprid shows high chronic toxicity to mayfly nymphs. Environ. Toxicol. Chem. 32, 1096–1100. doi:10.1002/etc.2201

Russian River Watershed Association (RRWA). 2016. Russian River Watershed – About Us. http://www.rrwatershed.org/about/

San Francisco Estuary Institute (SFEI). 2017. Contaminant Data Display and Download. cd3.sfei.org.

Scoy-DaSilva, A.V., Poulsen, A., Tjeerdema, R. 2014. The Potential of POCIS and SPMD Passive Samplers to Measure Pesticides in California Surface Waters. Department of Environmental Toxicology, University of California, Davis.

Smalling, K.L., Kuivila, K.M., Orlando, J.L., Phillips, B.M., Anderson, B.S., Siegler, K., Hunt, J.W., Hamilton, M. 2013a. Environmental fate of fungicides and other current-use pesticides in a central California estuary. Mar. Pollut. Bull. 73, 144–153. doi:10.1016/j.marpolbul.2013.05.028

Smalling, K.L., Reilly, T.J., Sandstrom, M.W., Kuivila, K.M. 2013b. Occurrence and persistence of fungicides in bed sediments and suspended solids from three targeted use areas in the United States. Sci. Total Environ. 447, 179–185. doi:10.1016/j.scitotenv.2013.01.021

State Water Resources Control Board, Division of Water Quality. 2017. Strategy to Optimize Resource Management of Stormwater, Attachment A: Establish Statewide Framework for Urban Pesticides Reduction. http://www.waterboards.ca.gov/water_issues/programs/stormwater/storms/docs/ obj6_proj6a/work_team_summary_8_4_17.pdf

United States Environmental Protection Agency (USEPA). 2003. Reregistration Eligibility Decision for Diuron, Case Number 0046. Office of Pesticide Programs. Washington, D.C. https://www3.epa.gov/pesticides/chem_search/reg_actions/reregistration/ red_PC-035505_30-Sep-03.pdf

United States Environmental Protection Agency (USEPA). 2008. EFED Problem Formulation for the Registration Review of Imidacloprid. Office of Pesticide Programs. Washington, D.C.

United States Environmental Protection Agency (USEPA). 2009a. Diuron. Drinking Water Treatability Database. Office of Pesticide Programs. Washington, D.C. https://iaspub.epa.gov/tdb/pages/contaminant/contaminantOverview.do?contaminantId= 10440

United States Environmental Protection Agency (USEPA). 2009b. Azoxystrobin Summary Document. Registration Review: Initial Docket. Case No. 7020. Office of Pesticide Programs. Washington, D.C. Docket Number EPA-HQ-OPP-2009-0835. https://www.regulations.gov/document?D=EPA-HQ-OPP-2009-0835-0002

United States Environmental Protection Agency (USEPA). 2011. Prodiamine Amended Final Work Plan. Registration Review. Case Number 7201. Office of Pesticide Programs. Washington, D.C. Docket Number EPA-HQ-OPP-2010-0920. https://www.regulations.gov/document?D=EPA-HQ-OPP-2010-0920-0015

United States Environmental Protection Agency (USEPA). 2012. *Registration Decision for the New Active Ingredient Fluxapyroxad*. May 2012. Office of Pesticide Programs. Washington, D.C. Docket Number EPA-HQ-OPP_2010-0421. https://www.regulations.gov/document?D=EPA-HQ-OPP-2010-0421-0020

United States Environmental Protection Agency (USEPA). 2013a. *Iprodione Final work Plan. Registration Review. Case Number 2335*. Docket Number EPA-HQ-OPP-2012-0392. https://www.regulations.gov/document?D=EPA-HQ-OPP-2012-0392-0016

United States Environmental Protection Agency (USEPA). 2013b. *Dithiopyr Preliminary Work Plan. Registration Review: Initial Docket. Case Number 7225.* Office of Pesticide Programs. Washington, D.C. Docket Number EPA-HQ-OPP-2013-0750. https://www.regulations.gov/document?D=EPA-HQ-OPP-2013-0750-0007

United States Environmental Protection Agency (USEPA). 2013c. *Simazine Final Work Plan. Registration Review. Case Number 70.* Office of Pesticide Programs. Washington, D.C. Docket Number EPA-HQ-OPP-2013-0251.https://www.regulations.gov/document?D=EPA-HQ-OPP-2013-0251-0008

United States Environmental Protection Agency (USEPA). 2014a.*Thiophanate Methyl & Carbendazim Preliminary Work Plan. Registration Review: Initial Docket. Case Number 2680.* Office of Pesticide Programs. Washington, D.C. Docket Number EPA-HQ-OPP-2014-0004. https://www.regulations.gov/document?D=EPA-HQ-OPP-2014-0004-0011

United States Environmental Protection Agency (USEPA). 2014b. *Flutolanil Proposed Interim Registration Review Decision*. *Case Number 7010*. Office of Pesticide Programs. Washington, D.C. Docket Number EPA-HQ-OPP-2008-0148. https://www.regulations.gov/document?D=EPA-HQ-OPP-2008-0148-0020

United States Environmental Protection Agency (USEPA). 2014c. *Oxadiazon Preliminary Work Plan. Registration Review: Initial Docket. Case Number 2485.* Office of Pesticide Programs. Washington, D.C. Docket Number EPA-HQ-OPP-2014-0782. https://www.regulations.gov/document?D=EPA-HQ-OPP-2014-0782-0002

United States Environmental Protection Agency (USEPA). 2016. Preliminary Aquatic Risk Assessment to Support the Registration Review of Imidacloprid. Office of Pesticide Programs. Washington, D.C. Docket Numbers EPA-HQ-OPP-2008-0844 and EPA-HQ-OPP-2017-0011. https://www.regulations.gov/document?D=EPA-HQ-OPP-2008-0844-1086

Weston, D.P., Chen, D., Lydy, M.J. 2015. Stormwater-related transport of the insecticides bifenthrin, fipronil, imidacloprid, and chlorpyrifos into a tidal wetland, San Francisco Bay, California. Sci. Total Environ. 527, 18–25. doi:10.1016/j.scitotenv.2015.04.095

Weston, D.P., Holmes, R.W., You, J., Lydy, M.J. 2005. Aquatic Toxicity Due to Residential Use of Pyrethroid Insecticides. Environ. Sci. Technol. 39, 9778–9784. doi:10.1021/es0506354

Weston, D.P., Lydy, M.J. 2014. Toxicity of the Insecticide Fipronil and Its Degradates to Benthic Macroinvertebrates of Urban Streams. Environ. Sci. Technol. 48, 1290–1297. doi:10.1021/es4045874

Weston, D.P., You, J., Harwood, A.D., Lydy, M.J. 2009. Whole sediment toxicity identification evaluation tools for pyrethroid insecticides: III. Temperature manipulation. Environ. Toxicol. Chem. 28, 173–180.

Wofford, P., Farnsworth, G., Verder-Carlos, M., Prichard, A., Goh, K.S., Singhasemanon, N., Alder, D., Wagner, S. 2017. US EPA Preliminary Aquatic Ecological Risk Assessment to Support the Registration Review of Imidacloprid (Case #7605, Docket ID #EPA-HQ-OPP-2008-0844). Comment Letter. California Department of Pesticide Regulation.

Appendix A. Agricultural Pesticide Prioritization Report

Introduction

This recommended agricultural pesticides monitoring list (**Table A-1**) was developed using the California Department of Pesticide Regulation's (DPR) Pesticides Use Reporting (PUR) database and Surface Water Prevention Program (SWPP) pesticide monitoring prioritization model, which utilizes pesticide chemical toxicity benchmarks and county use data to run a watershed-based pesticide prioritization algorithm (http://cdpr.ca.gov/docs/emon/surfwtr/sw_models.htm). Table A-1 provides a list of pesticides recommended for monitoring in the Russian River watershed. This recommended list is a modification of direct output from the PUR-based prioritization model, based on an aggregation of results over several different time periods and regions, more recent or external sources of toxicity information (the PUR database only includes toxicity and use data up to 2014), and best professional judgment. Factors considered in the development of this prioritization list include:

- Pesticide use volume
- Toxicity benchmarks
- Chemical properties (half-life, bioavailability)
- Recent use trends
- Seasonal and spatial use patterns
- Pesticide application method (e.g., ground vs. aerial application; low-flow vs. flood irrigation)

This document explains the data and parameters used to develop the monitoring priority analyte list, to help guide the use of the list in developing monitoring plans. Appendix A includes maps of total agricultural pesticide application volumes over the period 2012-2014 for several of the highest priority chemicals across a range of application types, and can be used to guide monitoring site selection.

Data Source

Pesticide use data were provided through the California Department of Pesticide Regulation's Pesticides Use Database. This database includes the total pounds of agricultural pesticides applied in each township-range section each month, but does not include chemicals used in seed coatings or adjuvants (substances added to improve performance of the pesticide, including dispersants, activators, wetter-spreaders, feeding stimulants, soil penetrants, etc.). Data in this database are also broken down by the product within which the chemical was applied and the application use type; however, for this prioritization, data were aggregated across these factors. Only agricultural pesticide applications within the boundaries of the Region 1 Russian River watershed were considered in this prioritization effort.

In some cases, additional chemicals were added to this list or recommended for future monitoring based on compounds of recent regulatory interest, compounds of high concern in other regions, and expert judgment.

Prioritization Method

DPR Pesticide Use Reporting – SWPP Monitoring Prioritization Model

For a specific region and time period, the DPR SWPP monitoring prioritization model (hereafter referred to as the "DPR prioritization tool") produces a ranked list of pesticides and monitoring recommendations. Each chemical is given a ranking (or "DPR Final Score") that is a product of the "DPR Use Score" and the "DPR Toxicity Score," which are described in greater detail below. The use, toxicity and final scores shown in Table A-1 are based on a prioritization of all pesticides applied within the entire Russian River watershed between 2012-2014.

Use score **–** The "DPR Use Score" is based on a ranking of all pesticides' usage within the given boundaries and time period. By default, the top 2% of pesticides with the highest use amounts are given the highest use score (5). The complete default probabilities for rankings are: score 1 = lowest 70%; score 2 = next 15%; score 3 = next 8%; score 4 = next 4%; and score 5 = top 2%.

Toxicity score **–** The "DPR Toxicity Score" is based on the lowest acute or chronic toxicity benchmark available for each chemical. The list of benchmarks considered includes the USEPA Aquatic Life Benchmarks (or estimated benchmark equivalents, as calculated by DPR based on toxicity data), USEPA Drinking Water Standards, and USEPA Human Health Benchmarks. The benchmark used to determine the toxicity score is noted in the "Toxicity Benchmark Type" column. Blanks indicate the use of the aquatic life benchmark; P refers to the benchmark equivalents, and H refers to the human health benchmarks. The toxicity scores are assigned as follows (Luo et al., 2013).

Table A-1. Ranking schemes for pesticide toxicity

Toxicity score	Lowest benchmarks (BM) (ppb)	Category description	
		SWPP [1]	USEPA [2]
8	BM≤0.001	Very highly toxic	Very highly toxic
7	0.001<BM≤0.01		
6	0.01<BM≤0.1		
5	0.1<BM≤1		
4	1<BM≤10	Highly toxic	
3	10<BM≤100		
2	100<BM≤1000		Highly toxic
1	BM>1000	Moderately to slightly toxic	Moderately toxic to practically non-toxic
0	No data		

[1] SWPP: Department of Pesticide Regulation's Surface Water Protection Program
[2] USEPA: United States Environmental Protection Agency

Chemical properties and indicators **–** Based on chemical properties influencing fate and transport processes, some chemicals may be included in the prioritization ranking but are not recommended for monitoring, even if use or toxicity scores are high. The DPR prioritization tool takes into account a total of 16 factors such as application method, use patterns, volatility, mobility, aquatic persistence, or bioavailability in water, using USEPA pesticide registration data and the EU FOOTPRINT Pesticide Properties DataBase (AERU, 2016). A full list of factors is described in greater detail in the DPR prioritization memo (Luo et al., 2014).

For example, chemicals with moderate to high use or toxicity scores in the Russian River that are not recommended for monitoring include:

- Mancozeb – short persistence in water (however, a degradate is recommended)
- Thiophanate-Methyl – low bioavailability in water-sediment systems (a degradate is recommended)
- Bifenzate – short persistence in water (a degradate is recommended)
- Naled – low use volume; all dominant products are registered with low-use risk patterns or low-risk application methods; there is also a low soil runoff potential

Degradates – The DPR prioritization tool will also recommend common pesticide degradates for monitoring based on the use volume and chemical characteristics of their parent compounds, although no data exist on the presence or concentrations of these compounds in the PUR database. Degradates recommended for monitoring are listed along with their parent compounds in Table 1. Analytical methods for many degradates are not currently available, but several key compounds should be considered for future monitoring or method development, including:

- Ethylene thiourea (mancozeb degradate)
- 1,2,4-triazole; triazole alanine; triazole acetic acid (myclobutanil degradates)

Prioritization Parameters

The DPR prioritization tool was run using both HUC-12 and customized watershed-based modes. The customized watershed-based prioritization uses pesticide application data within specified township-range sections, which for this study included all sections located wholly or partially within the boundaries of the Region 1 Russian River watershed. HUC-12 prioritization is based on chemicals applied within a designated HUC-12 watershed as well as in upstream tributaries that contribute to the same drainage area. The HUC-12 watersheds are outlined in purple in the attached use maps. The relationship between main stem and tributary streams are based on the USGS National Hydrography dataset (NHD) and its enhanced version, NHDPlus (Luo & Deng, 2015). This tool was run for all HUC-12 watersheds located at the base of the larger HUC-10 watersheds within the Russian River watershed in order to identify the variability among the highest priority pesticides in each sub-watershed. Across HUC-12 watersheds and both prioritization methods, variations in the ranking of priority pesticides were observed, but the top 20-30 pesticides used remained relatively constant.

The chemicals listed in Table 1 are those that were recommended for monitoring based on chemical properties, and assigned a DPR Final Score of at least 5 when considering the entire Russian River watershed during the period 2012-2014, or specific seasons within this time period and/or sub-watersheds within the Russian River watershed. In some cases, additional chemicals were added to this list or recommended for future monitoring based on professional judgment, including information about use or toxicity that have not yet been incorporated in the DPR prioritization tool.

Additional Prioritization Factors

***Compounds and degradates not included in the PUR database or prioritization tool* –** In some cases, common pesticide compounds and degradates have not yet been incorporated into the DPR's PUR database or prioritization tool. For example, paclobutrazole is a plant growth retardant and triazole fungicide that was reregistered in California in 2011 but is classified in the PUR database only as a "plant growth regulator," which causes it to be excluded from the DPR prioritization tool. Toxicity concerns for this compound are based primarily on human health benchmarks, which were not a focus of the current monitoring study, and the reported use volume, at least for this use type, in the Russian River watershed has been negligible. However, this compound could potentially become of interest in future monitoring efforts and may need to either be incorporated into the prioritization tool or tracked separately.

Additionally, degradates of priority pesticides that are not included in the prioritization tool but are recommended for monitoring include:

- THPA, 482-HA, and APF (flumioxazin degradates)
- Triazole alanine, triazole acetic acid (myclobutanil and other triazole degradates)

***Recent use patterns* –** In addition to current use volumes, use trends can be considered when prioritizing chemicals for monitoring. Chemicals that are used with increasing frequency and volume may be of greater interest than those that are being phased out. Table 1 conservatively includes chemicals that have been recommended as moderate to high monitoring priorities based on toxicity and use during 2012-2014 or a subset of this time period. However, certain chemicals, such as lambda-cyahlothrin and pyribaden, have shown decreasing use in recent years, and thus may be lower monitoring priorities.

***Historical monitoring results* –** Historical monitoring data can be useful in identifying high priority chemicals or monitoring sites that have caused concerns in the past and should be monitored again. However, limited pesticide data are available in the Russian River watershed to indicate which chemicals may be of concern.

***Other sources of pesticide toxicity* –** Metal-containing pesticides can cause aquatic toxicity via release of toxic metal ions, such as zinc and copper. However, in the Russian River watershed, the use volumes of these compounds were low and unlikely to be the region's major source of any zinc or copper toxicity in the watershed.

Monitoring Implementation: Time Period

The ideal sampling period is dependent on the pesticide application method and seasonal use pattern, as well as the chemical properties of the target compounds. In the Russian River watershed, the dominant agricultural pesticide use is on wine grapes, followed by apple and pear trees, which are predominantly irrigated using low-flow methods that reduce pesticide runoff into streams during the dry season. It is expected that higher pesticide concentrations will be detected in streams during periods when high use overlaps with the wet season. At the same time, stormwater runoff that occurs immediately following the dry season can be expected to deliver significant pesticide loads that have accumulated in soils during the dry season, when many prioritized pesticides are applied at higher quantities.

The DPR database provides pesticide use volumes by month. The total monthly use volume for each chemical recommended for monitoring, summed over the period 2012-2014, is shown in Table 1.Two of the highest-use chemicals, mancozeb (which is not recommended for monitoring, although the degradate ethylene thiourea is recommended) and glyphosate (which is considered to have low aquatic toxicity but has recently been identified as a probable human carcinogen), are predominantly applied between February and April. Among the remaining recommended chemicals, the highest volumes are typically applied in June and July. High priority pesticides cyprodinil, imidacloprid, pyraclostrobin, quinoxifen, difenoconazole, and pyrimethanil are predominantly applied during the summer months and are considered moderately persistent to very persistent in soils (AERU, 2016). It is expected that a portion of pesticides applied during this period will be transported to streams in fall “first flush” stormwater runoff.

In addition to mancozeb and glyphosate, other pesticides in the recommended list that are predominantly applied during early spring months include flumioxazin, oxyfluorfen, pendimethalin, oxytetracycline, thiophanate-methyl, chlorpyrifos, oryazlin, and simazine. These chemicals or their degradates would be best monitored during the spring, during concurrent periods of high use and high rainfall.

