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Study 310: Surface Water Monitoring for Pesticides in Agricultural Areas of Northern California, 2017

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June 22, 2017

1. INTRODUCTION

The California Department of Pesticide Regulation (CDPR) regularly monitors for pesticides in urban and agricultural surface waters throughout the state (Budd, 2016; DaSilva, 2016a; Deng, 2017; Ensminger, 2016). Agricultural monitoring has focused on intensively irrigated regions of the Central Coast, Imperial County, and the northern-most part of the state. In Northern California's Sacramento Valley, there are two major monitoring programs: the Sacramento Valley Water Quality Coalition (SVWQC) and the California Rice Commission (CRC). The SVWQC is designed to fulfill Irrigated Land Regulatory Program requirements, as directed through the Central Valley Regional Water Quality Control Board (CVRWQCB) while the CRC program focuses primarily on rice pesticides. Therefore, some pesticides of interest may not be monitored on a regular basis for long-term evaluations. The objectives of this study are to establish long-term monitoring sites and monitor for a broader range of pesticide classes of interest.

CDPR recently developed a watershed prioritization model that systematically ranks monitoring watersheds based on pesticide uses at the spatial resolution of the USGS hydrologic unit codes (Luo et al., 2017). The watershed rankings provided by the model helped prioritize our monitoring efforts in identifying long term monitoring watersheds. The initial model screen results indicate that many of the current sites monitored by other programs are not in the watersheds identified by the model. Therefore, the monitoring watersheds and sites identified by CDPR could provide data sets that fill the spatial gaps that are not covered by the other monitoring programs. Data from this study will be used to evaluate the spatial and temporal pesticide concentrations in runoff and receiving waters in these agriculturally-dominated regions of Northern California.

Agricultural monitoring in Northern California began in 2016 (DaSilva, 2016a). The monitoring study at that time was designed to focus on agricultural areas with limited monitoring data. However, the small number of pesticide detections at low concentrations (all below the US EPA chronic aquatic life benchmark) across all sites suggested that monitoring at other sites in Northern California could be more effective (DaSilva, 2016b). In the current study, we aim to fill spatial and temporal data gaps in the Sacramento Valley. According to the Pesticide Use Reports (PUR), the Sacramento Valley contains watersheds where some of the most intense agricultural pesticide applications occur in Northern California. In these watersheds of high pesticide use, candidates for monitoring were identified using the prioritization method developed by CDPR (Luo et al., 2017). Watersheds in Colusa, Glenn, Sutter, Solano, Yolo, and Yuba counties were identified by the methodology as candidates for monitoring (Table 1). In keeping with the objectives of this study (stated below), we selected sites within or near the watersheds identified by the prioritization method, but not all prioritized watersheds or represented counties will be monitored. Specific pesticides were then identified for monitoring within each watershed using the Monitoring Prioritization Model (Luo et al., 2013, 2015).

2. OBJECTIVES

The objectives of the study are to:

1) Prioritize pesticide monitoring candidates based on current use reports at the watershed level;
2) Determine the presence and concentrations of selected pesticides in surface waters of selected monitoring regions; and
3) Analyze chemistry data to evaluate potential impacts on aquatic life

3. PERSONNEL

The study will be conducted by SWPP staff under the general direction of Nan Singhasemanon, Senior Environmental Scientist (Supervisory). Key personnel are listed below:

- Project Leader: Scott Wagner
- Field Coordinator: KayLynn Newhart
- Reviewing Scientist: Xin Deng, Ph.D.
- Statistician: Dan Wang, Ph.D.
- Laboratory Liaison: Sue Peoples
- Analytical Chemistry, water: Center for Analytical Chemistry, California Department of Food and Agriculture (CDFA)

Please direct questions regarding this study to Scott Wagner, Environmental Scientist, at 916-324-4087 or Scott.Wagner@cdpr.ca.gov.

4. STUDY PLAN

4.1. Selection of monitoring sites

Monitoring sites were selected within or near watersheds that were identified by the site prioritization methodology. Specific sites were selected after field scouting trips to the sites to determine ease of access, water flow, and nearby land use. Not all watersheds that appeared in the site prioritization list were selected for monitoring due to accessibility issues, site monitoring feasibility, or concerns about water flow during the dry summer months. A total of ten sites will be monitored in Colusa, Solano, Yolo, and Yuba counties (Figures 1–5; Table 2). Some locations were selected since they are historical monitoring sites that have not been sampled in years; others have limited historical monitoring data that warrants current monitoring efforts. Selected sites include a combination of tributaries, drainage canals, and main waterways that simultaneously meet the objectives of the study and allow for source identification should there be detections at these sites.