References

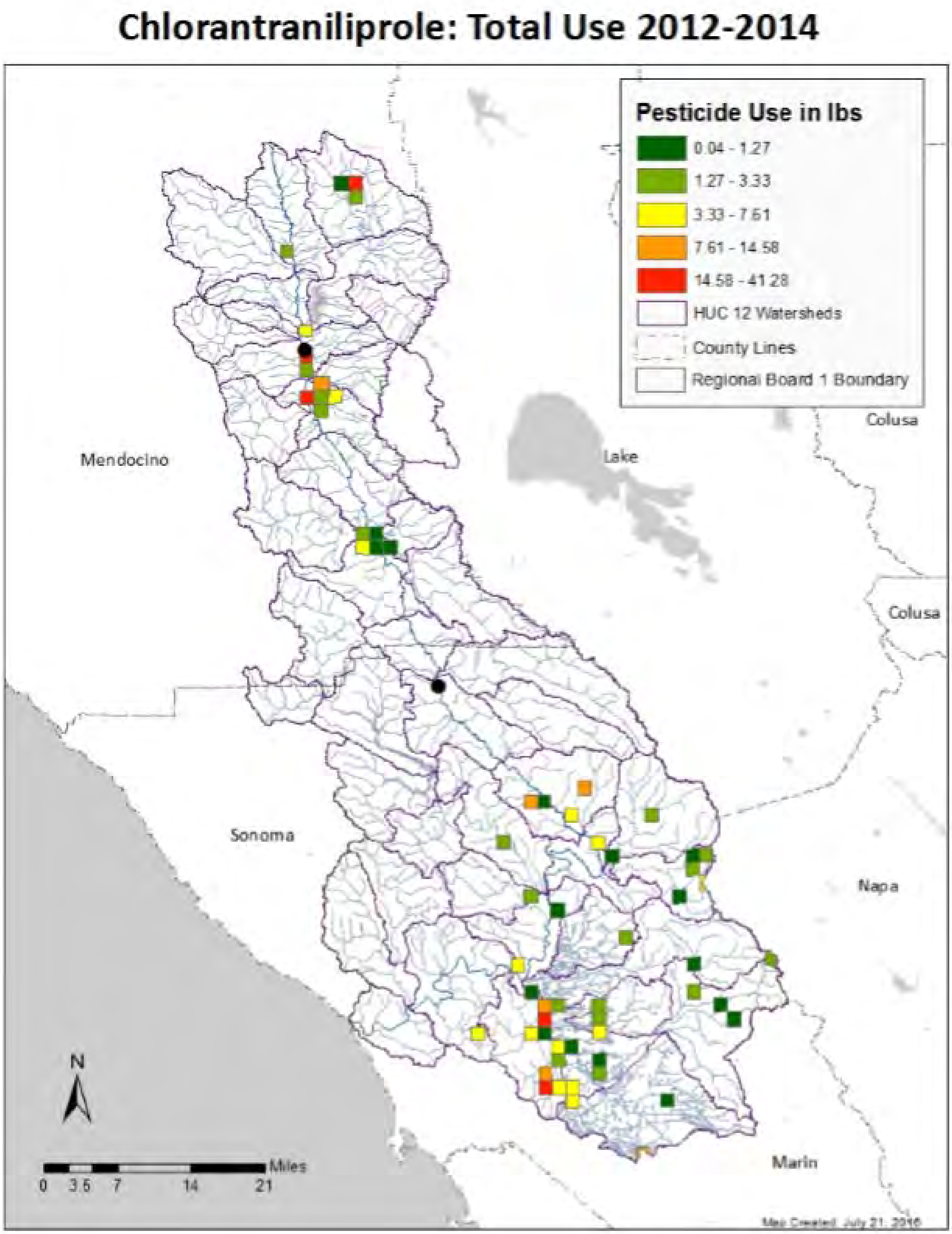
Agriculture & Environmental Research Unit, University of Hertfordshire. 2016. Pesticide Properties DataBase. Version March 2016. Hertfordshire, England. Accessed June 2016. http://sitem.herts.ac.uk/aeru/ppdb/en/search.htm

Luo, Y., Deng, X., Budd, R., Starner, K., and Ensminger, M. 2013. Methodology for Prioritization Pesticides for Surface Water Monitoring in Agricultural and Urban Areas. Department of Pesticide Regulation. Sacramento, CA. http://cdpr.ca.gov/docs/emon/pubs/ehapreps/analysis_memos/prioritization_report.pdf

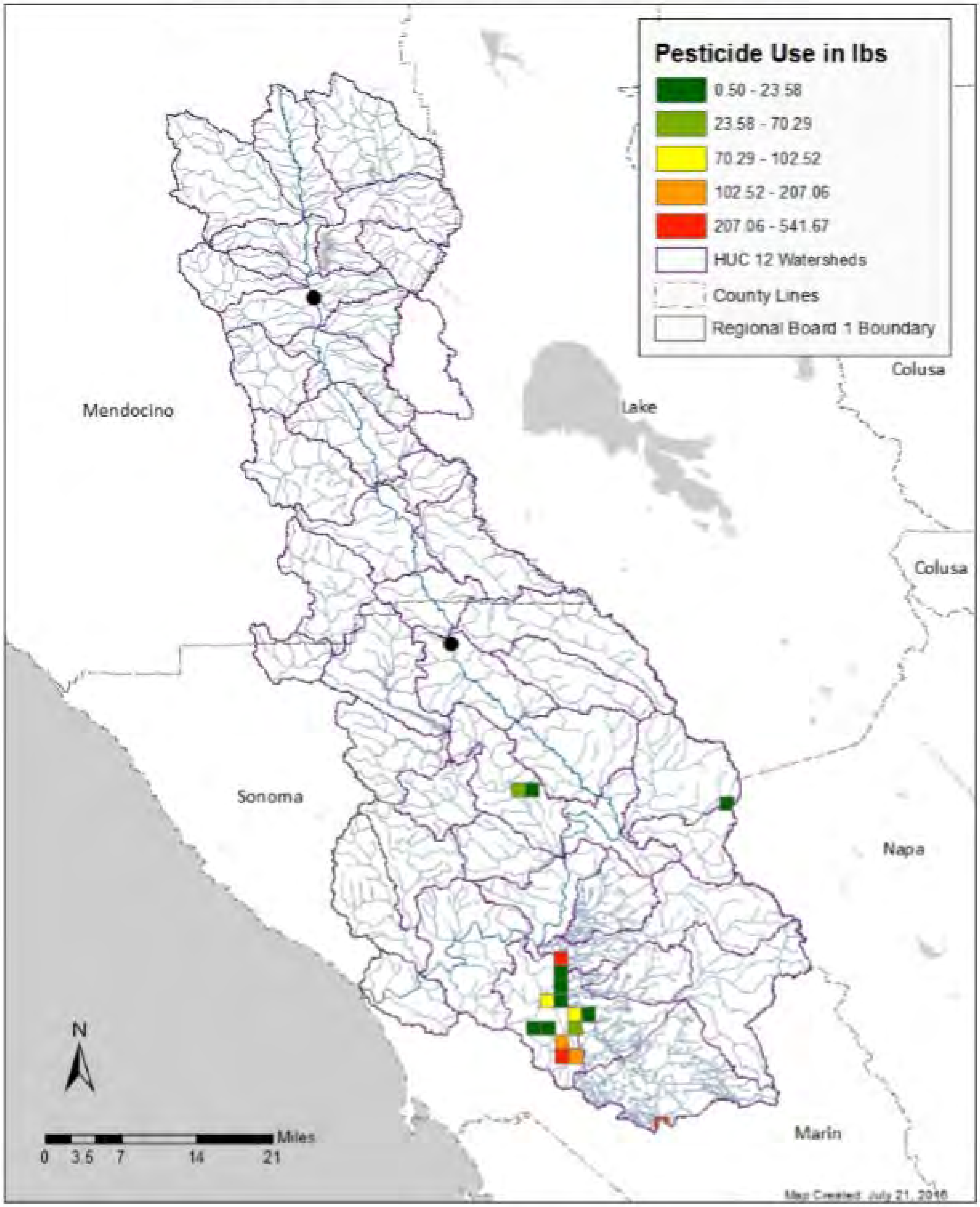
Luo, Y., Ensminger, M., Budd, R., Deng, X., and DaSilva, A. 2014. Methodology for Prioritizing Pesticides for Surface Water Monitoring in Agricultural and Urban Areas II: Refined Priority List. Department of Pesticide Regulation. Sacramento, CA. http://cdpr.ca.gov/docs/emon/pubs/ehapreps/analysis_memos/prioritization_report_2.pdf

Luo, Y and Deng, X. 2015. Methodology for Prioritizing Pesticides for Surface Water Monitoring in Agricultural and Urban Areas III: Watershed-Based Prioritization. Department of Pesticide Regulation. Sacramento, CA. http://www.cdpr.ca.gov/docs/emon/pubs/ehapreps/analysis_memos/luo_prioritization_3.pdf