4.2. Selection of pesticides

Results from CDPR's Surface Water Monitoring Prioritization Model were used as a guide in selecting pesticides for monitoring (Luo et al., 2013, 2015). A range of pesticide classes were identified by the model for each watershed (Tables 3–8). The prioritized lists for each watershed were combined into one list. As a result, each of the ten selected sites will be monitored for the same suite of pesticides.

Active ingredients, for the four counties and selected watersheds, were chosen based on the following criteria:

1. Pesticides with a final ranking score ≥9 are of high priority and were considered for monitoring. Those with a final score <9 are considered low priority due to low use score (use score <2) and/or low toxicity (toxicity score <3).
2. Pesticides with a use score ≥2 were considered for monitoring. Pesticides that were not in the priority list or had use scores <2 may be analyzed because they were in the multiresidue analytical methods that were monitored
3. Pesticides that were ranked very low by the model are not included in the final monitoring list (Table 9) unless they are in the chosen analytical method groups. Historical monitoring data and/or current availability of analytical methods at the CDFA lab were additional factors to help arrive at a final list for monitoring.

4.3. Sampling plan

There will be two sampling events at each site in 2017: one event in July and the other in September. Events will be coordinated with rice field water release and peak irrigation events. At each site, surface water grab samples will be collected into 1-liter amber glass bottles. Samples will be transported on ice and stored in a refrigerator (4°C) until analyzed. CDPR staff will transport samples following procedures outlined in CDPR SOP QAQC004.01 (Jones, 1999). A chain-of-custody record will be completed for each sample.

5. LABORATORY ANALYSES

5.1. Chemical Analysis

The Center for Analytical Chemistry, CDFA will conduct the chemical analyses for this study. The lab will utilize four pesticide screens, which includes 37 chemical compounds (Table 9). The Liquid Chromatography (LC) short screen used by the CDFA analytical laboratory has the ability to analyze for a variety of compounds from different pesticide classes (Table 10). The method detection limit and reporting limit for each analyte are listed as well (Table 11). Laboratory QA/QC will follow CDPR guidelines provided in the

Standard Operating Procedure QAQC001.00 (Segawa, 1995). Extractions will include laboratory blanks and matrix spikes. The analytical methods, method detection limits, reporting limits and detected compounds will be reported by the lab for each sample set.

5.2. Organic Carbon and Suspended Solid Analysis

Total organic carbon (TOC) and dissolved organic carbon (DOC) in water samples will be analyzed by CDPR staff using a TOC-V CSH/CNS analyzer (Shimadzu Corporation, Kyoto, Japan) (Ensminger, 2013a). Water samples will also be analyzed for suspended sediment (Ensminger, 2013b). Lab blanks and calibration standards will be run before every sample set to ensure the quality of the data.

6. DATA ANALYSIS

Concentrations of pesticides in water will be reported as micrograms per liter (µg/L)/parts per billion (ppb) or nanograms per liter (ng/L)/parts per trillion (ppt). Data from this study will be stored in a Microsoft Office Access database that holds all field measurements and lab data. Pesticide concentrations will be evaluated against aquatic life toxicity benchmarks, water quality limits or other toxicity data (US EPA, 2016; CCVRWQCB, 2012). Patterns and trends in detections may be identified as data from multiple years of monitoring accumulate in the database.

7. TIMETABLE

Field Sampling: June 2017 – September 2017
Chemical Analysis: June 2016 – October 2017
Summary Report: March 2018

8. LABORATORY BUDGET

The expected cost for chemical analysis of samples through the CDFA lab is $80,300 (Table 12). This estimate includes laboratory QC samples.

9. REFERENCES

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Table 1. Watersheds identified by the prioritization model as candidates for monitoring. This list was considered when selecting final sites for monitoring.

HUC	HUCNAME	type
18020163:		
180201630502	Gibson Canyon Creek-Sweany Creek	mainstem
180201630102	Lamb Valley Slough-South Fork Willow Slough	mainstem
180201630203	South Fork Ditch-Willow Slough	mainstem
180201630501	McCune Creek-Sweany Creek	tributary
180201630301	Knights Landing Ridge Cut	tributary
180201630602	Tremont School	tributary
18020104:		
180201040703	Salt Creek	mainstem
180201040203	Lower Walker Creek	mainstem
180201040504	Lower Logan Creek	mainstem
180201041201	Deadmans Reach-Sacramento River	tributary
180201041008	Smith Creek-Colusa Basin Drainage Canal	tributary
180201041003	Clarks Ditch-Colusa Basin Drainage Canal	tributary
18020159:		
180201590400	Gilsizer Slough-Snake River	tributary
180201590107	Wilson Creek-North Honcut Creek	tributary
180201590502	Ellis Lake-Feather River	tributary
180201590107	Wilson Creek-North Honcut Creek	mainstem
180201590302	Reeds Creek	mainstem

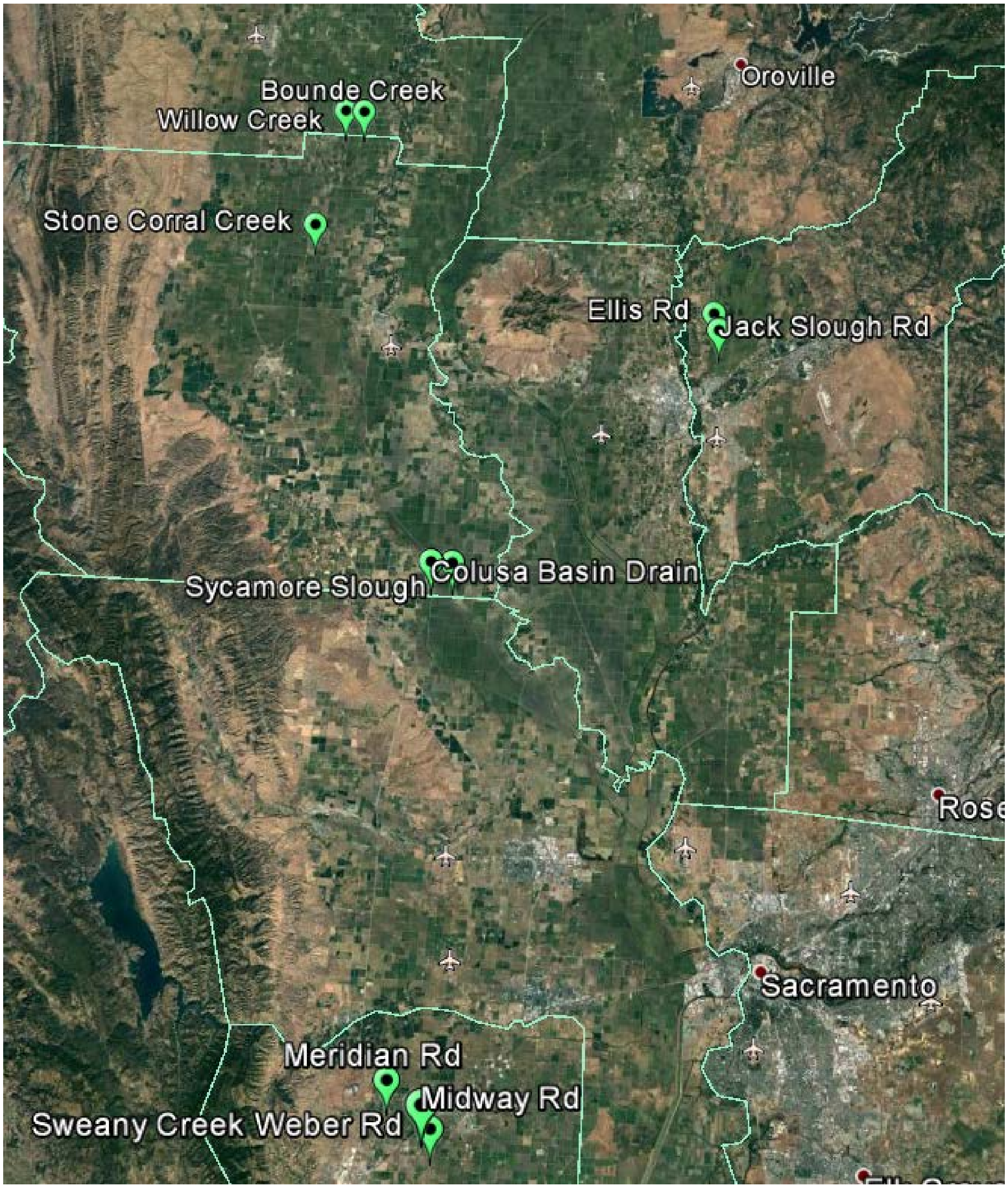

Figure 1. Monitoring sites in Colusa, Yuba, Yolo, and Solano counties, Calif.