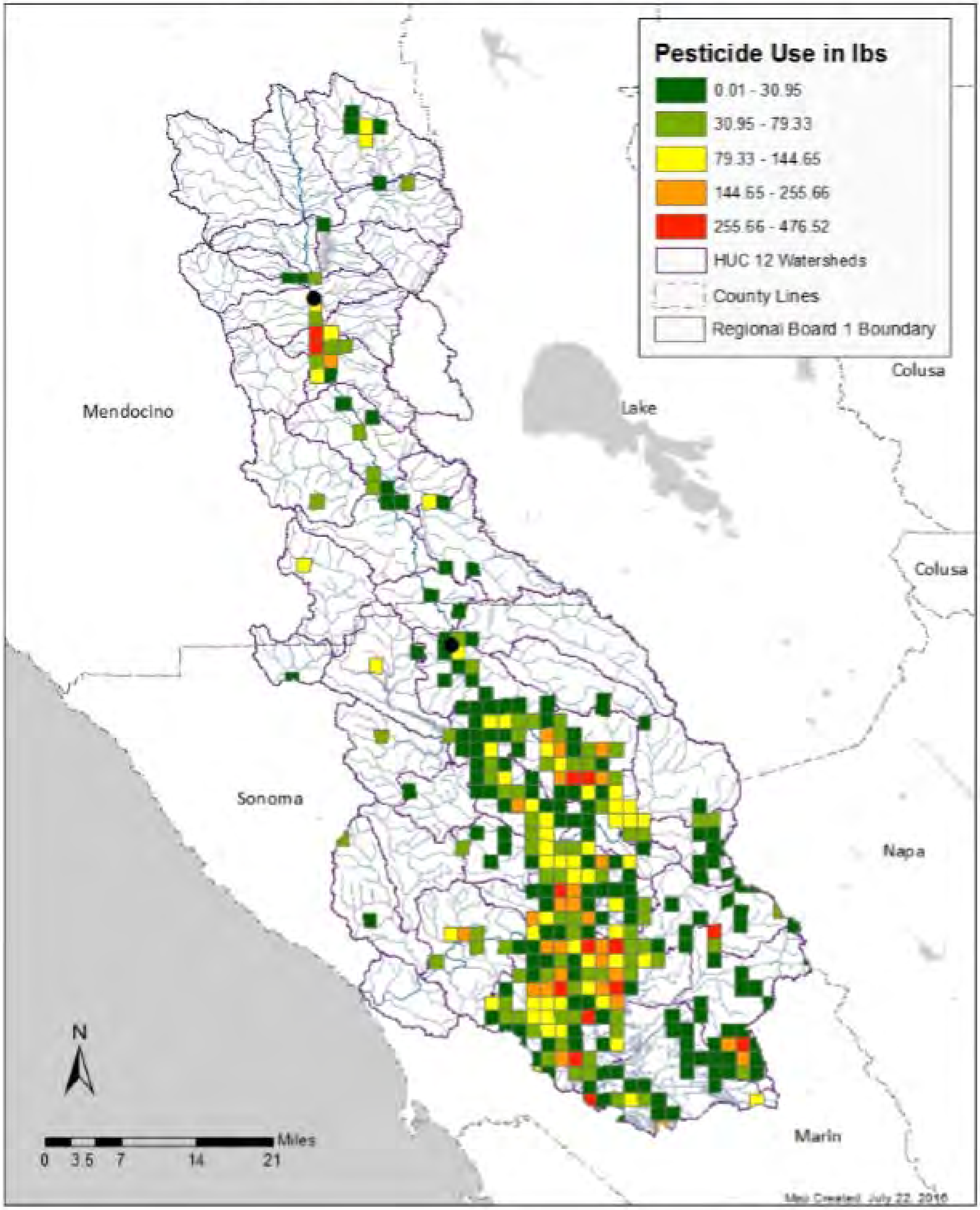
Appendix A1: Pesticide Use Maps



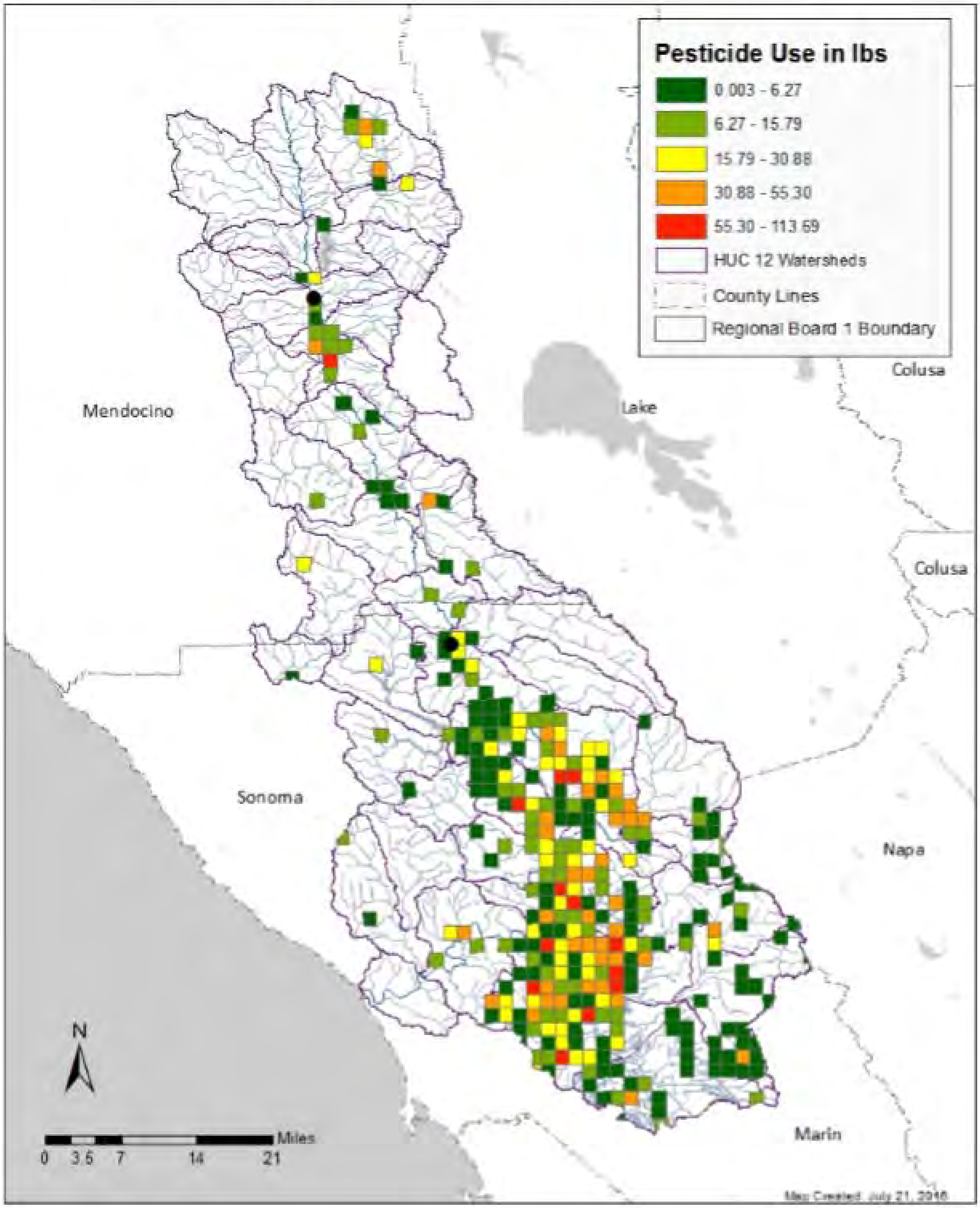
Chlorpyrifos: Total Use 2012-2014



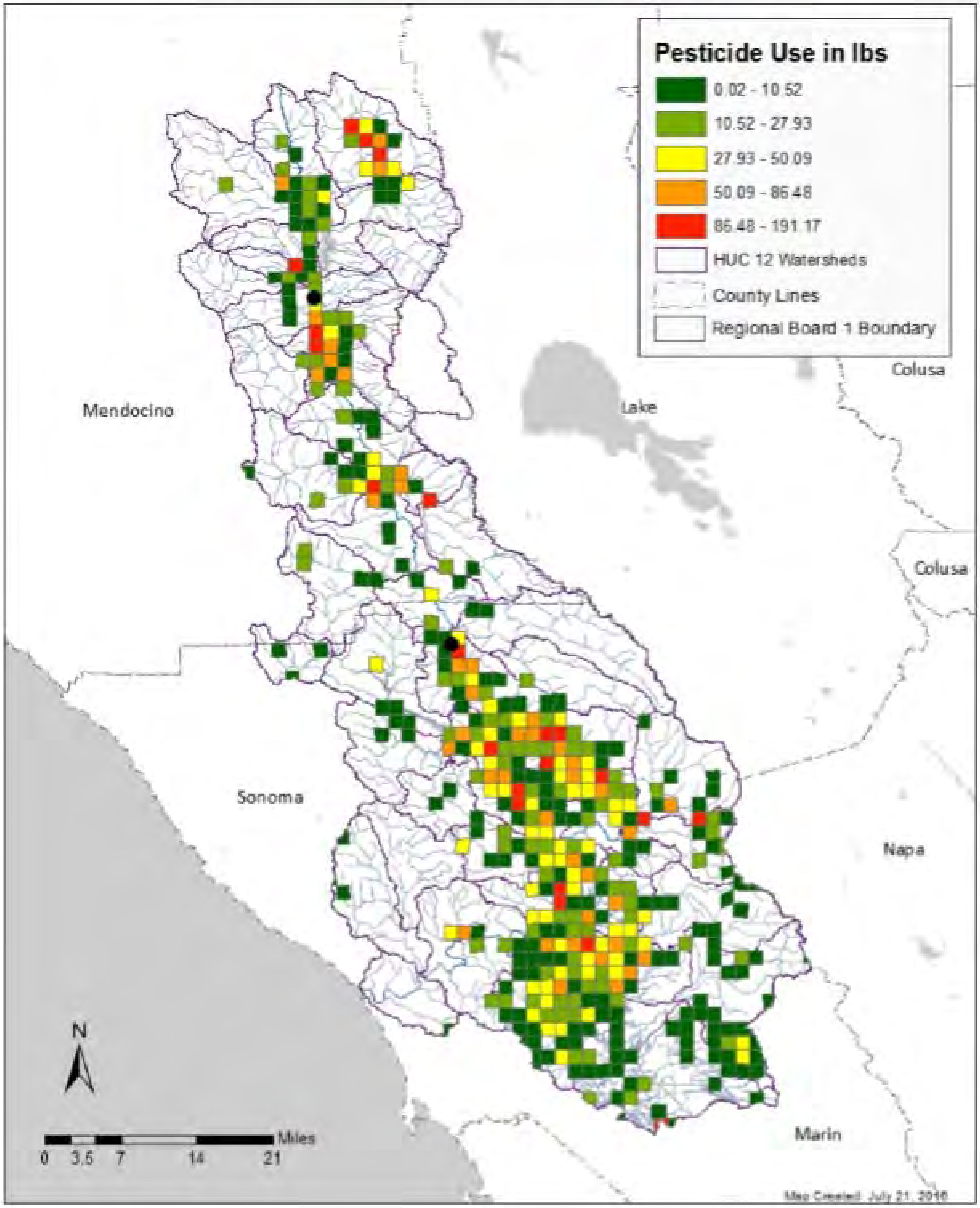
Cyprodinil: Total Use 2012-2014



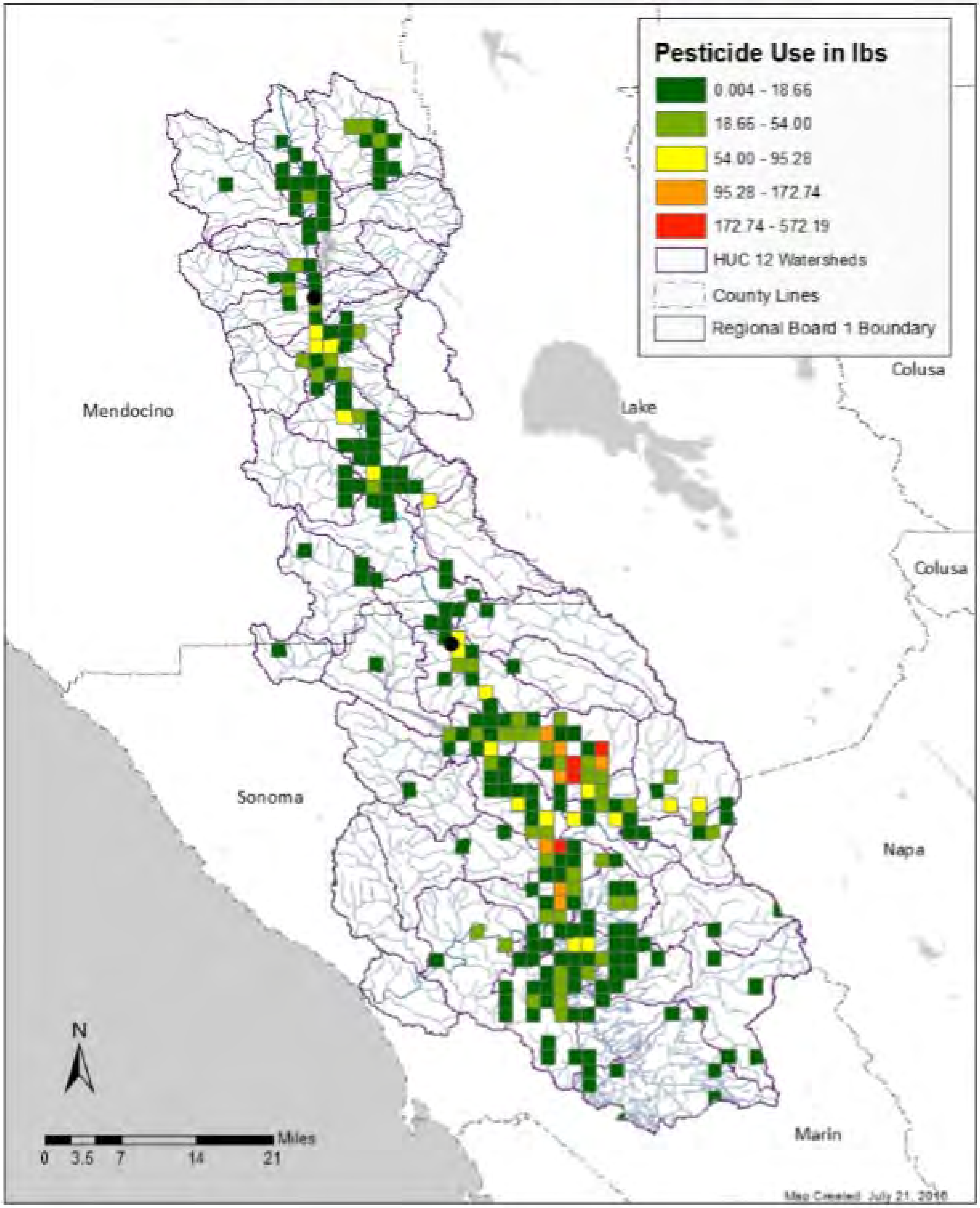
Difenoconazole: Total Use 2012-2014



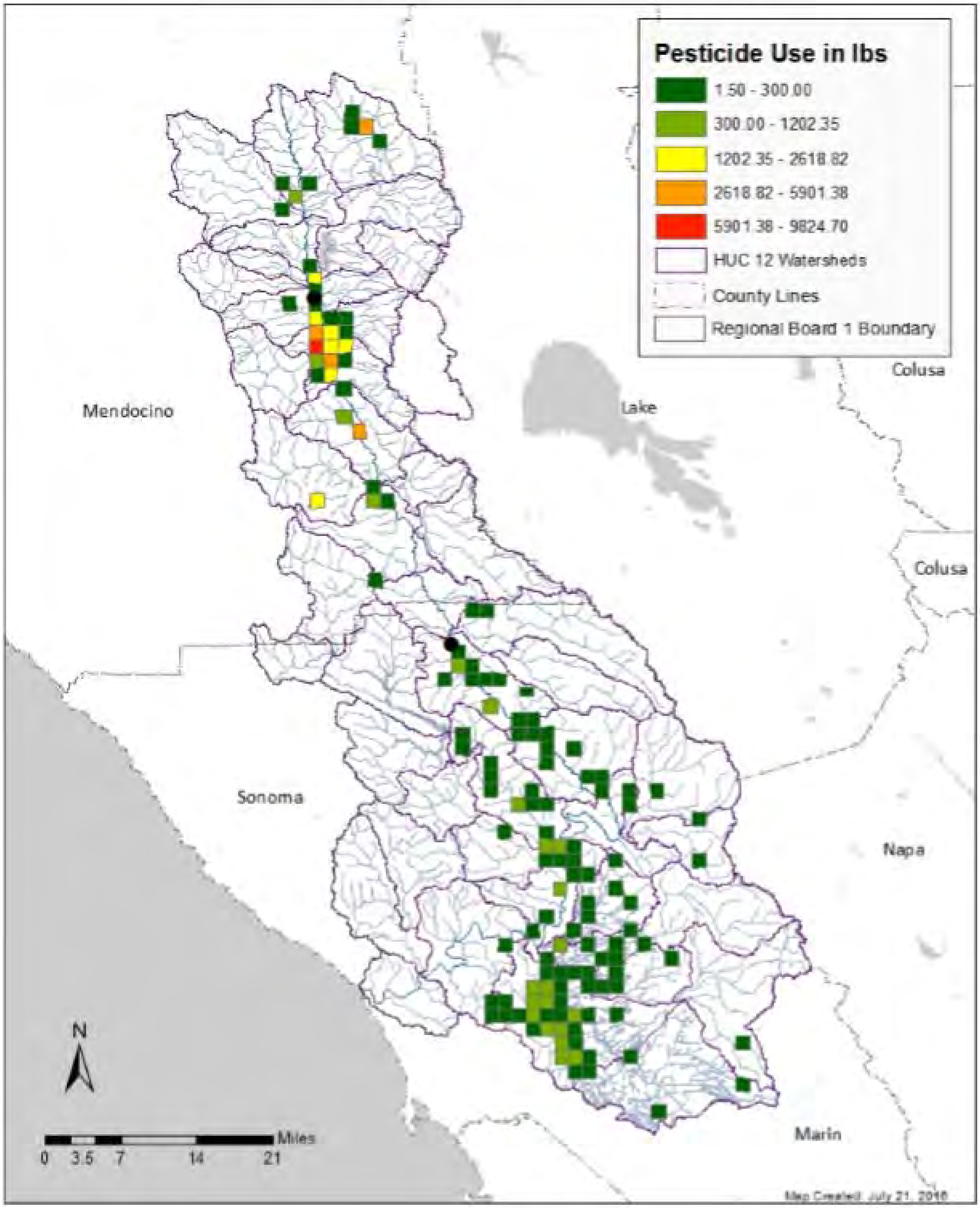
Flumioxazin: Total Use 2012-2014



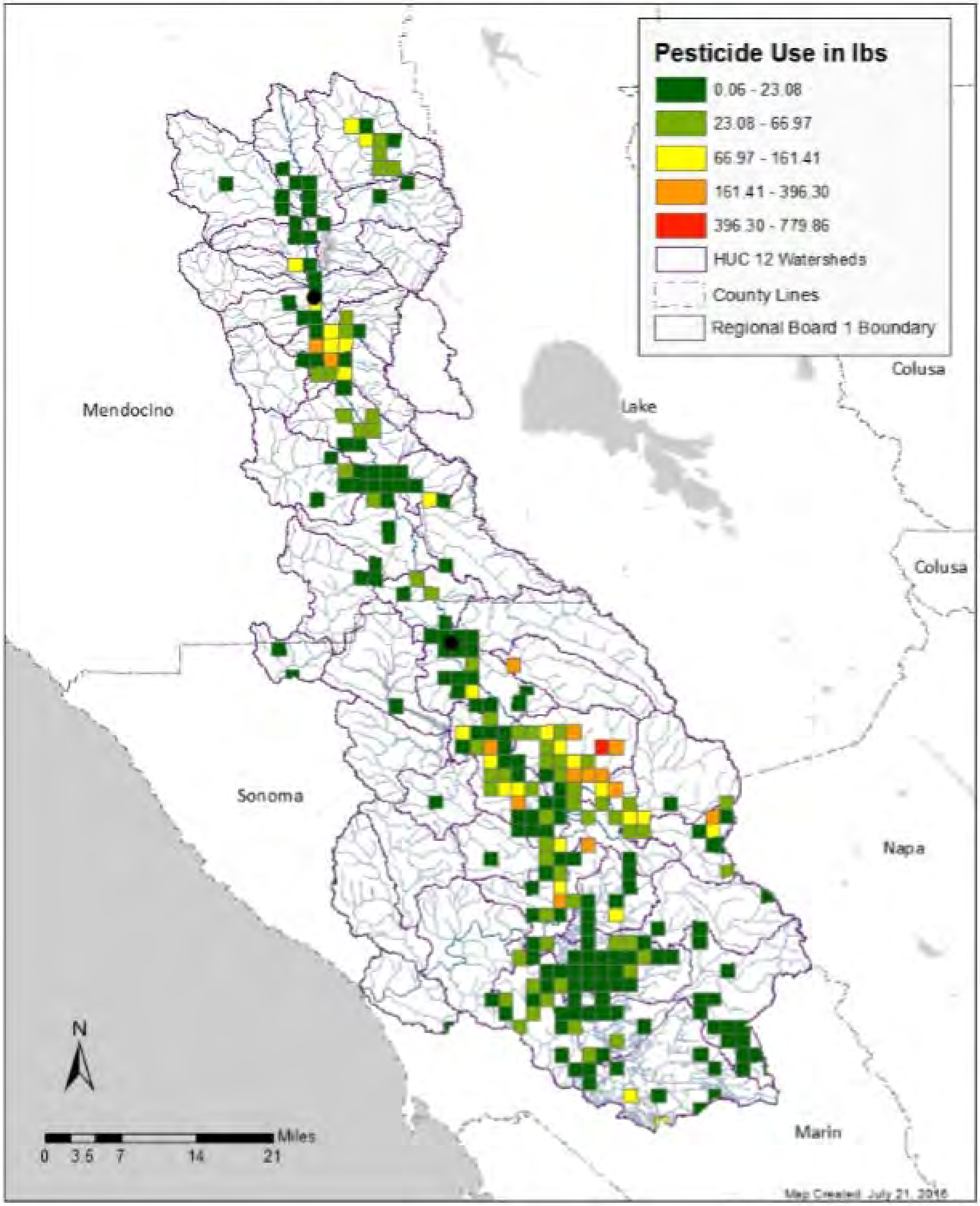
Imidacloprid: Total Use 2012-2014



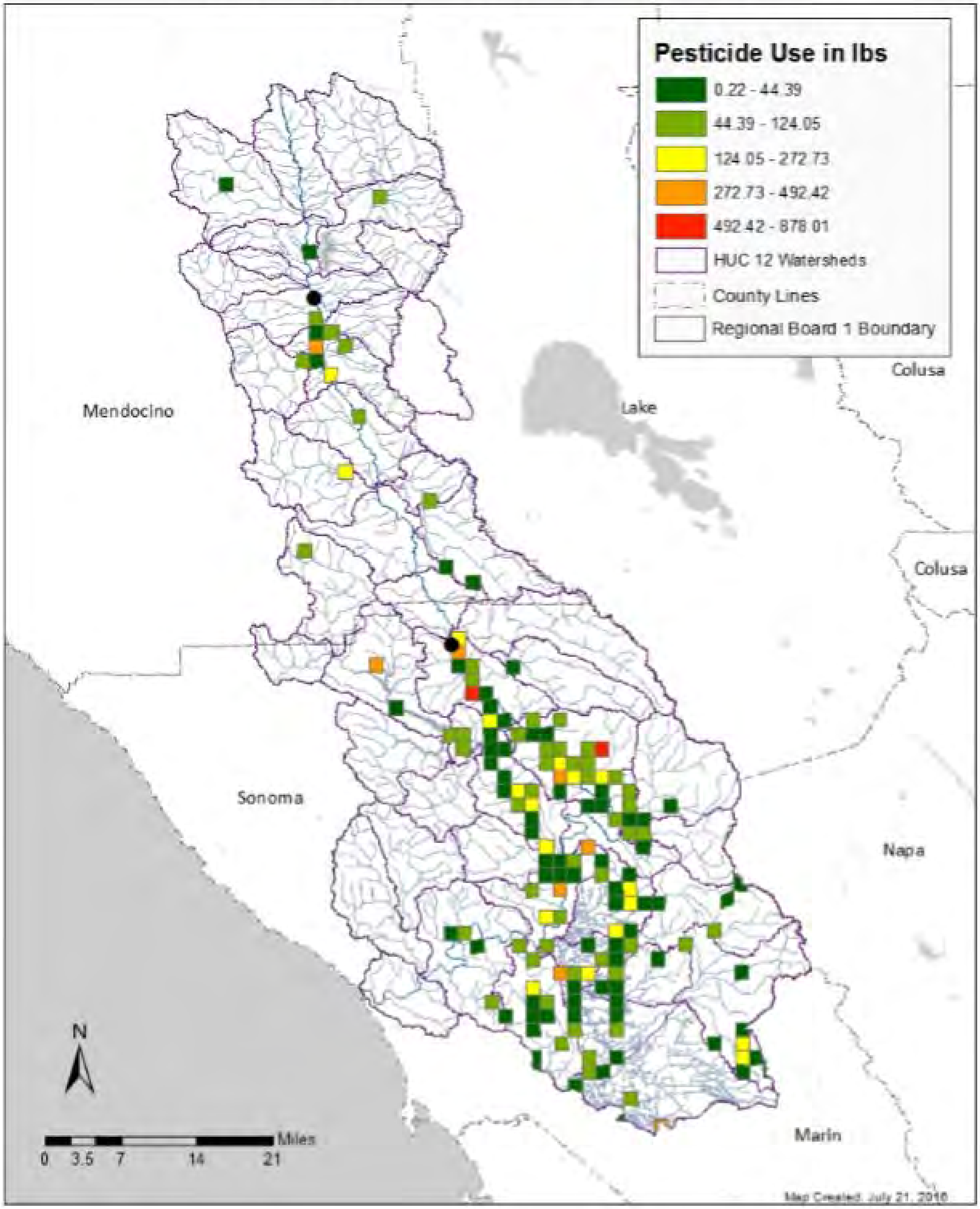
Mancozeb: Total Use 2012-2014



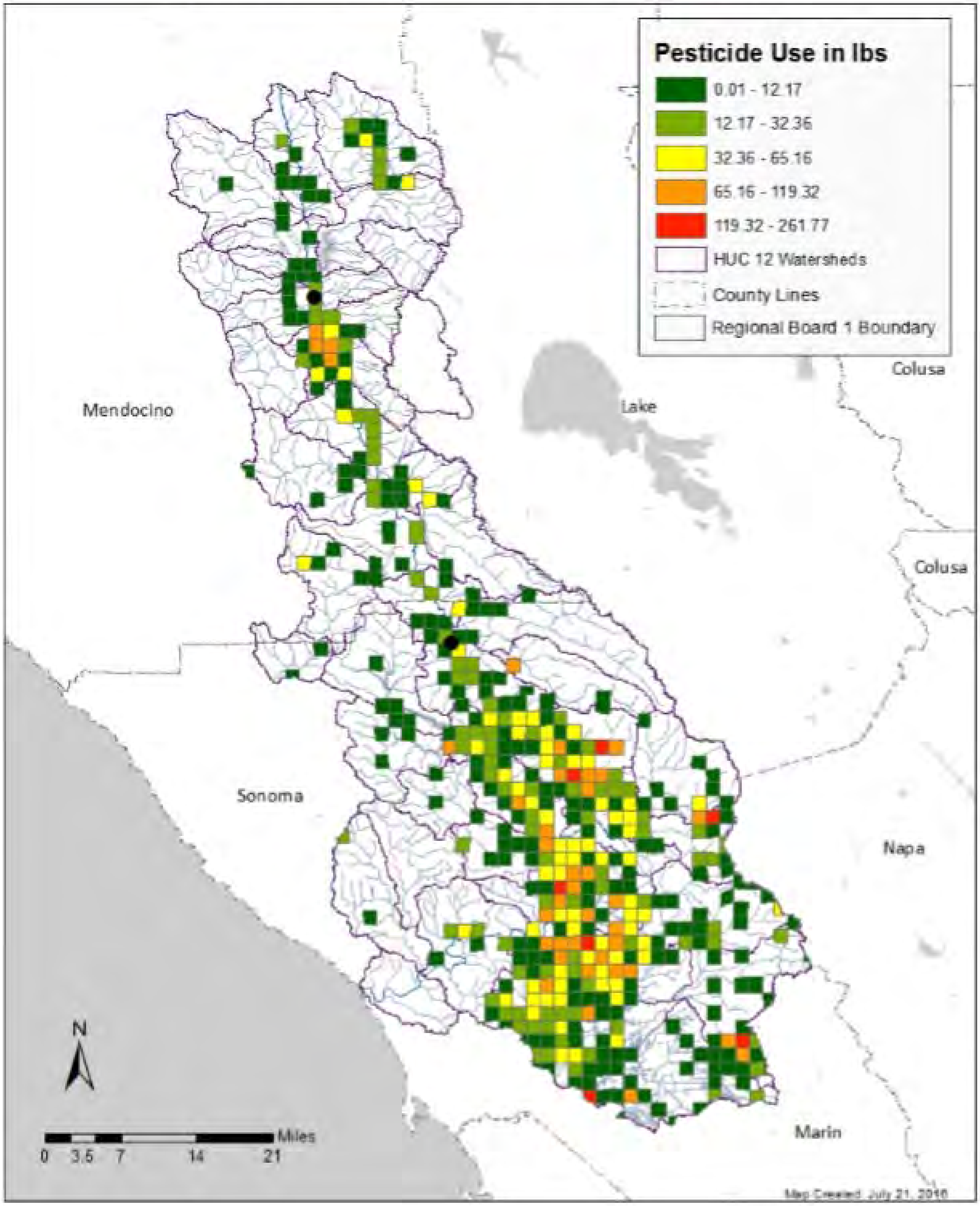
Oxyfluorfen: Total Use 2012-2014



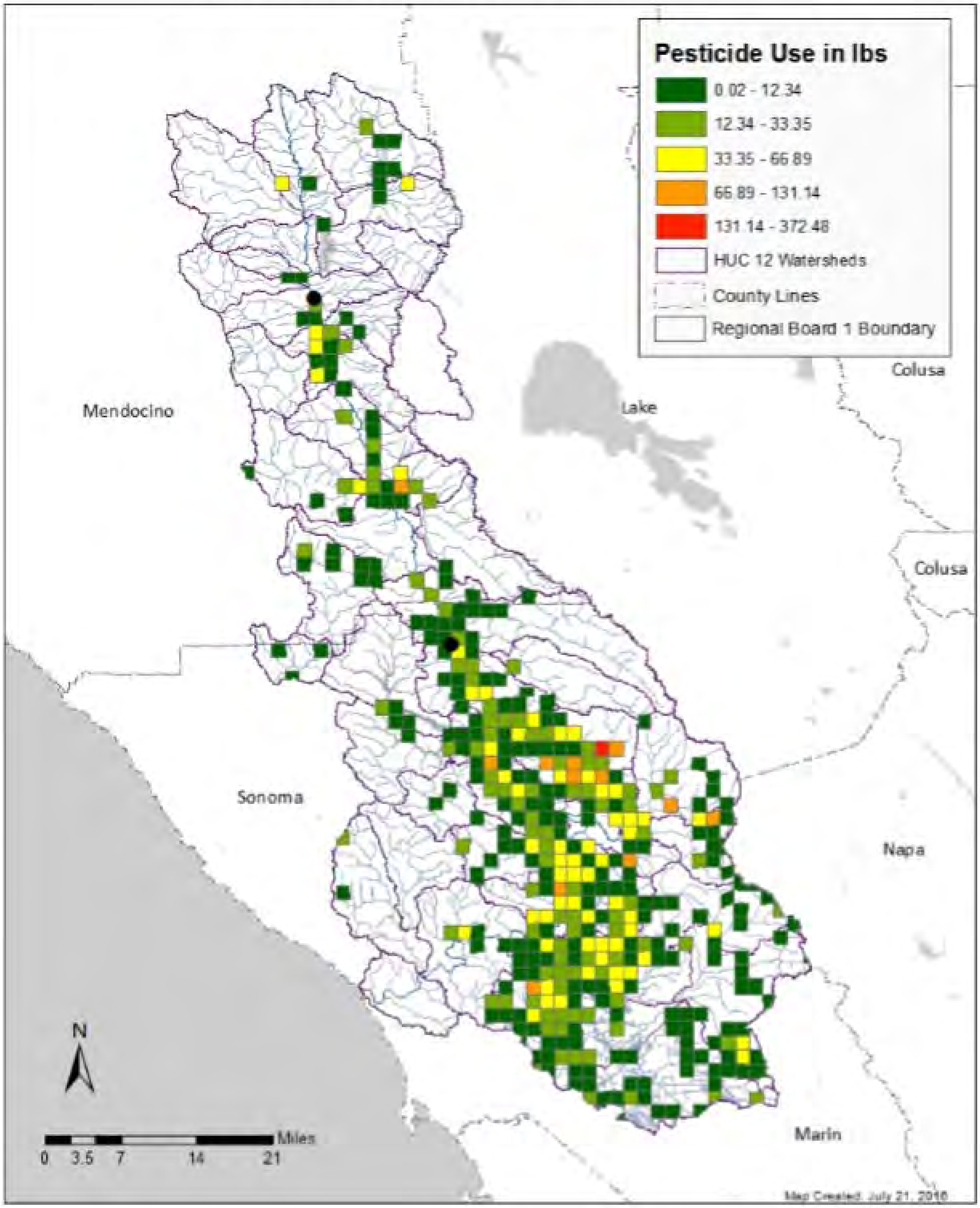
Pendimethalin: Total Use 2012-2014



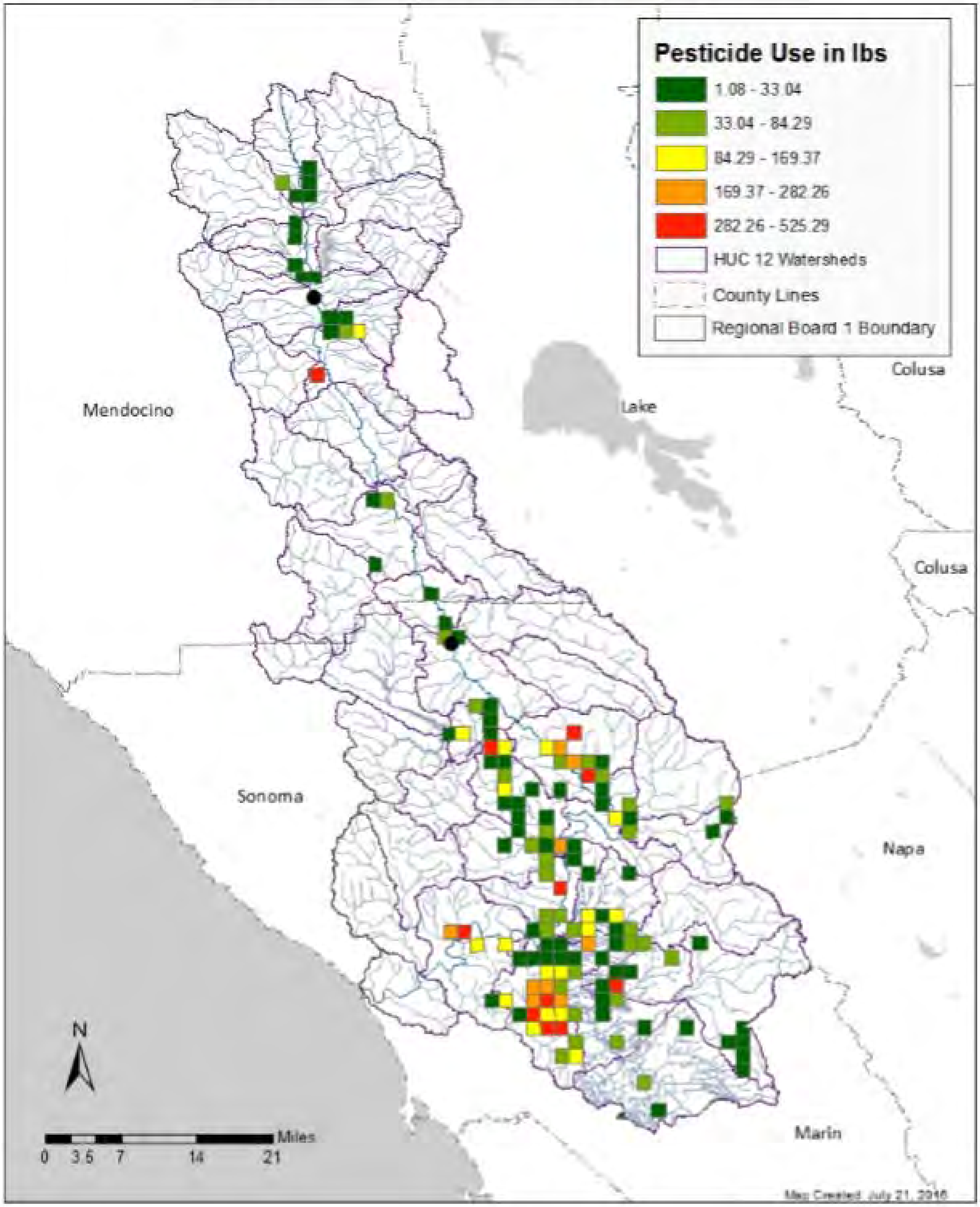
Pyraclostrobin: Total Use 2012-2014



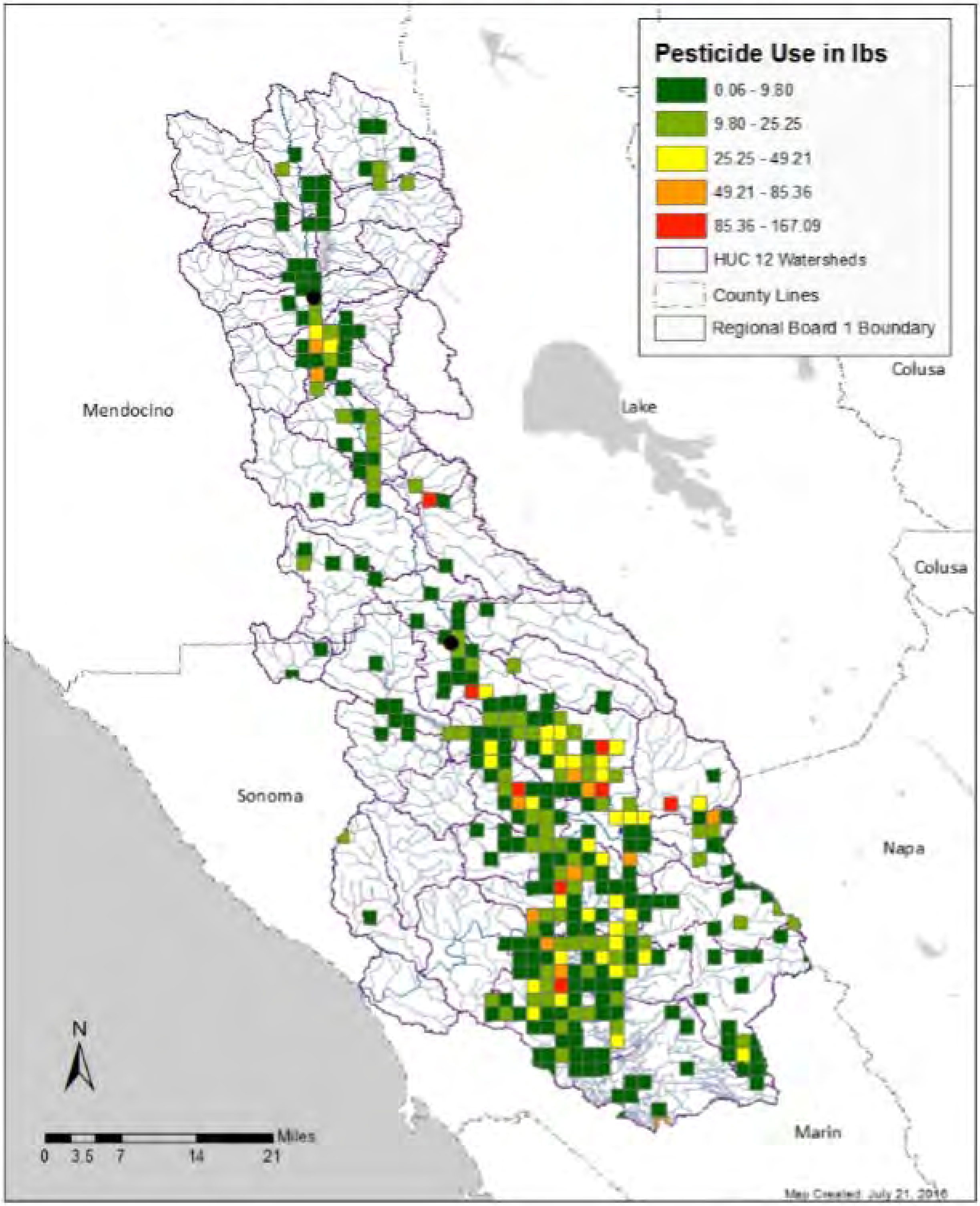
Quinoxyfen: Total Use 2012-2014



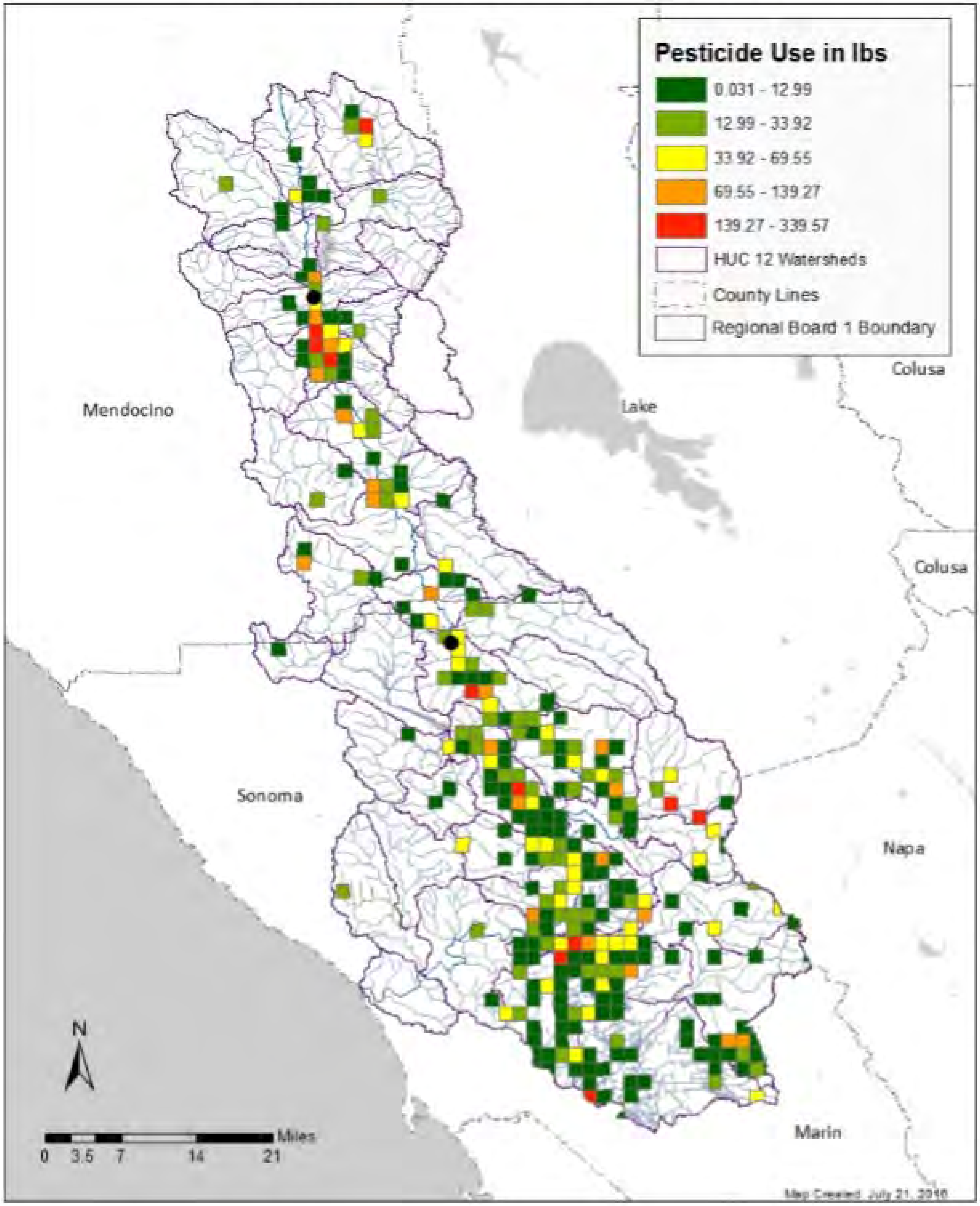
Simazine: Total Use 2012-2014



Trifloxystrobin: Total Use 2012-2014



Triflumizole: Total Use 2012-2014



Appendix B. Current Use Pesticides Monitoring Pilot Study Russian River Watershed

Introduction

The agricultural regions of the Russian River Watershed are subjected to the application of a broad range of current use pesticides, many of which have not yet been monitored. The purpose of this study is to prioritize pesticides for monitoring based on pesticide use and toxicity information, and conduct an initial screening of current use pesticides impacting the Russian River and its tributaries.

In fall 2016, water and sediment samples were collected for pesticide analyses at five sites along the Russian River and its tributaries in the Russian River Watershed (Table B-1, Figure B-1). Samples were collected by the North Coast Regional Water Quality Control Board. Sediment samples were collected prior to the wet season just downstream of high application volume regions. These samples were expected to capture hydrophobic compounds that slowly washed off the landscape and accumulated in the stream beds during the dry season, before heavy rains might scour these surface sediments and transport them further downstream. Water samples were collected during the first major storm of the season. These samples are expected to capture hydrophobic pesticides that have accumulated in agricultural soils during the dry season and are flushed off the landscape and transported downstream by significant stormwater volumes, as well as hydrophilic pesticides that are being actively applied during the fall wet season.

Figure B-1. Site map of locations sampled for water and sediment. The locations of the USGS stream gages used to create the hydrographs shown in Figure B-2 are also labeled, although these locations are not visible at some sites where samples were collected at the same location as the stream gage site

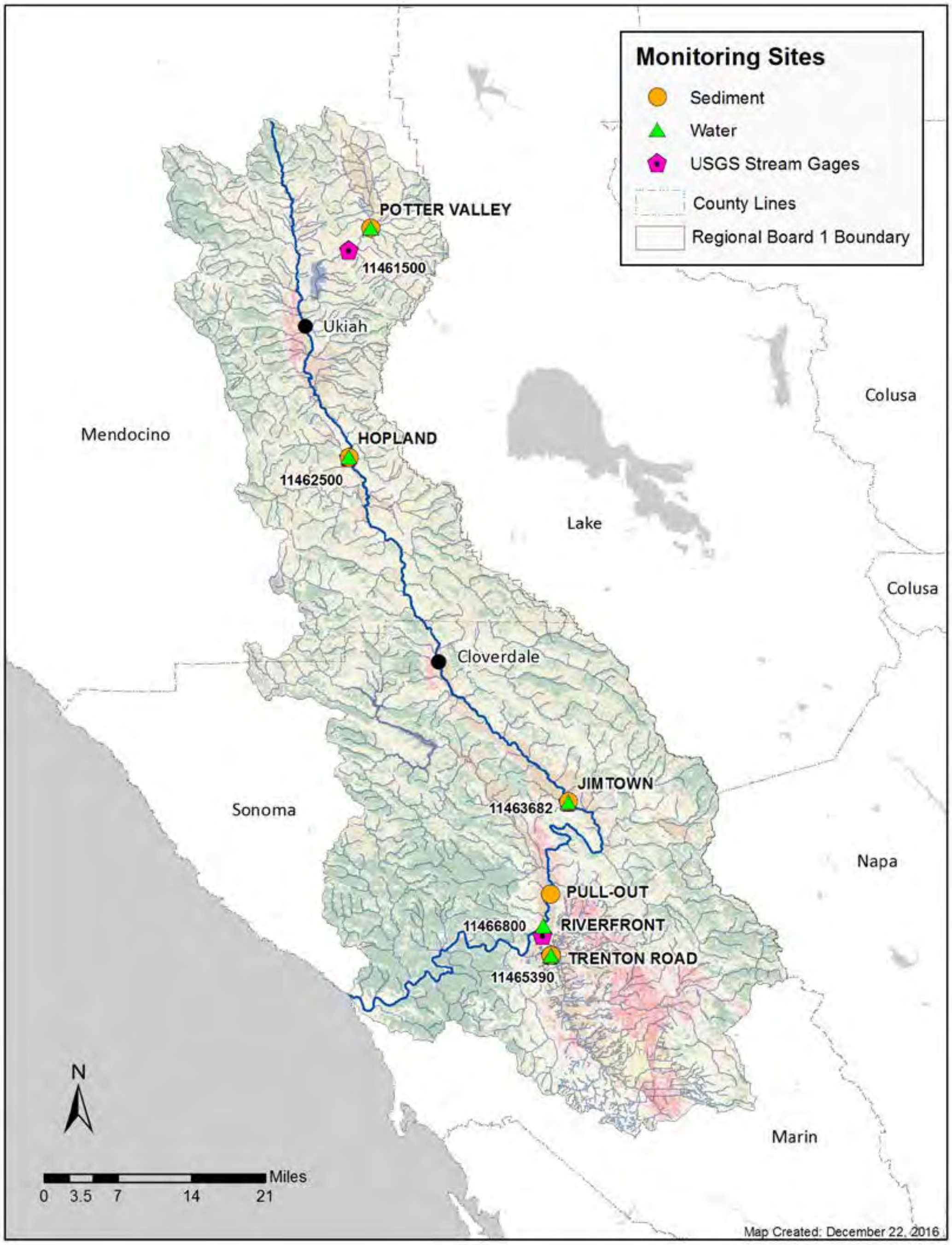


Table B-1. Sediment and water sites sampled in fall 2016.