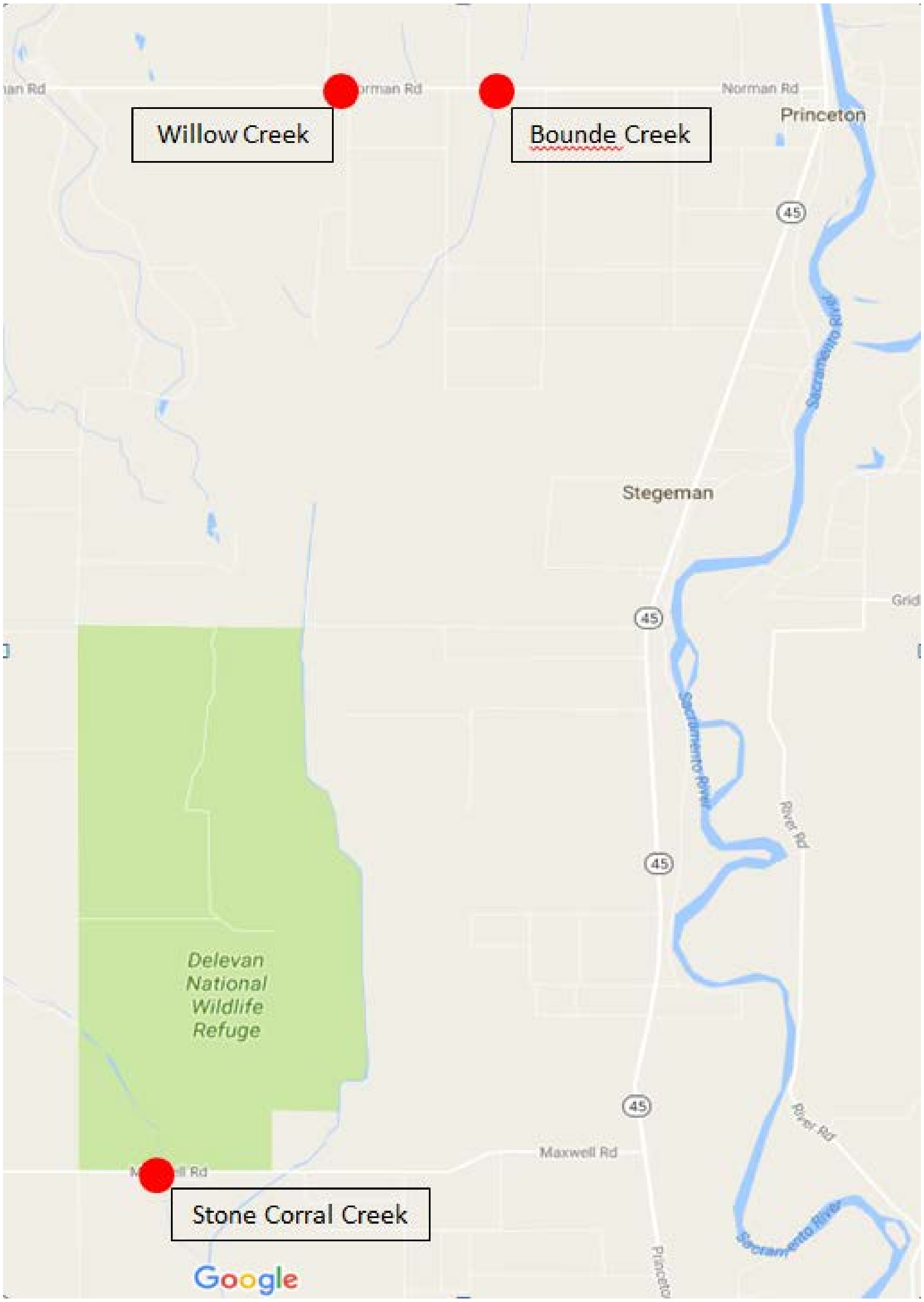

Figure 2. Monitoring sites in Colusa County, Calif.