Station Code	Station Name	Map Name	Sampling Date	Sampling Time	Latitude	Longitude	USGS Gauge Number
SEDIMENT							
114EF6000	East Fork Russian River above Mewhinney Creek	POTTER VALLEY	9/28/2016	11:45	39.27026	-123.10091	11461500
114RR7396	Russian River above Hopland	HOPLAND	9/28/2016	12:45	39.02629	-123.13036	11462500
114RR4234	Russian River at Alexander Valley Road	JIMTOWN	9/28/2016	14:45	38.65873	-122.8296	11463682
114RR2655	Russian River below Kabutts Road	PULL-OUT	9/29/2016	12:45	38.55993	-122.85423	11465390
114MW0930	Mark West Creek at Trenton-Healdsburg Road	TRENTON ROAD	9/28/2016	17:15	38.49399	-122.85316	11466800
WATER							
114EF6000	East Fork Russian River above Mewhinney Creek	POTTER VALLEY	10/28/2016	12:15	39.27008	-123.1009	11461500
114RR7396	Russian River above Hopland	HOPLAND	10/28/2016	11:15	39.02666	-123.13043	11462500
114RR4234	Russian River at Alexander Valley Road	JIMTOWN	10/28/2016	10:00	38.65843	-122.82928	11463682
114RR2401	Russian River above Riverfront Park	RIVERFRONT	10/28/2016	9:15	38.52573	-122.8638	11465390
114MW0930	Mark West Creek at Trenton-Healdsburg Road	TRENTON ROAD	10/28/2016	8:45	38.49412	-122.85316	11466800

Sediment

Sediment samples were collected prior to the wet season on September 28, 2016 between 11:45 am and 5:15 pm (Table B-1). Samples were collected at five sites according to protocols established in the SWAMP SPoT program QAPP (Figure B-1; SWAMP 2012). Each sediment sample was a composite of subsamples collected from at least three locations along the stream bank, and included only the top 2 cm of sediment from each depositional zone. Samples were collected with a polycarbonate scoop and were not sieved, but large debris were not found present in the samples. Water was poured off from each subsample before subsamples were homogenized within a pre-cleaned 250 mL glass jar.

One laboratory replicate and one matrix spike analysis was conducted in the laboratory. Sediment samples were chilled in the field and shipped frozen overnight to the USGS laboratory. Samples were analyzed for pesticides using the USGS GC/MS pesticide method (Table B-2; Hladik and McWayne 2012). Samples were stored on wet ice in the field and shipped to the analytical laboratory for analysis overnight and subsequently stored frozen in the laboratory until analysis.

Each site was characterized by measurements of water velocity, stream width and distance of the sampling site from the right stream bank when facing downstream**.** Ancillary field parameters collected included water temperature, specific conductivity, salinity, dissolved oxygen, pH, and barometric pressure, measured with a YSI 600XL Data Sonde. Additional parameters qualitatively assessed included site and water odor, water clarity, water color, dominant substrate, cloud condition, precipitation, wind, overland runoff volume (light/heavy/etc.), and the presence of hydromodifications.

Table B-2. Pesticide target analyte list.

Compound	Type	Class	Method	Target Water MDL (ng/L)	Water Method/MDL Reference #	Target Sediment MDL	Sediment Method/MDL Reference #
3,4-DCA	Degradate	Urea	GC/MS	8.3	2,3,4	1.3	6
3,5-DCA	Degradate	Aniline	GC/MS	7.6	2,3,4	1.5	6
Acibenzolar-S-methyl	Fungicide	Benzothiadiazole	GC/MS	3	2,3,4	Not yet determined	6
Alachlor	Herbicide	Chloroacetanilide	GC/MS	1.7	2,3,4	0.6	6
Allethrin	Insecticide	Pyrethroid	GC/MS	1	1	1.7	6
Atrazine	Herbicide	Triazine	GC/MS	2.3	2,3,4	1.5	6
Azinphos methyl	Insecticide	Organophosphate	GC/MS	9.4	2,3,4	1.7	6
Azoxystrobin	Fungicide	Strobilurin	GC/MS	3.1	2,3,4	0.9	6
Benefin (Benfluralin)	Herbicide	Dinitroaniline	GC/MS	2	2,3,4	1.7	6
Bifenthrin	Insecticide	Pyrethroid	GC/MS	0.7	1	0.6	6
Boscalid	Fungicide	Pyridine	GC/MS	2.8	2,3,4	1.2	6
Butralin	Herbicide	Dinitroaniline	GC/MS	2.6	2,3,4	1.6	6
Butylate	Herbicide	Thiocarbamate	GC/MS	1.8	2,3,4	1.3	6
Captan	Fungicide	Phthalimide	GC/MS	10.2	2,3,4	3.1	6
Carbaryl	Insecticide	Carbamate	GC/MS	6.5	2,3,4	1.2	6
Carbofuran	Insecticide	Carbamate	GC/MS	3.1	2,3,4	1.2	6
Chlorothalonil	Fungicide	Chloronitrile	GC/MS	4.1	2,3,4	1.1	6
Chlorpyrifos	Insecticide	Organophosphate	GC/MS	2.1	2,3,4	0.9	6
Chlorpyrifos OA	Degradate	Organophosphate	GC/MS	5	2,3,4	Not yet determined	6
Clomazone	Herbicide	Isoxazlidinone	GC/MS	2.5	2,3,4	2	6

Compound	Type	Class	Method	Target Water MDL (ng/L)	Water Method/MDL Reference #	Target Sediment MDL	Sediment Method/MDL Reference #
Coumaphos	Insecticide	Organophosphate	GC/MS	3.1	2,3,4	1.2	6
Cycloate	Herbicide	Thiocarbamate	GC/MS	1.1	2,3,4	0.8	6
Cyfluthrin	Insecticide	Pyrethroid	GC/MS	1	1	1.3	6
Cyhalofop-butyl	Herbicide	Aryloxyphenoxypropionate	GC/MS	1.9	2,3,4	0.8	6
Cyhalothrin	Insecticide	Pyrethroid	GC/MS	0.5	1	0.7	6
Cypermethrin	Insecticide	Pyrethroid	GC/MS	1	1	1.2	6
Cyproconazole	Fungicide	Triazole	GC/MS	4.7	2,3,4	1	6
Cyprodinil	Fungicide	Pyrimidine	GC/MS	7.4	2,3,4	1.7	6
DCPA	Herbicide	Benzenedicarboxylic acid	GC/MS	2	2,3,4	1.7	6
Deltamethrin	Insecticide	Pyrethroid	GC/MS	0.6	1	1.3	6
Diazinon	Insecticide	Organophosphate	GC/MS	0.9	2,3,4	1.6	6
Diazinon OA	Degradate	Organophosphate	GC/MS	5	2,3,4	Not yet determined	6
Difenoconazole	Fungicide	Triazole	GC/MS	10.5	2,3,4	1	6
Dimethomorph	Fungicide	Morpholine	GC/MS	6	2,3,4	1.5	6
Dithiopyr	Herbicide	Pyridine	GC/MS	1.6	2,3,4	1.3	6
EPTC	Herbicide	Thiocarbamate	GC/MS	1.5	2,3,4	0.8	6
Esfenvalerate	Insecticide	Pyrethroid	GC/MS	0.5	1	1	6
Ethalfluralin	Herbicide	Aniline	GC/MS	3	2,3,4	1.2	6
Etofenprox	Insecticide	Pyrethroid	GC/MS	2.2	2,3,4	1	6
Famoxadone	Fungicide	Oxazole	GC/MS	2.5	2,3,4	1.7	6
Fenamidone	Fungicide	Imidazole	GC/MS	5.1	2,3,4	Not yet determined	6

Compound	Type	Class	Method	Target Water MDL (ng/L)	Water Method/MDL Reference #	Target Sediment MDL	Sediment Method/MDL Reference #
Fenarimol	Fungicide	Pyrimidine	GC/MS	6.5	2,3,4	1.4	6
Fenbuconazole	Fungicide	Triazole	GC/MS	5.2	2,3,4	1.8	6
Fenhexamide	Fungicide	Anilide	GC/MS	7.6	2,3,4	2.5	6
Fenpropathrin	Insecticide	Pyrethroid	GC/MS	0.6	1	1	6
Fenpyroximate	Insecticide	Pyrazole	GC/MS	5.2	2,3,4	1.9	6
Fenthion	Insecticide	Organophosphate	GC/MS	5.5	2,3,4	2	6
Fipronil	Insecticide	Phenylpyrazole	GC/MS	2.9	2,3,4	1.6	6
Fipronil desulfinyl	Degradate	Phenylpyrazole	GC/MS	1.6	2,3,4	1.8	6
Fipronil desulfinyl amide	Degradate	Phenylpyrazole	GC/MS	3.2	2,3,4	2	6
Fipronil sulfide	Degradate	Phenylpyrazole	GC/MS	1.8	2,3,4	1.5	6
Fipronil sulfone	Degradate	Phenylpyrazole	GC/MS	3.5	2,3,4	1	6
Fluazinam	Fungicide	Pyridine	GC/MS	4.4	2,3,4	2.1	6
Fludioxinil	Fungicide	Pyrrole	GC/MS	7.3	2,3,4	2.5	6
Flufenacet	Herbicide	Anilide	GC/MS	4.7	2,3,4	1	6
Flumethralin	Plant growth regulator	Dinitroaniline	GC/MS	5.8	2,3,4	1.2	6
Fluopicolide	Fungicide	Pyrimidine	GC/MS	3.9	2,3,4	Not yet determined	6
Fluoxastrobin	Fungicide	Strobilurin	GC/MS	9.5	2,3,4	1.2	6
Flusilazole	Fungicide	Triazole	GC/MS	4.5	2,3,4	2.2	6
Flutolanil	Fungicide	Anilide	GC/MS	4.4	2,3,4	2.1	6
Flutriafol	Fungicide	Triazole	GC/MS	4.2	2,3,4	1.1	6
Fluxapyroxad	Fungicide	Anilide	GC/MS	4.8	2,3,4	Not yet determined	6

Compound	Type	Class	Method	Target Water MDL (ng/L)	Water Method/MDL Reference #	Target Sediment MDL	Sediment Method/MDL Reference #
Hexazinone	Herbicide	Triazone	GC/MS	8.4	2,3,4	0.9	6
Imazalil	Fungicide	Triazole	GC/MS	10.5	2,3,4	1.8	6
Indoxacarb	Insecticide	Oxadiazine	GC/MS	4.9	2,3,4	2.4	6
Ipconazole	Fungicide	Azole	GC/MS	Not yet determined	2,3,4	Not yet determined	6
Iprodione	Fungicide	Dicarboxamide	GC/MS	4.4	2,3,4	0.9	6
Kresoxim-methyl	Fungicide	Strobilurin	GC/MS	4	2,3,4	0.5	6
Malathion	Insecticide	Organophosphate	GC/MS	3.7	2,3,4	1	6
Malathion OA	Degradate	Organophosphate	GC/MS	5	2,3,4	Not yet determined	6
Metalaxyl	Fungicide	Phenylamide	GC/MS	5.1	2,3,4	1.9	6
Metconazole	Fungicide	Azole	GC/MS	5.2	2,3,4	1.2	6
Methidathion	Insecticide	Organophosphate	GC/MS	7.2	2,3,4	1.8	6
Methoprene	Insecticide	Terpene	GC/MS	6.4	2,3,4	1.6	6
Methylparathion	Insecticide	Organophosphate	GC/MS	3.4	2,3,4	1.1	6
Metolachlor	Herbicide	Chloroacetanilide	GC/MS	1.5	2,3,4	0.7	6
Molinate	Herbicide	Thiocarbamate	GC/MS	3.2	2,3,4	1	6
Myclobutanil	Fungicide	Triazole	GC/MS	6	2,3,4	1.7	6
Napropamide	Herbicide	Amide	GC/MS	8.2	2,3,4	0.9	6
Novaluron	Herbicide	Benzoylurea	GC/MS	2.9	2,3,4	1.1	6
Oxadiazon	Herbicide	Oxadiazolone	GC/MS	2.1	2,3,4	1.4	6
Oxyfluorfen	Herbicide	Nitrophenyl ether	GC/MS	3.1	2,3,4	1.9	6
p,p'-DDD	Degradate	Organochlorine	GC/MS	4.1	2,3,4	1	6

Compound	Type	Class	Method	Target Water MDL (ng/L)	Water Method/MDL Reference #	Target Sediment MDL	Sediment Method/MDL Reference #
p,p'-DDE	Degradate	Organochlorine	GC/MS	3.6	2,3,4	1	6
p,p'-DDT	Insecticide	Organochlorine	GC/MS	4	2,3,4	0.8	6
Paclobutrazol	Fungicide	Triazole	GC/MS	6.2	2,3,4	Not yet determined	6
Pebulate	Herbicide	Thiocarbamate	GC/MS	2.3	2,3,4	0.9	6
Pendimethalin	Herbicide	Aniline	GC/MS	2.3	2,3,4	0.8	6
Pentachloroanisole (PCA)	Insecticide	Organochlorine	GC/MS	4.7	2,3,4	1.1	6
Pentachloronitrobenzene (PCNB)	Fungicide	Organochlorine	GC/MS	3.1	2,3,4	1.1	6
Permethrin	Insecticide	Pyrethroid	GC/MS	0.6	1	0.9	6
Phenothrin	Insecticide	Pyrethroid	GC/MS	1	1	0.9	6
Phosmet	Insecticide	Organophosphate	GC/MS	4.4	2,3,4	0.9	6
Picoxystrobin	Fungicide	Strobilurin	GC/MS	4.2	2,3,4	Not yet determined	6
Piperonyl butoxide	Synergist	Unclassified	GC/MS	2.3	2,3,4	1.2	6
Prodiamine	Herbicide	Dinitroaniline	GC/MS	5.2	2,3,4	Not yet determined	6
Prometon	Herbicide	Triazine	GC/MS	2.5	2,3,4	2.7	6
Prometryn	Herbicide	Triazine	GC/MS	1.8	2,3,4	1.3	6
Propanil	Herbicide	Anilide	GC/MS	10.1	2,3,4	2.2	6
Propargite	Insecticide	Sulfite ester	GC/MS	6.1	2,3,4	2.2	6
Propiconazole	Fungicide	Azole	GC/MS	5	2,3,4	1.1	6
Propyzamide	Herbicide	Benzamide	GC/MS	5	2,3,4	1.7	6
Pyraclostrobin	Fungicide	Strobilurin	GC/MS	2.9	2,3,4	1.1	6
Pyridaben	Insecticide	Pyridazinone	GC/MS	5.4	2,3,4	1.2	6

Compound	Type	Class	Method	Target Water MDL (ng/L)	Water Method/MDL Reference #	Target Sediment MDL	Sediment Method/MDL Reference #
Pyrimethanil	Fungicide	Pyrmidine	GC/MS	4.1	2,3,4	1.1	6
Quinoxyfen	Fungicide	Quinoline	GC/MS	3.3	2,3,4	Not yet determined	6
Resmethrin	Insecticide	Pyrethroid	GC/MS	1	1	1.3	6
Sedaxane	Fungicide	Anilide	GC/MS	Not yet determined	2,3,4	Not yet determined	6
Simazine	Herbicide	Triazine	GC/MS	5	2,3,4	1.3	6
Tebuconazole	Fungicide	Azole	GC/MS	3.7	2,3,4	1.2	6
Tebupirimfos	Insecticide	Organophosphate	GC/MS	1.9	2,3,4	1.5	6
Tebupirimfos OA	Degradate	Organophosphate	GC/MS	2.8	2,3,4	2	6
Tefluthrin	Insecticide	Pyrethroid	GC/MS	0.6	1	0.7	6
Tetraconazole	Fungicide	Azole	GC/MS	5.6	2,3,4	1.1	6
Tetradifon	Insecticide	Bridged diphenyl	GC/MS	3.8	2,3,4	2	6
Tetramethrin	Insecticide	Pyrethroid	GC/MS	0.5	1	0.9	6
t-Fluvalinate	Insecticide	Pyrethroid	GC/MS	0.7	1	1.2	6
Thiazopyr	Herbicide	Pyridine	GC/MS	4.1	2,3,4	1.9	6
Thiobencarb	Herbicide	Thiocarbamate	GC/MS	1.9	2,3,4	0.6	6
Triadimefon	Fungicide	Triazole	GC/MS	8.9	2,3,4	1.5	6
Triadimenol	Fungicide	Triazole	GC/MS	8	2,3,4	1.5	6
Triallate	Herbicide	Carbamate	GC/MS	2.4	2,3,4	1.4	6
Tribufos	Herbicide	Organophosphate	GC/MS	3.1	2,3,4	2.2	6
Trifloxystrobin	Fungicide	Strobilurin	GC/MS	4.7	2,3,4	1	6
Triflumizole	Fungicide	Azole	GC/MS	6.1	2,3,4	1.1	6

Compound	Type	Class	Method	Target Water MDL (ng/L)	Water Method/MDL Reference #	Target Sediment MDL	Sediment Method/MDL Reference #
Trifluralin	Herbicide	Aniline	GC/MS	2.1	2,3,4	0.9	6
Triticonazole	Fungicide	Azole	GC/MS	6.9	2,3,4	1.8	6
Zoxamide	Fungicide	Benzamide	GC/MS	3.5	2,3,4	1.1	6
3,4-DCA (diuron degradate)	Degradate	Urea	LC-MS/MS	3.2	5		
Acetamiprid	Insecticide	Neonicotinoid	LC-MS/MS	3.3	5		
Carbendazim	Fungicide/Degradate	Benzimidazole	LC-MS/MS	4.2	5		
Chlorantraniliprole	Insecticide	Anthranilic diamide	LC-MS/MS	4	5		
Clothianidin	Insecticide	Neonicotinoid	LC-MS/MS	3.9	5		
Cyantraniliprole	Insecticide	Anthranilic diamide	LC-MS/MS	4.2	5		
Cyazofamid	Fungicide	Azole	LC-MS/MS	4.1	5		
Cymoxanil	Fungicide	Unclassified	LC-MS/MS	3.9	5		
DCPMU (diuron degradate)	Degradate	Urea	LC-MS/MS	3.5	5		
DCPU (diuron degradate)	Degradate	Urea	LC-MS/MS	3.4	5		
Desthio-Prothioconazole	Fungicide	Azole	LC-MS/MS	3	5		
Dinotefuran	Insecticide	Neonicotinoid	LC-MS/MS	4.5	5		
Diuron	Herbicide	Urea	LC-MS/MS	3.2	5		
Ethaboxam	Fungicide	Unclassified	LC-MS/MS	3.8	5		
Flonicamid	Insecticide	Unclassified	LC-MS/MS	3.4	5		
Fluridone	Herbicide	Unclassified	LC-MS/MS	3.7	5		
Imidacloprid	Insecticide	Neonicotinoid	LC-MS/MS	3.8	5		
Mandipropamid	Fungicide	Mandelamide	LC-MS/MS	3.3	5		
Methoxyfenozide	Insecticide	Diacylhydrazine	LC-MS/MS	2.7	5		

Compound	Type	Class	Method	Target Water MDL (ng/L)	Water Method/MDL Reference #	Target Sediment MDL	Sediment Method/MDL Reference #
Oryzalin	Herbicide	2,6-Dinitroaniline	LC-MS/MS	5	5		
Penoxsulam	Herbicide	Triazolopyrimidine	LC-MS/MS	3.5	5		
Thiabendazole	Fungicide	Benzimidazole	LC-MS/MS	3.6	5		
Thiacloprid	Insecticide	Neonicotinoid	LC-MS/MS	3.2	5		
Thiamethoxam	Insecticide	Neonicotinoid	LC-MS/MS	3.4	5		
Tofenpyrad	Insecticide	Pyrazole	LC-MS/MS	2.9	5		

Method Reference Number – Reference

1 - Hladik, M.L., Smalling, K.L., and Kuivila, K.M., 2009, Methods of analysis—Determination of pyrethroid insecticides in water and sediment using gas chromatography/mass spectrometry: U.S. Geological Survey Techniques and Methods 5–C2, 18 p
2 - Hladik, M.L., Smalling, K.L., and Kuivila, K.M., 2008, A multi-residue method for the analysis of pesticides and pesticide degradates in water using Oasis HLB solid phase extraction and gas chromatography-ion trap mass spectrometry: Bulletin of Environmental Contamination and Toxicology, v. 80, p. 139–144.
3 - Smalling, K.L., Orlando, J.L., Calhoun, Daniel, Battaglin, W.A., and Kuivila, K.M., 2012, Occurrence of pesticides in water and sediment collected from amphibian habitats located throughout the United States, 2009–10: U.S. Geological Survey Data Series 707, 40p.
4 - Orlando, J.L., McWayne, Megan, Sanders, Corey, and Hladik, Michelle, Dissolved pesticide concentrations in the Sacramento-San Joaquin Delta and Grizzly Bay, California, 2011–12: U.S. Geological Survey Data Series 779, 24 p.
5 - Hladik, M.L., and Calhoun, D.L., 2012, Analysis of the herbicide diuron, three diuron degradates, and six neonicotinoid insecticides in water—Method details and application to two Georgia streams: U.S. Geological Survey Scientific Investigations Report 2012–5206, 10 p.
6 - Hladik, M.L., and McWayne, M.M., 2012, Methods of analysis—Determination of pesticides in sediment using gas chromatography/mass spectrometry: U.S. Geological Survey Techniques and Methods 5–C3, 18 p. Available at http://pubs.usgs.gov/tm/tm5c3

Water

Water samples were collected during a precipitation event on October 28, 2016 between 8:45 am and 12:15 pm (Table B-1). Samples were collected from the same five sites at which sediment samples were collected in September. However, the Pull-Out sediment site on the Russian River below Kabutts Road was relocated to the Riverfront Park site during water sampling due to private property access restrictions during the storm (Figure B-1).

Samples were estimated to have taken place after less than a centimeter of rain had fallen during this particular rain event, but following a separate rain event that took places several days earlier. Runoff from this earlier event had not fully receded at the time of sampling collection. Figure B-2 shows the timing of sample collection relative to the storm period and runoff volume. At the northernmost site on the East Fork of the Russian River (Potter Valley site), samples were collected during the falling limb of what was a small runoff event. Samples collected farther south on the main stem of the Russian River (Hopland, Jimtown, and Riverfront sites) and on Mark West Creek (Trenton Road site) were collected during the rising limb of the storm period. However, at these downstream sites, nearby stream gage measurements suggest that a significant volume of runoff created by the earlier rain event was captured by this sampling event.

Grab samples were collected by submerging a 1-L amber glass jar, provided by the USGS analytical laboratory, approximately 0.5 m below the water surface. One trip blank and one replicate sample were collected, along with enough sample for laboratory analysis of a matrix spike and matrix spike replicate. Samples were stored on wet ice in the field and shipped overnight to the analytical laboratory for analysis. No field filtering or chemical preservation was conducted. Samples were analyzed for pesticides both in total water and on suspended sediment with the USGS GC/MS method (Hladik et al. 2008, Hladik et al. 2009, Smalling et al. 2012, Orlando et al. 2012), and in total water with the USGS LC/MS/MS method (Table B-2; Hladik and Calhoun, 2012).

Field measurements were collected for the same parameters using the same methods as during sediment sampling.

Figure B-2. Hydrographs of stormwater runoff measured at USGS stream gages at or just downstream of each sampling location. The time of water sample collection is marked on each hydrograph in red.

Figure B-2A. Storm hydrograph near the Potter Valley sampling site

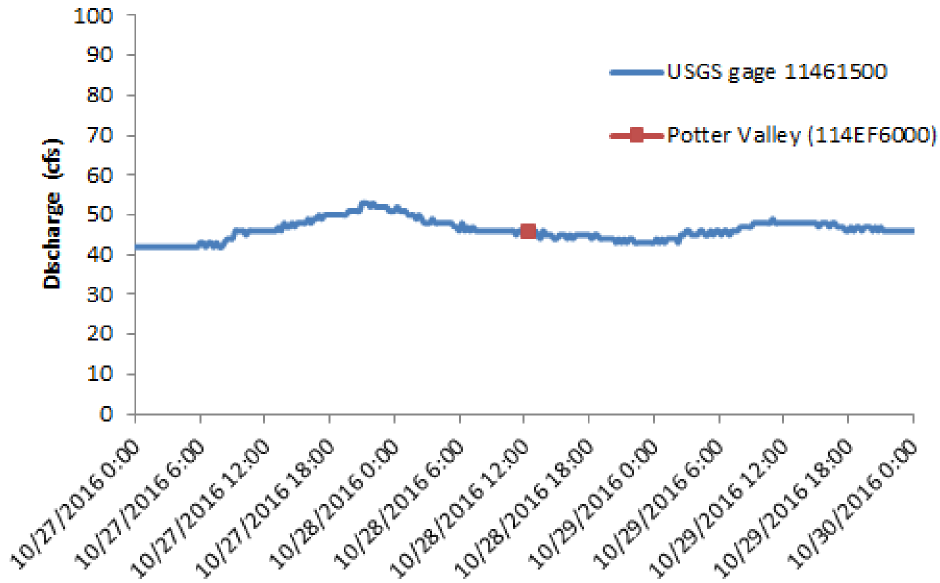


Figure B-2B. Storm hydrograph at the Hopland sampling site

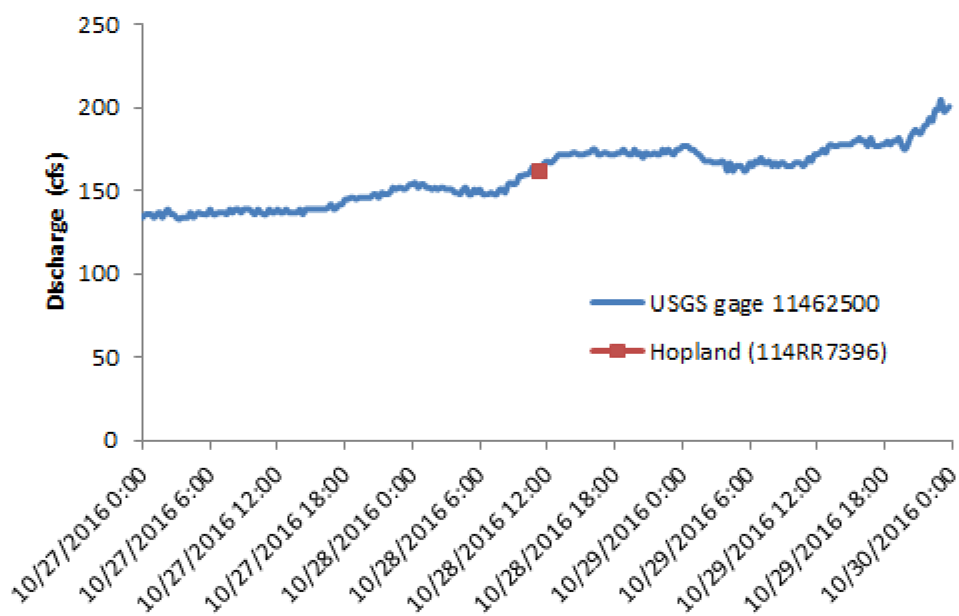
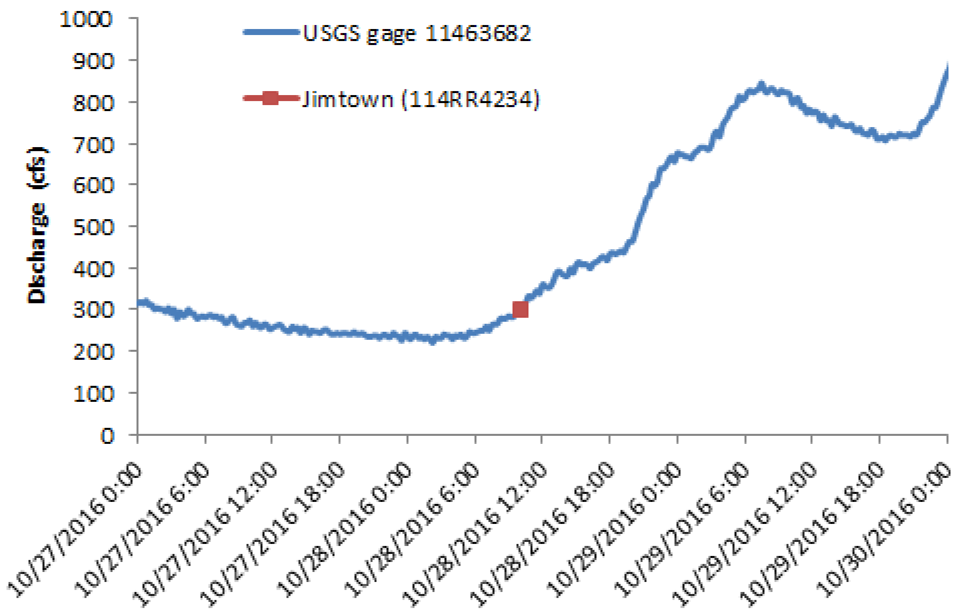


Figure B-2C. Storm hydrograph at the Jimtown sampling site



Figures B-2D. Storm hydrograph near the Riverfront sampling site

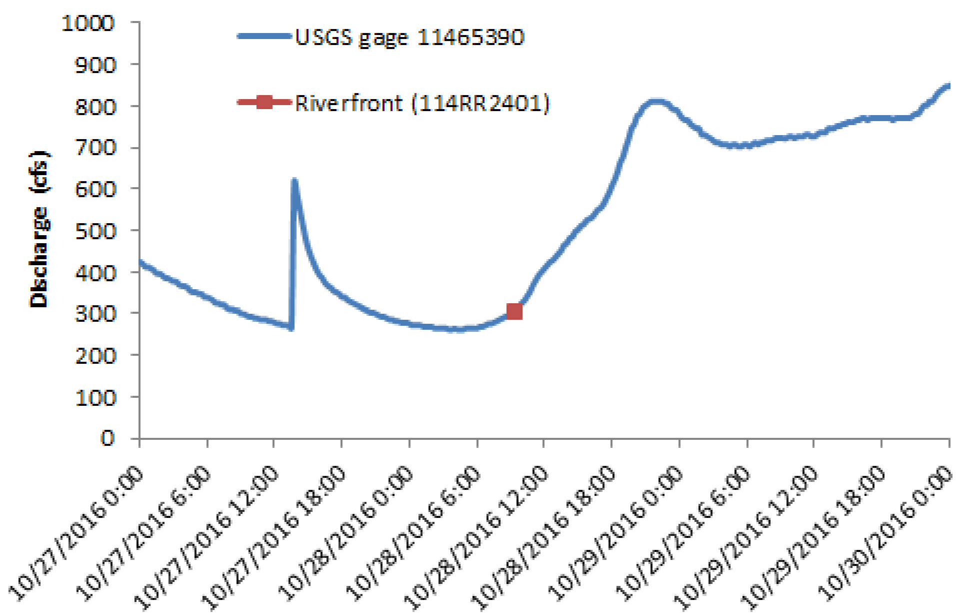
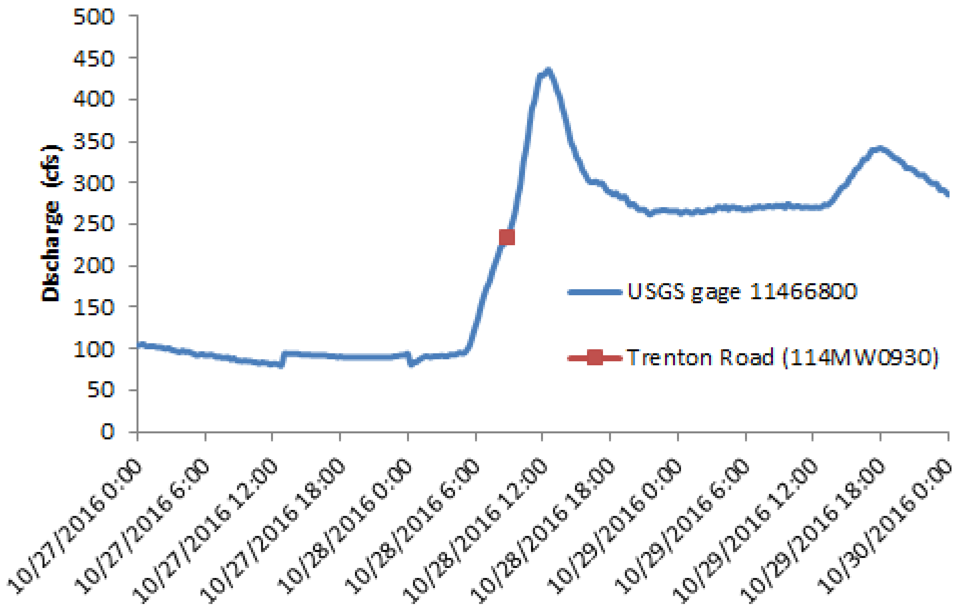


Figure B-2E. Storm hydrographs near the Trenton Road sampling site



References

Hladik, M.L., Smalling, K.L., and Kuivila, K.M., 2008, A multi-residue method for the analysis of pesticides and pesticide degradates in water using Oasis HLB solid phase extraction and gas chromatography-ion trap mass spectrometry: Bulletin of Environmental Contamination and Toxicology, v. 80, p. 139–144.

Hladik, M.L., Smalling, K.L., and Kuivila, K.M., 2009, Methods of analysis—Determination of pyrethroid insecticides in water and sediment using gas chromatography/mass spectrometry: U.S. Geological Survey Techniques and Methods 5–C2, 18 p

Smalling, K.L., Orlando, J.L., Calhoun, Daniel, Battaglin, W.A., and Kuivila, K.M., 2012, Occurrence of pesticides in water and sediment collected from amphibian habitats located throughout the United States, 2009–10: U.S. Geological Survey Data Series 707, 40p.

Orlando, J.L., McWayne, Megan, Sanders, Corey, and Hladik, Michelle, Dissolved pesticide concentrations in the Sacramento-San Joaquin Delta and Grizzly Bay, California, 2011–12: U.S. Geological Survey Data Series 779, 24 p.

Hladik, M.L., and Calhoun, D.L., 2012, Analysis of the herbicide diuron, three diuron degradates, and six neonicotinoid insecticides in water—Method details and application to two Georgia streams: U.S. Geological Survey Scientific Investigations Report 2012–5206, 10 p.

Hladik, M.L., and McWayne, M.M., 2012, Methods of analysis—Determination of pesticides in sediment using gas chromatography/mass spectrometry: U.S. Geological Survey Techniques and Methods 5–C3, 18 p. Available at http://pubs.usgs.gov/tm/tm5c3

Surface Water Ambient Monitoring Program. 2012. Statewide Stream Pollution Trends Monitoring Program - Quality Assurance Project Plan. UC Davis Marine Pollution Studies Laboratory Granite Canyon. http://www.waterboards.ca.gov/water_issues/programs/swamp /qapp/qapp_spot_strms_pollute_final.pdf

Appendix C. Analyte Lists, Toxicity Thresholds, and Method Details

Table C-1. Water Analyte List (dissolved phase), toxicity thresholds (µg/L), and method details

Pesticide	**OW Aquatic Life Criteria[1]**		**OPP Aquatic Life Benchmarks[2]** *(italicized: OPP benchmark equivalents, Luo et al. 2013[3])*						**OPP Benchmark Equivalents[4]**	**MDLs (µg/L)**	**Detection Frequency**	**Analysis[5]**
			Fish		Invertebrates		Nonvascular plants	Vascular plants	Lowest reported			
	Acute	Chronic	Acute	Chronic	Acute	Chronic	Acute	Acute	Acute			
Fungicides												
Acibenzolar-S-methyl	—	—	—	—	—	—	—	—	***200***	0.003		GC/MS
Azoxystrobin	—	—	235	147	130	**44**	49	3400	—	0.0031	1 / 5	GC/MS
Boscalid	—	—	1350	**116**	>2665	790	1340	>3900	—	0.0028	4 / 5	GC/MS
Bromoconazole	—	—	—	—	—	—	—	—	—	0.0032		GC/MS
Captan	—	—	**13.1**	16.5	4200	560	320	>12700	—	0.0102		GC/MS
Carbendazim	—	—	*190*	—	*150*	—	*7700*	—	***75***	0.0042	4 / 5	LC/MS
Carboxin	—	—	600	—	42,200	—	370	670	—	0.0045		GC/MS (D)
Chlorothalonil	—	—	5.25	3	1.8	**0.6**	6.8	630	—	0.0041		GC/MS
Cyazofamid	—	—	>53.5	90.1	>650	**<87**	—	>1220	—	0.0041		LC/MS
Cymoxanil	—	—	*29000*	—	*27000*	—	***254***	—	*254*	0.0039		LC/MS
Cyproconazole	—	—	—	—	—	—	—	—	***99***	0.0047		GC/MS
Cyprodinil	—	—	1205	230	16	**8**	2250	—	—	0.0074		GC/MS
Desthio-prothioconazole	—	—	—	—	—	—	—	—	—	0.003		LC/MS
Difenoconazole	—	—	405	8.7	385	**5.6**	98	1900	—	0.0105		GC/MS
Dimethomorph	—	—	3100	<341	>5300	**110**	—	—	—	0.006		GC/MS
Ethaboxam	—	—	1090	880	185	**50**	>3600			0.0038		LC/MS
Famoxadone	—	—	*11*	—	*12*	—	*22*	—	***5.5***	0.0025		GC/MS
Fenamidone	—	—	370	**4.7**	24.5	12.5	70	>880	—	0.0051		GC/MS
Fenarimol	—	—	450	180	3400	113	**100**	—	—	0.0065		GC/MS
Fenbuconazole	—	—	*1500*	—	*2300*	—	***330***	—	*330*	0.0052		GC/MS
Fenhexamid	—	—	670	**101**	>9400	1000	4820	>2300	—	0.0076		GC/MS
Fluazinam	—	—	18	**0.69**	90	68	1.1	—	—	0.0044		GC/MS

Table C-1. Water Analyte List (dissolved phase), toxicity thresholds (µg/L), and method details