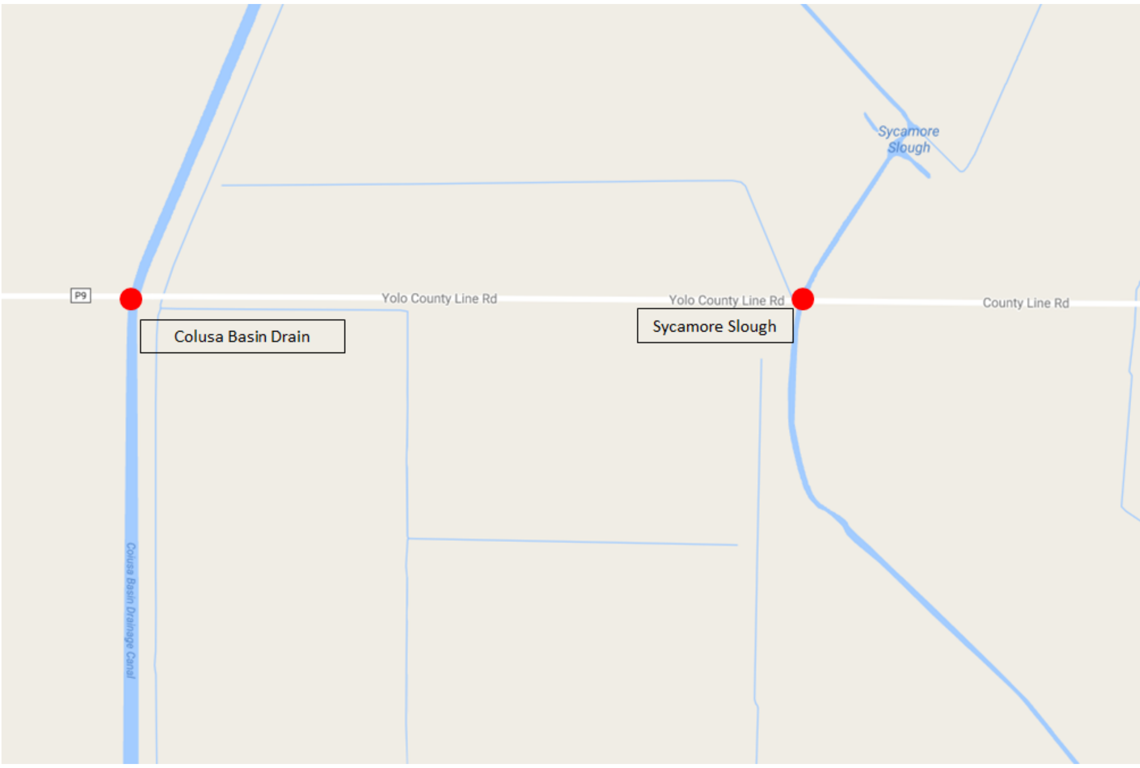

Figure 3. Monitoring sites in Yolo County, Calif.

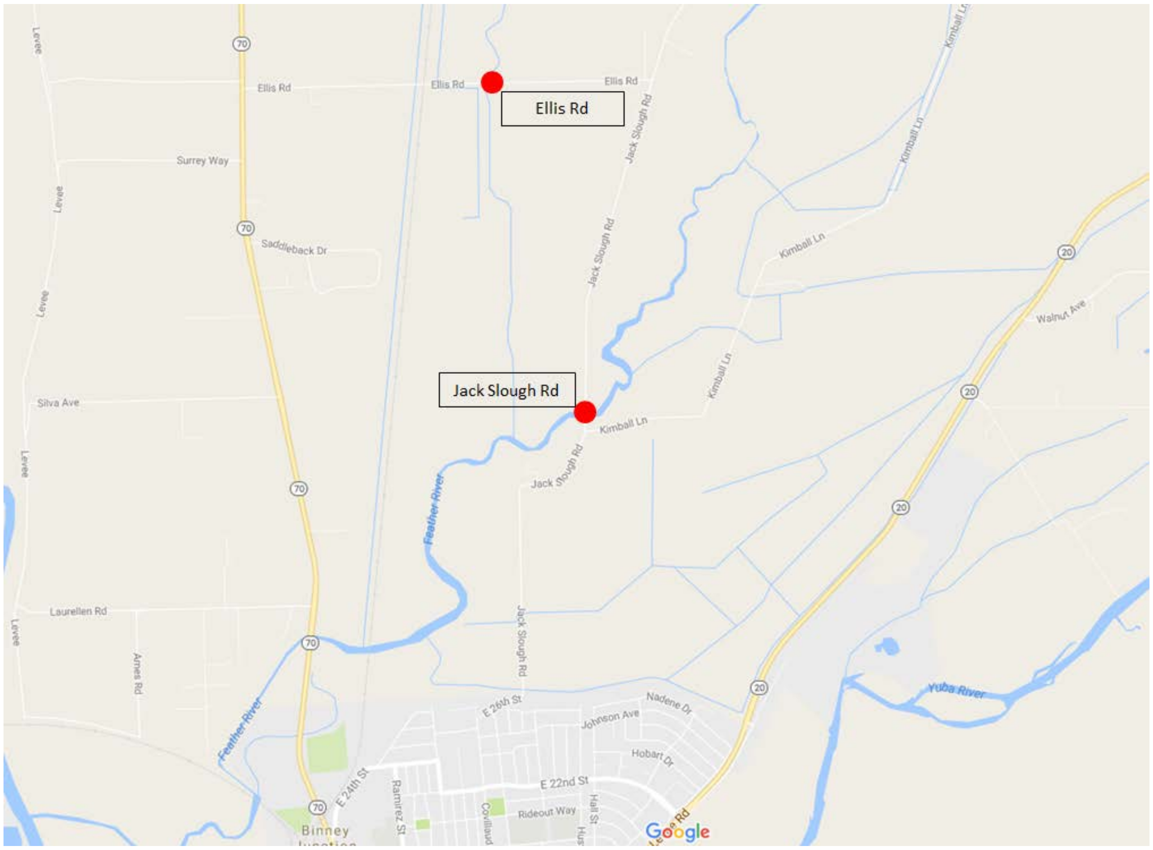

Figure 4. Monitoring sites in Yuba County, Calif.

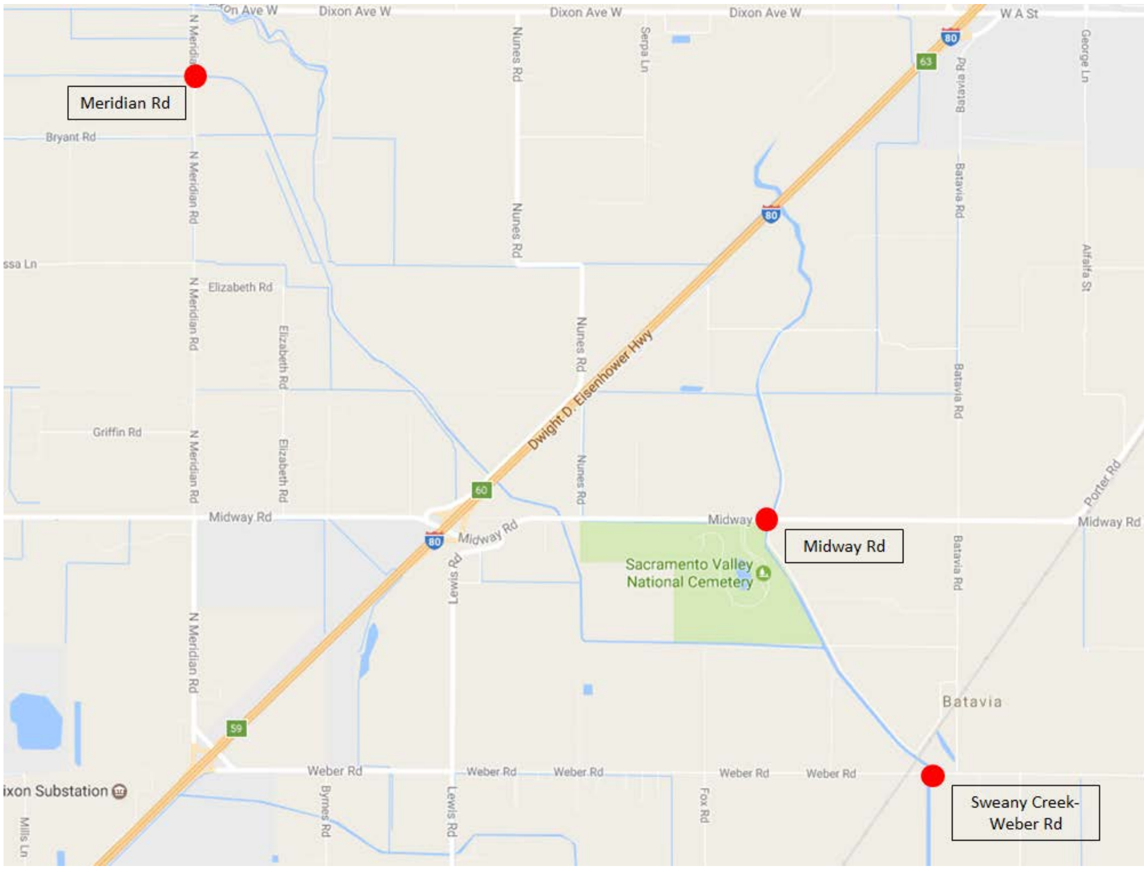

Figure 5. Monitoring sites in Solano County, Calif.

Table 2. Description of sampling sites for Northern California counties in 2017.

Site ID	Site Location	County	Watershed	Latitude	Longitude
Stone Corral Creek	Stone Corral Creek near Maxwell Rd	Colusa	Lower Logan Creek	39.2751	-122.1043
Willow Creek	Willow Creek at Norman Rd		Willow Creek	39.406432	-122.080504
Bounde Creek	Bounde Creek at Norman Rd		Colusa Drain	39.406297	-122.055885
Jack Slough Rd	Feather River at Jack Slough Rd	Yuba	Jack Slough	39.180349	-121.571142
Ellis Rd	Simmerly Slough at Ellis Rd			39.198074	-121.578178
CBD	Colusa Basin Drain at County Line Rd	Yolo	Clarks Ditch-Colusa Basin Drain	38.924458	-121.913986
Sycamore Slough	Sycamore Slough at County Line Rd			38.925162	-121.888634
Weber Rd	Sweany Creek at Weber Rd	Solano	Gibson Canyon Creek-Sweany Creek	38.40257	-121.86064
Meridian Rd	Sweany Creek at N. Meridian Rd			38.442209	-121.91559
Midway Rd	Sweany Creek at Midway Rd			38.416865	-121.873421

Table 3. Highest scoring pesticides recommended for monitoring using the Pesticide Prioritization Model, based on the 2012-2015 pesticide use reports for Lower Logan Creek watershed in Colusa County.