Pesticide	**OW Aquatic Life Criteria**[1]		**OPP Aquatic Life Benchmarks**[2] *(italicized: OPP benchmark equivalents, Luo et al. 2013*[3]*)*						**OPP Benchmark Equivalents**[4]	**MDLs (µg/L)**	**Detection Frequency**	**Analysis**[5]
			Fish		Invertebrates		Nonvascular plants	Vascular plants	Lowest reported			
	Acute	Chronic	Acute	Chronic	Acute	Chronic	Acute	Acute	Acute			
Fludioxonil	—	—	235	19	450	**<19**	70	>1000	—	0.0073		GC/MS
Fluopicolide	—	—	174.5	151	>850	190	**<1.4**	>3200	—	0.0039		GC/MS
Fluoxastrobin	—	—	*435*	—	*480*	—	*350*	—	***217.5***	0.0095		GC/MS
Flusilazole	—	—	—	—	—	—	—	—	***600***	0.0045		GC/MS
Flutolanil	—	—	1250	**233**	>3400	530	8010	8010	—	0.0044	1 / 5	GC/MS
Flutriafol	—	—	16500	4800	33550	**310**	460	780	—	0.0042		GC/MS
Fluxapyroxad	—	—	—	—	—	—	—	—	***18***	0.0048	1 / 5	GC/MS
Imazalil	—	—	*1480*	—	*3500*	—	*870*	—	***740***	0.0105		GC/MS
Ipconazole	—	—	765	0.18	850	—	—	—	—	0.0078		GC/MS
Iprodione	—	—	—	260	**120**	—	>130	>12640	—	0.0044	1 / 5	GC/MS
Kresoxim-methyl	—	—	95	87	166	55	**29.2**	>301	—	0.004		GC/MS
Mandipropamid	—	—	—	**220**	3550	—	>2500	>7400	—	0.0033		LC/MS
Metalaxyl	—	—	65000	9100	14000	**100**	140000	92000	—	0.0051		GC/MS
Metconazole	—	—	*2100*	—	*4200*	—	*1700*	—	***1050***	0.0052		GC/MS
Myclobutanil	—	—	1200	980	5500	—	**830**	—	—	0.006		GC/MS
Oxathiapiprolin	—	—	>345	460	>280	750	>140	>790	—	0.0032		GC/MS (D)
Paclobutrazol	—	—	7950	49	120	9	40800	**8**	—	0.0062		GC/MS
Pentachloronitrobenzene	—	—	50	**13**	385	18	—	—	—	0.0031		GC/MS
Penthiopyrad	—	—	145	***100***	1266	471	1200	>1205	—	0.0032		GC/MS (D)
Picoxystrobin	—	—	32.5	36	12	**1**	4	210	—	0.0042		GC/MS
Fluopyram	—	—	—	—	—	—	—	—	***67.5***	0.0038	1 / 5	GC/MS
Propiconazole	—	—	425	95	650	260	**21**	4828	—	0.005		GC/MS
Pyraclostrobin	—	—	3.1	2.35	7.85	4	**1.5**	1720	—	0.0029		GC/MS
Pyrimethanil	—	—	5050	**20**	1500	1000	1800	7800	—	0.0041		GC/MS
Quinoxyfen	—	—	—	—	—	—	—	—	***27***	0.0033		GC/MS

Table C-1. Water Analyte List (dissolved phase), toxicity thresholds (µg/L), and method details

Pesticide	OW Aquatic Life Criteria[1]		OPP Aquatic Life Benchmarks[2] *(italicized: OPP benchmark equivalents, Luo et al. 2013[3])*						OPP Benchmark Equivalents[4]	MDLs (µg/L)	Detection Frequency	Analysis[5]
			Fish		Invertebrates		Nonvascular plants	Vascular plants	Lowest reported			
	Acute	Chronic	Acute	Chronic	Acute	Chronic	Acute	Acute	Acute			
Sedaxane	—	—	—	—	—	—	—	—	—	0.0052		GC/MS
Tebuconazole	—	—	1135	**12**	1440	120	1450	151.5	—	0.0037		GC/MS
Tetraconazole	—	—	1925	300	1315	**190**	—	310	—	0.0056		GC/MS
Thiabendazole	—	—	280	110	155	**42**	3060	2320	—	0.0036		LC/MS
Triadimefon	—	—	2050	**41**	800	52	17000	—	—	0.0089		GC/MS
Triadimenol	—	—	—	—	—	—	—	—	***9600***	0.008		GC/MS
Tricyclazole	—	—	—	—	—	—	—	—	***3650***	0.0041		GC/MS (D)
Trifloxystrobin	—	—	7.15	4.3	12.65	**2.76**	37.1	>1930	—	0.0047		GC/MS
Triflumizole	—	—	290	**33**	695	67	140	720	—	0.0061		GC/MS
Triticonazole	—	—	—	—	—	—	—	—	***1000***	0.0069		GC/MS
Zoxamide	—	—	78	**3.48**	>390	39	10	19	—	0.0035		GC/MS
Herbicides												
Alachlor	—	—	900	187	1250	110	**1.64**	2.3	—	0.0017		GC/MS
Atrazine	—	—	2650	—	360	60	**<1**	4.6	—	0.0023		GC/MS
Benfluralin			34.85	**1.9**	1090	15.5	>100			0.002		GC/MS
Butralin	—	—	—	—	—	—	—	—	***60***	0.0026		GC/MS
Butylate	—	—	**105**	—	5950	—	—	—	—	0.0018		GC/MS
Clomazone	—	—	1450	350	2700	2200	**167**	30200	—	0.0025		GC/MS
Cycloate	—	—	2250	—	**1300**	—	—	—	—	0.0011		GC/MS
Cyhalofop-butyl	—	—	*790*	—	*2700*	—	*960*	—	***395***	0.0019		GC/MS
Dacthal	—	—	15000	—	13500	—	**>11000**	**>11000**	—	0.002		GC/MS
Dichlorobenzenamine, 3,4-	—	—	—	—	—	—	—	—	—	0.0032	1 / 5	GC/MS (P); LC/MS (D)
Dichloroaniline, 3,5-	—	—	—	—	—	—	—	—	—	0.0076		GC/MS
Dichlorophenyl Urea, 3,4-	—	—	—	—	—	—	—	—	—	0.0034	3 / 5	LC/MS

Table C-1. Water Analyte List (dissolved phase), toxicity thresholds (µg/L), and method details

Pesticide	OW Aquatic Life Criteria[1]		OPP Aquatic Life Benchmarks[2] *(italicized: OPP benchmark equivalents, Luo et al. 2013[3])*						OPP Benchmark Equivalents[4]	MDLs (µg/L)	Detection Frequency	Analysis[5]
			Fish		Invertebrates		Nonvascular plants	Vascular plants	Lowest reported			
	Acute	Chronic	Acute	Chronic	Acute	Chronic	Acute	Acute	Acute			
Dichlorophenyl-3-methyl Urea, 3,4-	—	—	—	—	—	—	—	—	—	0.0035	1 / 5	LC/MS
Dithiopyr			235	56	>850	81	**20**			0.0016	1 / 5	GC/MS
Diuron	—	—	200	26.4	80	200	**2.4**	15	—	0.0032	3 / 5	LC/MS
EPTC	—	—	7000	—	3250	**800**	1,400	5600	—	0.0015		GC/MS
Ethalfluralin	—	—	16	**0.4**	30	24	25	—	—	0.003		GC/MS
Flufenacet	—	—	—	—	—	—	—	—	***2.04***	0.0047		GC/MS
Fluridone	—	—	2800	**480**	680	—	—	—	—	0.0037		LC/MS
Hexazinone	—	—	137000	17000	75800	20000	**7**	37.4	—	0.0084		GC/MS
Metolachlor	—	—	1900	30	550	**1**	10	48	—	0.0015		GC/MS
Molinate	—	—	**105**	390	170	340	220	3300	—	0.0032		GC/MS
Napropamide	—	—	3200	**1100**	7150	**1100**	3400	—	—	0.0082		GC/MS
Novaluron	—	—	>490	6.16	0.075	**0.03**	3549	>75.4	—	0.0029		GC/MS
Oryzalin	—	—	1440	220	750	358	42	**>15.4**	—	0.005		LC/MS
Oxadiazon	—	—	600	33	1090	33	**5.2**	41	—	0.0021	1 / 5	GC/MS
Oxyfluorfen	—	—	100	1.3	750	13	1.1	**0.49**	—	0.0031		GC/MS
Pebulate	—	—	3150	—	3315	—	**230**	1800	—	0.0023		GC/MS
Pendimethalin	—	—	69	6.3	140	14.5	**5.2**	12.5	—	0.0023		GC/MS
Penoxsulam	—	—	>51000	10200	>49250	2950	92	**3**	—	0.0035		LC/MS
Prodiamine	—	—	>6.5	—	>6.5	**1.5**	—	—	—	0.0052	1 / 5	GC/MS
Prometon	—	—	6000	19700	12850	3450	**98**	—	—	0.0025		GC/MS
Prometryn	—	—	1455	620	4850	1000	**1.04**	11.9	—	0.0018		GC/MS
Propyzamide	—	—	36000	7700	>2800	**600**	>4000	1180	—	0.005		GC/MS
Propanil	—	—	1150	**9.1**	600	86	16	110	—	0.0101		GC/MS

Table C-1. Water Analyte List (dissolved phase), toxicity thresholds (µg/L), and method details

Pesticide	OW Aquatic Life Criteria[1]		OPP Aquatic Life Benchmarks[2] *(italicized: OPP benchmark equivalents, Luo et al. 2013[3])*						OPP Benchmark Equivalents[4]	MDLs (µg/L)	Detection Frequency	Analysis[5]
			Fish		Invertebrates		Nonvascular plants	Vascular plants	Lowest reported			
	Acute	Chronic	Acute	Chronic	Acute	Chronic	Acute	Acute	Acute			
Simazine	—	—	3200	—	500	—	**2.24**	140	—	0.005	1 / 5	GC/MS
Thiazopyr	—	—	*3400*	—	*6100*	—	***40***	—	*40*	0.0041		GC/MS
Thiobencarb	—	—	220	21	50.6	**1**	17	770	—	0.0019		GC/MS
Triallate	—	—	600	38	45.5	**14**	21	2400	—	0.0024		GC/MS
Tributyl Phosphorotrithioate, S,S,S-	—	—	122.5	3.5	3.4	**1.56**	148	1100	—	0.0031		GC/MS
Trifluralin	—	—	20.5	**1.14**	280	2.4	7.52	43.5	—	0.0021		GC/MS
Insecticides												
Acetamiprid	—	—	>50000	19200	10.5	**2.1**	>1000	>1000	—	0.0033		LC/MS
Allethrin	—	—	—	—	**1.05**	—	—	—	—	0.001		GC/MS
Azinphos Methyl	—	—	0.18	0.055	0.08	**0.036**	—	—	—	0.0094		GC/MS
Azinphos Methyl Oxon	—	—	—	—	—	—	—	—	—	0.0094		GC/MS
Bifenthrin	—	—	0.075	0.04	0.8	**0.001**	—	—	—	0.0007		GC/MS
Carbaryl	2.1	2.1	110	6	0.85	**0.5**	660	1500	—	0.0065		GC/MS
Carbofuran	—	—	44	5.7	1.115	**0.75**	—	—	—	0.0031		GC/MS
Chlorantraniliprole	—	—	>600	110	4.9	**4.5**	1800	2000	—	0.004	1 / 5	LC/MS
Chlorpyrifos	0.083	0.041	0.9	0.57	0.05	0.04	140	—	**0.025**	0.0021		GC/MS
Chlorpyrifos Oxon	—	—	—	—	—	—	—	—	—	0.005		GC/MS
Clothianidin	—	—	>50750	9700	**11**	**11**	64000	121000	—	0.0039	1 / 5	LC/MS
Coumaphos	—	—	140	11.7	0.037	**0.034**	—	—	—	0.0031		GC/MS
Cyantraniliprole	—	—	>5000	10700	10.2	**6.56**	>10000	12100	—	0.0042		LC/MS
Cyfluthrin, total	—	—	0.034	0.01	0.013	**0.007**	>181	—	—	0.001		GC/MS
Cyhalothrin			0.105	0.031	0.004	**0.002**	>310			0.0005		GC/MS
Cypermethrin, Total	—	—	0.195	0.14	0.21	**0.069**	—	—	—	0.001		GC/MS

Table C-1. Water Analyte List (dissolved phase), toxicity thresholds (µg/L), and method details

Pesticide	OW Aquatic Life Criteria[1]		OPP Aquatic Life Benchmarks[2] *(italicized: OPP benchmark equivalents, Luo et al. 2013[3])*						OPP Benchmark Equivalents[4]	MDLs (µg/L)	Detection Frequency	Analysis[5]
			Fish		Invertebrates		Nonvascular plants	Vascular plants	Lowest reported			
	Acute	Chronic	Acute	Chronic	Acute	Chronic	Acute	Acute	Acute			
DDD(p,p')	—	—	—	—	—	—	—	—	—	0.0041		GC/MS
DDE(p,p')	—	—	—	—	—	—	—	—	—	0.0036		GC/MS
DDT(p,p')	1.1	**0.001**	—	—	—	—	—	—	—	0.004		GC/MS
Deltamethrin	—	—	0.29	0.017	0.055	**0.004**	—	—	—	0.0006		GC/MS
Diazinon	0.17	0.17	45	<0.55	**0.105**	0.17	3700	—	0.16	0.0009		GC/MS
Diazoxon	—	—	—	—	—	—	—	—	—	0.005		GC/MS
Dinotefuran	—	—	>49550	**>6360**	>484150	>95300	>97600	>110000	—	0.0045		LC/MS
Esfenvalerate	—	—	0.035	0.035	0.025	**0.017**	—	—	—	0.0005		GC/MS
Ethofenprox	—	—	1.35	23	0.4	**0.17**	>18.8	>26	—	0.0022		GC/MS
Fenpropathrin	—	—	1.1	0.091	0.265	**0.064**	—	—	—	0.0006		GC/MS
Fenpyroximate	—	—	0.22	**0.11**	0.8	0.56	1.9	>190	—	0.0052		GC/MS
Fenthion	—	—	415	7.5	2.6	**0.013**	400	>2800	—	0.0055		GC/MS
Fipronil	—	—	41.5	6.6	0.11	**0.011**	140	>100	—	0.0029	1 / 5	GC/MS
Fipronil Desulfinyl	—	—	10	**0.59**	100	10.3	140	>100	—	0.0016	1 / 5	GC/MS
Fipronil Desulfinyl Amide	—	—	—	—	—	—	—	—	—	0.0032		GC/MS
Fipronil Sulfide	—	—	41.5	6.6	1.065	**0.11**	140	>100	—	0.0018	1 / 5	GC/MS
Fipronil Sulfone	—	—	12.5	0.67	0.36	**0.037**	140	>100	—	0.0035	1 / 5	GC/MS
Flonicamid	—	—	*100000*	—	*1E+05*	—	***3300***	—	*3300*	0.0034		LC/MS
Flupyradifurone	—	—	—	—	—	—	—	—	—	0.003		GC/MS (D)
Imidacloprid	—	—	114500	9000	0.385	**0.01**	>10000	—	—	0.0038	1 / 5	LC/MS
Indoxacarb	—	—	145	150	300	**75**	>110	>84	—	0.0049		GC/MS
Malaoxon	—	—	—	—	—	—	—	—	—	0.005		GC/MS
Malathion	—	0.1	16.5	8.6	0.295	**0.035**	2400	>9630	—	0.0037		GC/MS
Methidathion	—	—	1.1	6.3	1.5	**0.66**	—	—	—	0.0072		GC/MS

Table C-1. Water Analyte List (dissolved phase), toxicity thresholds (µg/L), and method details

Pesticide	OW Aquatic Life Criteria[1]		OPP Aquatic Life Benchmarks[2] *(italicized: OPP benchmark equivalents, Luo et al. 2013[3])*						OPP Benchmark Equivalents[4]	MDLs (µg/L)	Detection Frequency	Analysis[5]
			Fish		Invertebrates		Nonvascular plants	Vascular plants	Lowest reported			
	Acute	Chronic	Acute	Chronic	Acute	Chronic	Acute	Acute	Acute			
Methoprene	—	—	380	**48**	165	51	—	—	—	0.0064		GC/MS
Methoxyfenozide	—	—	>2100	530	25	**6.3**	>3400	—	—	0.0027		LC/MS
Parathion, Methyl	—	—	925	<10	0.485	**0.25**	15000	18000	—	0.0034		GC/MS
Pentachloroanisole	—	—	**28**	—	150	—	—	—	—	0.0047		GC/MS
Permethrin, Total	—	—	0.395	0.0515	0.011	**0.001**	68	—	—	0.0006		GC/MS
Phenothrin	—	—	7.9	1.1	2.2	**0.47**	—	—	—	0.001		GC/MS
Phosmet	—	—	35	3.2	1	**0.8**	—	—	—	0.0044		GC/MS
Propargite	—	—	59	16	37	**9**	66.2	75000	—	0.0061		GC/MS
Pyridaben	—	—	—	—	—	—	—	—	—	0.0054		GC/MS
Resmethrin	—	—	**0.14**	0.35	1.55	—	—	—	—	0.001		GC/MS
Sulfoxaflor	—	—	>181,500	660	>200,000	50,500	81,200	>99,000	—	0.0044		GC/MS (D)
Tebufenozide	—	—	1500	<48	1900	4.3	>740	—	—	0.003		GC/MS (D)
Tebupirimfos	—	—	44.5	130	0.039	**0.011**	630	8800	—	0.0019		GC/MS
Tebupirimfos oxon	—	—	—	—	—	—	—	—	—	0.0028		GC/MS
Tefluthrin	—	—	0.03	**0.004**	0.035	0.008	—	—	—	0.0006		GC/MS
Tetradifon	—	—	—	—	—	—	—	—	***1000***	0.0038		GC/MS
Tetramethrin	—	—	**1.85**	—	22.5	—	—	—	—	0.0005		GC/MS
T-Fluvalinate	—	—	0.175		0.47	**0.1**				0.0007		GC/MS
Thiacloprid	—	—	12600	918	18.9	**0.97**	45000	>95400	—	0.0032		LC/MS
Thiamethoxam	—	—	>50000	20000	**17.5**	—	>97000	>90000	—	0.0034		LC/MS
Tolfenpyrad	—	—	**0.0815**	0.188	0.5	0.244	1	>30	—	0.0029		LC/MS
Synergists												
Flumetralin	—	—	—	—	—	**—**	—	—	***12.5***	0.0058		GC/MS
Piperonyl Butoxide	—	—	950	40	255	**30**	—	—	—	0.0023		GC/MS

1 - EPA. 2015. National Recommended Water Quality Criteria - Aquatic Life Criteria Table. URL: http://www2.epa.gov/wqc/national-recommended-water-quality-criteria-aquatic-life-criteria-table. Accessed on November 23, 2015.

2 - EPA. 2017. Aquatic Life Benchmarks for Pesticide Registration. URL: http://www2.epa.gov/pesticide-science-and-assessing-pesticide-risks/aquatic-life-benchmarks-pesticide-registration#benchmarks. Accessed on November 30, 2017.

3 - Luo, Y., Deng, X., Budd, R., Starner, K. and Ensminger, M. 2013. Methodology for Prioritizing Pesticides for Surface Water Monitoring in Agricultural and Urban Areas (http://www.cdpr.ca.gov/docs/emon/surfwtr/monitoring_methods.htm). California Department of Pesticide Regulation, Sacramento, CA.