Lower Logan Creek Watershed, Drainage Area= 137 km^2 HUC12: 180201040504				
Active Ingredient	**Use Score**	**Toxicity Score**	**Final Score**	**Does Model Recommend Monitoring?**
PROPANIL	5	3	15	YES
THIOBENCARB	5	3	15	YES
PARAQUAT DICHLORIDE[1]	3	5	15	YES
LAMBDA-CYHALOTHRIN	2	7	14	YES
S-METOLACHLOR	3	4	12	YES
CHLOROTHALONIL[2]	3	4	12	NO
CHLORPYRIFOS	2	6	12	YES
BIFENTHRIN	2	6	12	YES
CARBARYL	2	5	10	YES
AZOXYSTROBIN	3	3	9	YES
PENDIMETHALIN	2	4	8	YES

[1] Analytical method not currently available

[2] Short persistence defined by the prioritization model

Table 4. Highest scoring pesticides recommended for monitoring using the Pesticide Prioritization Model, based on the 2012-2015 pesticide use reports for Willow Creek watershed in Colusa County.

Willow Creek Watershed, Drainage Area = 92 km^2 HUC12: 180201040303				
Active Ingredient	**Use Score**	**Toxicity Score**	**Final Score**	**Does Model Recommend Monitoring?**
CHLORPYRIFOS	3	6	18	YES
PROPANIL	5	3	15	YES
THIOBENCARB	5	3	15	YES
MALATHION	3	5	15	YES
PARAQUAT DICHLORIDE[1]	3	5	15	YES
LAMBDA-CYHALOTHRIN	2	7	14	YES
AZOXYSTROBIN	4	3	12	YES
PENDIMETHALIN	3	4	12	YES

[1] Analytical method not currently available

Table 5. Highest scoring pesticides recommended for monitoring using the Pesticide Prioritization Model, based on the 2012-2015 pesticide use reports for Colusa Drain watershed in Colusa County.

Colusa Drain Watershed, Drainage Area = 321 km^2 HUC12: 180201040400				
Active Ingredient	**Use Score**	**Toxicity Score**	**Final Score**	**Does Model Recommend Monitoring?**
ZIRAM[1]	5	4	20	NO
CHLORPYRIFOS	3	6	18	YES
CHLOROTHALONIL[1]	4	4	16	NO
PENDIMETHALIN	4	4	16	YES
PROPANIL	5	3	15	YES
THIOBENCARB	5	3	15	YES
PARAQUAT DICHLORIDE[2]	3	5	15	YES
OXYFLUORFEN	3	5	15	YES
MALATHION	2	5	10	YES

[1] Short persistence defined by the prioritization model

[2] Analytical method not currently available

Table 6. Highest scoring pesticides recommended for monitoring using the Pesticide Prioritization Model, based on 2012-2015 pesticide use reports for Clarks Ditch-Colusa Basin Drain watershed in Yolo County.

Clarks Ditch-Colusa Basin Drain Watershed, Drainage Area = 152 km^2 HUC12: 180201041003				
Active Ingredient	**Use Score**	**Toxicity Score**	**Final Score**	**Does Model Recommend Monitoring?**
CHLOROTHALONIL[1]	5	4	20	NO
ZIRAM[1]	5	4	20	NO
OXYFLUORFEN	4	5	20	YES
BIFENTHRIN	3	6	18	YES
PENDIMETHALIN	4	4	16	YES
PARAQUAT DICHLORIDE[2]	3	5	15	YES
MANCOZEB[1]	4	3	12	NO
PROPANIL	4	3	12	YES
PYRACLOSTROBIN	3	4	12	YES
TRIFLURALIN	3	4	12	YES

[1] Short persistence defined by the prioritization model

[2] Analytical method not currently available

Table 7. Highest scoring pesticides recommended for monitoring using the Pesticide Prioritization Model, based on the 2012-2015 pesticide use reports for Jack Slough watershed in Yuba County.

Jack Slough Watershed, Drainage Area = 134 km^2 HUC12: 180201590501				
Active Ingredient	**Use Score**	**Toxicity Score**	**Final Score**	**Does Model Recommend Monitoring?**
PROPANIL	5	3	15	YES
CARBARYL	3	5	15	YES
LAMBDA-CYHALOTHRIN	2	7	14	YES
THIOBENCARB	4	3	12	YES
CHLOROTHALONIL[1]	3	4	12	NO
PENDIMETHALIN	3	4	12	YES
CLOMAZONE[2]	5	2	10	NO
AZOXYSTROBIN	3	3	9	YES
MALATHION	1	5	5	YES

[1] Short persistence defined by the prioritization model

[2] Low soil runoff potential, based on vapor pressure, as defined by the prioritization model

Table 8. Highest scoring pesticides recommended for monitoring using the Pesticide Prioritization Model, based on the 2012–2015 pesticide use reports for Gibson Canyon Creek-Sweany Creek watershed in Solano County.