4 - See footnote 3. New benchmarks calculated after 2013 were provided by Yuzhou Luo (DPR) and shown in red text. Both acute and chronic benchmarks are used in the SWMP model and are shown here if lower than the acute benchmarks, but the process for calculating chronic benchmark equivalent values has not yet been formalized by DPR. The benchmarks shown for fluopyram and fluxapyroxad are chronic benchmark equivalents; all others are acute benchmark equivalents.

5 - GC/MS method described in Hladik and McWayne 2012; LC/MS method described in Hladik and Calhoun 2012. Samples were analyzed in the dissolved phase (D) using both GC/MS and LC/MS; samples were analyzed in the particulate phase (P) using GC/MS only. Six compounds were analyzed by GC/MS but not in the particulate phase and are marked with a (D); one compound was analyzed by both LC/MS (dissolved phase) and GC/MS (particulate phase).

Table C-2. Sediment Analyte List, USGS toxicity benchmarks, and method detection limits

Analyte Name	Min MDL (µg/g-OC), TOC=2.89%	Max MDL (µg/g-OC), TOC=0.4%	TEB Threshold (µg/g-oc)	LEB Threshold (µg/g-oc)
Fungicides				
Azoxystrobin	0.03	0.23	19	110
Boscalid	0.04	0.30	240	860
Captan	0.11	0.78	54	810
Chlorothalonil	0.04	0.28	0.95	5.7
Cyproconazole	0.03	0.25	2200	22000
Cyprodinil	0.06	0.42	5700	57000
Difenoconazole	0.03	0.25	--	--
Dimethomorph	0.05	0.37	38	3700
Famoxadone	0.06	0.43	4.5	45
Fenarimol	0.05	0.35	83	5000
Fenbuconazole	0.06	0.46	1000	10000
Fenhexamid	0.09	0.62	--	--
Fluazinam	0.07	0.51	1100	3000
Fludioxonil	0.09	0.64	1400	68000
Fluoxastrobin	0.04	0.31	48	480
Flusilazole	0.07	0.54	570	5700
Flutolanil	0.07	0.53	390	5000
Flutriafol	0.04	0.26	78	17000
Imazalil	0.06	0.46	1500	15000
Iprodione	0.03	0.22	16	160
Kresoxim-methyl	0.02	0.13	17	100
Metalaxyl	0.07	0.47	5	1400
Metconazole	0.04	0.30	470	4700
Myclobutanil	0.06	0.44	550	5500
Pentachloronitrobenzene	0.04	0.27	81	3500
Propiconazole	0.04	0.27	170	840
Pyraclostrobin	0.04	0.27	35	350
Pyrimethanil	0.04	0.26	300	900
Tebuconazole	0.04	0.30	92	2200
Tetraconazole	0.04	0.28	220	3000
Triadimefon	0.05	0.37	16	480
Triadimenol	0.05	0.39	68	680
Trifloxystrobin	0.04	0.26	6.6	60
Triflumizole	0.04	0.26	92	1900

Table C-2. Sediment Analyte List, USGS toxicity benchmarks, and method detection limits

Analyte Name	Min MDL (µg/g-OC), TOC=2.89%	Max MDL (µg/g-OC), TOC=0.4%	TEB Threshold (µg/g-oc)	LEB Threshold (µg/g-oc)
Triticonazole	0.06	0.44	450	4500
Vinclozolin	0.04	0.30	240	1200
Zoxamide	0.04	0.28	48	950
Herbicides				
2-Chloro-2,6-Diethylacetanilide	0.05	0.33	--	--
Alachlor	0.02	0.14	--	--
Atrazine	0.05	0.37	130	1500
Benfluralin	0.06	0.42	--	--
Butralin	0.06	0.40	560	5600
Butylate	0.04	0.32	360	3600
Clomazone	0.07	0.49	630	1500
Cycloate	0.03	0.20	71	710
Cyhalofop-butyl	0.03	0.20	52000	520000
Dacthal	0.06	0.43	--	--
Dichloroaniline, 3,5-	0.05	0.37	35	350
Dichlorobenzenamine, 3,4-	0.05	0.33	630	6300
Dithiopyr	0.04	0.31	420	4200
EPTC	0.03	0.20	160	1300
Ethalfluralin	0.04	0.29	120	310
Flufenacet	0.03	0.25	620	6200
Hexazinone	0.03	0.23	760	5800
Metolachlor	0.03	0.18	0.18	200
Molinate	0.03	0.24	28	28
Napropamide	0.03	0.22	510	6600
Oxadiazon	0.05	0.34	--	--
Oxyfluorfen	0.07	0.47	63	630
Pebulate	0.03	0.22	280	2800
Pendimethalin	0.03	0.20	190	3800
Prodiamine	0.05	0.36	19	170
Prometon	0.09	0.67	1200	8900
Prometryn	0.05	0.33	400	3900
Propanil	0.08	0.56	1800	18000
Propyzamide	0.05	0.37	890	8900
Simazine	0.05	0.33	5.2	130
Thiazopyr	0.06	0.47	240	2400

Table C-2. Sediment Analyte List, USGS toxicity benchmarks, and method detection limits

Analyte Name	Min MDL (µg/g-OC), TOC=2.89%	Max MDL (µg/g-OC), TOC=0.4%	TEB Threshold (µg/g-oc)	LEB Threshold (µg/g-oc)
Thiobencarb	0.02	0.15	0.9	90
Triallate	0.05	0.34	31	220
Tributyl Phosphorotrithioate, S,S,S-	0.08	0.55	12	52
Trifluralin	0.03	0.22	21000	210000
Insecticides				
Allethrin	0.06	0.43	--	--
Azinphos Methyl	0.06	0.42	--	--
Bifenthrin	0.02	0.15	0.17	0.6
Carbaryl	0.04	0.30	0.11	0.39
Carbofuran	0.04	0.31	0.043	0.43
Chlorpyrifos	0.03	0.22	0.41	4.1
Coumaphos	0.04	0.30	0.61	1.3
Cyfluthrin, total	0.04	0.32	0.046	0.46
Cyhalothrin	0.02	0.17	0.023	0.23
Cypermethrin, Total	0.04	0.31	0.049	0.49
DDD(p,p')	0.03	0.24	66	240
DDE(p,p')	0.03	0.24	55	550
DDT(p,p')	0.03	0.21	33	200
Deltamethrin	0.04	0.31	0.02	0.2
Diazinon	0.05	0.39	1.9	19
Esfenvalerate	0.03	0.25	0.055	0.55
Ethofenprox	0.03	0.25	180	1800
Fenpropathrin	0.04	0.26	0.11	1.1
Fenpyroximate	0.07	0.47	29	83
Fenthion	0.07	0.50	0.02	7.9
Fipronil	0.06	0.40	0.01	0.1
Fipronil Desulfinyl	0.06	0.44	--	--
Fipronil Desulfinyl Amide	0.07	0.49	--	--
Fipronil Sulfide	0.05	0.37	--	--
Fipronil Sulfone	0.03	0.24	--	--
Indoxacarb	0.08	0.60	1.1	11
Malathion	0.03	0.25	0.064	1.1
Methidathion	0.06	0.44	0.26	1.2

Table C-2. Sediment Analyte List, USGS toxicity benchmarks, and method detection limits

Analyte Name	Min MDL (µg/g-OC), TOC=2.89%	Max MDL (µg/g-OC), TOC=0.4%	TEB Threshold (µg/g-oc)	LEB Threshold (µg/g-oc)
Methoprene	0.06	0.41	130	840
Novaluron	0.04	0.28	0.046	0.46
Parathion, Methyl	0.04	0.27	--	--
Pentachloroanisole	0.04	0.28	110	1100
Permethrin, Total	0.03	0.23	0.42	9.3
Phenothrin	0.03	0.22	--	--
Phosmet	0.03	0.23	0.5	1.3
Propargite	0.08	0.55	58	580
Pyridaben	0.04	0.31	2.9	35
Resmethrin	0.05	0.33	31	310
Tebupirimfos	0.07	0.51	0.046	0.32
Tebupirimfos oxon	0.05	0.38	--	--
Tefluthrin	0.02	0.17	0.29	2.9
Tetradifon	0.07	0.49	--	--
Tetramethrin	0.03	0.24	6.4	64
T-Fluvalinate	0.04	0.29	75	710
Synergists				
Flumetralin	0.04	0.31	17	170
Piperonyl Butoxide	0.04	0.31	--	--

1 - MDLs shown in orange are greater than the TEB threshold. MDLs shown in red are greater than the LEB threshold.

Total Organic Carbon

Bed sediment samples were analyzed at the USGS Organic Chemistry Research Laboratory in Sacramento, Calif. for organic carbon content according to a modified version of USEPA 440.0 (Zimmerman et al. 2007). Sediment samples were freeze-dried then homogenized using a mortar and pestle before sub-sampling. 5 to 10 mg of sediment were weighed into silver capsules and exposed to concentrated hydrochloric acid fumes in a desiccator for 14 hours to remove inorganic carbon. The sediment samples were then dried in an oven at 60 °C to remove any remaining acid or water before being pressed into sealed balls. Samples were analyzed by using a Costech ECS 4010 CHNSO analyzer (Costech Analytical Technologies Inc., Valenica, CA) in carbon nitrogen mode. The combustion furnace temperature was 980 °C, the reduction furnace temperature was 650 °C, the gas chromatographic column temperature was 65 °C, and the carrier gas flow rate was 110 mL per min. The instrument was calibrated using blanks and a five point calibration curve using acetanilide reference standards with a minimum correlation coefficient of 99.9%. Reference standards were analyzed every 10 samples to verify the calibration.

Reference

Zimmerman, C. F., C. W. Keefe, AND J. Bashe. 2007. Method 440.0 Determination of Carbon and Nitrogen in Sediments and Particulatesof Estuarine/Coastal Waters Using Elemental Analysis. U.S. Environmental Protection Agency, Washington, DC, EPA/600/R-15/009, 1997.

Appendix D. Hydrographs and Rainfall Data

Figure D-1. Hydrograph measured downstream of Potter Valley site. Data from USGS stream gauge 11461500. Green dots represent sampling dates for sediment (September) and water (October).

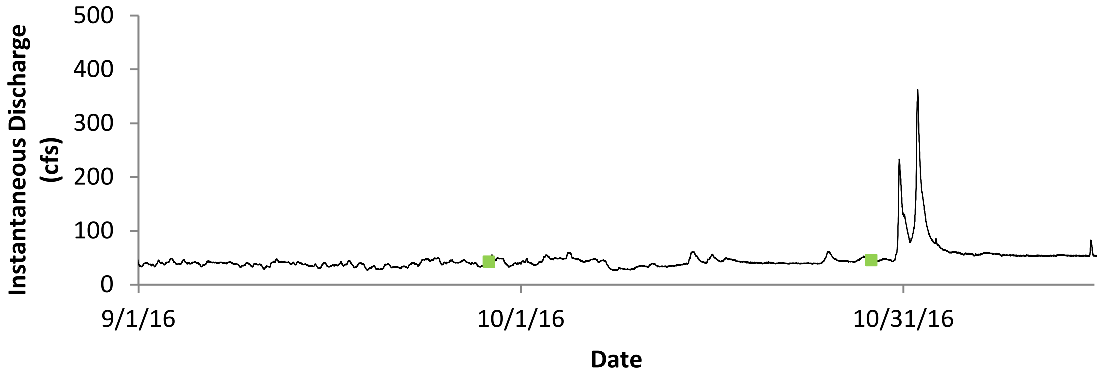


Figure D-2. Hydrograph measured at the Hopland site. Data from USGS stream gauge 11462500. Green dots represent sampling dates for sediment (September) and water (October).

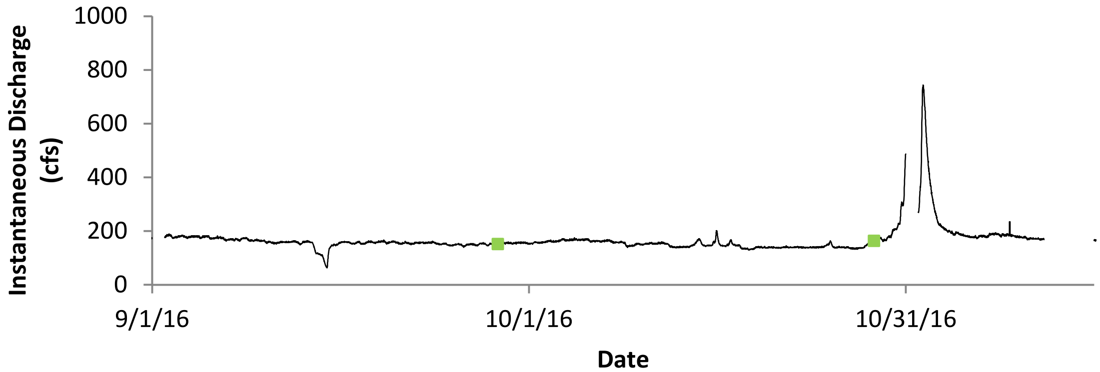


Figure D-3. Hydrograph at the Jimtown site. Data from USGS stream gauge 11463682. Green dots represent sampling dates for sediment (September) and water (October).

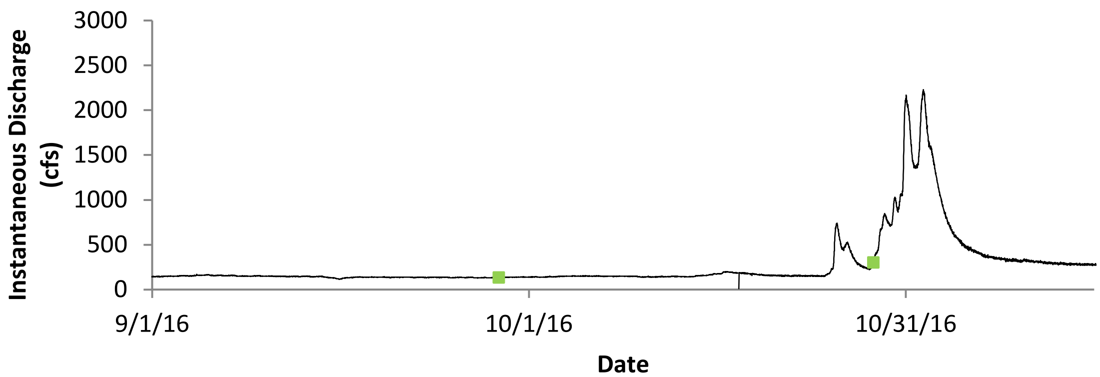


Figure D-4. Hydrograph at the Riverfront site. Data from USGS stream gauge 11465390. Green dots represent sampling dates for sediment (September) and water (October).

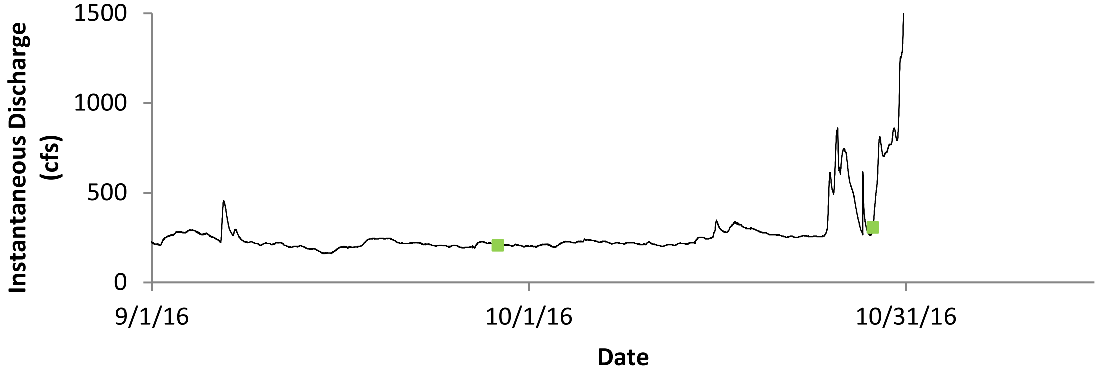


Figure D-5. Hydrograph at the Trenton Road site. Data from USGS stream gauge 11466800. Green dots represent sampling dates for sediment (September) and water (October).

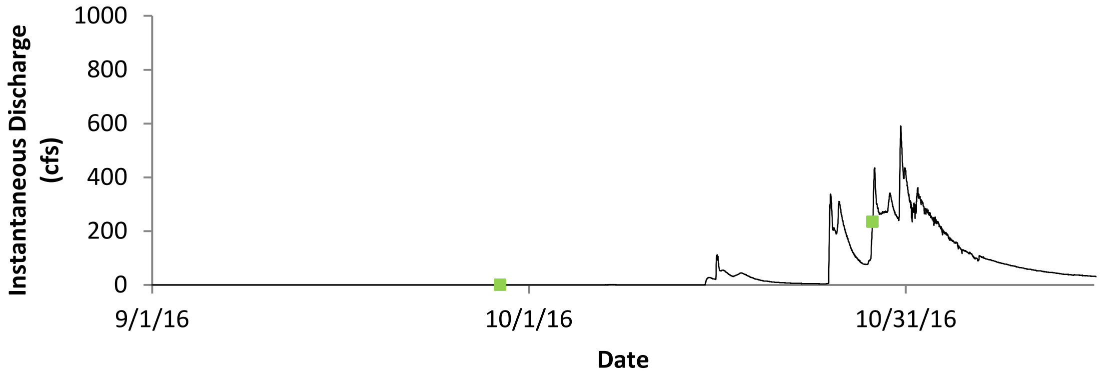


Figure D-6. Rainfall at Ukiah Airport. Green points represent the approximate timing of water sample collection at the Potter Valley and Hopland sites, which are in the vicinity of the NOAA Ukiah Municipal Airport rain gauge station (Station ID 72590523275).

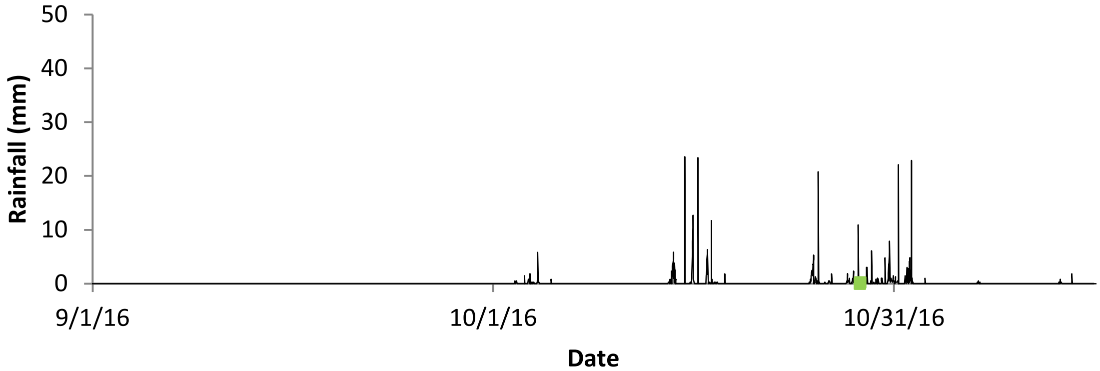


Figure D-7. Rainfall at Sonoma Airport. Green points represent the approximate timing of water sample collection at the Jimtown, Riverfront, and Trenton Road sites, which are in the vicinity of the NOAA Sonoma County Airport rain gauge station (Station ID 74295723213).