Gibson Canyon Creek-Sweany Creek, Drainage Area = 46 km^2 HUC12: 180201630502				
Active Ingredient	**Use Score**	**Toxicity Score**	**Final Score**	**Does Model Recommend Monitoring?**
PARAQUAT DICHLORIDE[1]	5	5	25	YES
CHLORPYRIFOS	3	6	18	YES
PENDIMETHALIN	4	4	16	YES
OXYFLUORFEN	3	5	15	YES
ORYZALIN	4	3	12	YES
S-METOLACHLOR	3	4	12	YES
CHLOROTHALONIL[2]	3	4	12	NO
BIFENTHRIN	2	6	12	YES
DIAZINON	2	5	10	YES
MALATHION	1	5	5	YES

[1] Analytical method not currently available

[2] Short persistence defined by the prioritization model

Table 9. Pesticides in the pyrethroid, dinitroaniline and malathion analytical methods used by the CDFA lab.

Liquid Chromatography Screen (LC) short	Pyrethroid Screen (PYR)	Dinitroaniline Screen (DN)	Malathion-acidified
(See Table 10)	Bifenthrin Permethrin Cypermethrin Lambda-cyhalothrin Esfenvalerate/fenvalerate	Benfluralin Ethalfluralin Oryzalin Oxyfluorfen Pendimethalin Prodiamine Trifluralin	Malathion

Table 10. Analytes included in the LC Screen (short).

Abamectin Atrazine Azoxystrobin Carbaryl Chlorantraniliprole Chlorpyrifos Cyprodinil Diazinon Diflubenzuron	Dimethoate Diuron Hexazinone Imidacloprid Methidathion Propanil Propargite Propiconazole Pyraclostrobin Pyriproxyfen	Quinoxyfen Simazine S-Metolachlor Thiobencarb Trifloxystrobin

Table 11. Reporting Limit and Method Detection Limit for Pesticides Monitored in 2017

Analytical Screen	**Analyte**	**Method Detection Limit (µg/L)**	**Reporting Limit (µg/L)**
Liquid chromatography multi-analyte screen (LC)	Abamectin	0.004	0.02
	Atrazine	0.004	0.02
	Azoxystrobin	0.004	0.02
	Carbaryl	0.004	0.02
	Chlorantraniliprole	0.004	0.02
	Chlorpyrifos	0.004	0.02
	Cyprodinil	0.004	0.02
	Diazinon	0.004	0.02
	Diflubenzuron	0.004	0.02
	Dimethoate	0.004	0.02
	Diuron	0.004	0.02
	Hexazinone	0.004	0.02
	Imidacloprid	0.004	0.02
	Methidathion	0.004	0.02
	Propanil	0.004	0.02
	Propargite	0.004	0.02

	Propiconazole	0.004	0.02
	Pyraclostrobin	0.004	0.02
	Pyriproxyfen	0.004	0.02
	Quinoxyfen	0.004	0.02
	Simazine	0.004	0.02
	S-Metolachlor	0.004	0.02
	Thiobencarb	0.004	0.02
	Trifloxystrobin	0.004	0.02
Pyrethroid Screen (PYR)	Bifenthrin	0.00091	0.001
	Permethrin (cis)	0.00105	0.002
	Permethrin (trans)	0.00105	0.002
	Cypermethrin	0.00154	0.005
	Lambda-cyhalothrin	0.00174	0.002
	Esfenvalerate/fenvalerate	0.00166	0.005
Dinitroaniline Screen (DN)	Benfluralin	0.015	0.05
	Ethalfluralin	0.017	0.05
	Oryzalin	0.021	0.05
	Oxyfluorfen	0.023	0.05
	Pendimethalin	0.019	0.05
	Prodiamine	0.02	0.05
	Trifluralin	0.015	0.05
Malathion-acidified	Malathion	0.00935	0.02

Table 12. Analytical cost estimate for agricultural samples for Northern California, 2017.

Analytical Screen	Total Samples*	Cost per sample	Cost estimate
LC screen (short)	22	$1,700	$37,400
Pyrethroid screen	22	$600	$13,200
Dinitroaniline screen	22	$840	$18,480
Malathion-acidified[1]	22	$510	$11,220
Total cost			$80,300

*QC samples included in the total number of samples

[1] A separate sample will be taken for malathion because it breaks down rapidly in alkaline water; therefore acid is added to the water sample to preserve the malathion concentration