Department of Pesticide Regulation
Environmental Monitoring Branch
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Study 310: Surface Water Monitoring for Pesticides in Agricultural Areas of Northern California, 2019

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1. INTRODUCTION

The California Department of Pesticide Regulation (CDPR) routinely monitors for pesticides in urban and agricultural surface waters throughout the state (Budd, 2016; DaSilva, 2016a; Deng, 2017; Ensminger, 2016; Wagner, 2018). Agricultural monitoring has focused on intensively irrigated regions of the Central Coast, Imperial County, and the northernmost part of the state. In 2017, CDPR expanded monitoring into the Sacramento Valley (Wagner, 2018). In 2019, CDPR proposes to continue monitoring in the Sacramento Valley and further expand monitoring coverage into the San Joaquin Valley.

The Sacramento and San Joaquin valleys are regions of high pesticide use. Total agricultural pesticide use in 2016 was 20,021,141 and 41,299,492 pounds in the Sacramento and San Joaquin river basins, respectively (CDPR, Pesticide Use Reports 2016). Several groups monitor pesticides in surface waters throughout the two regions including watershed-based, water quality coalitions and the California Rice Commission (CRC) coalition. Water quality coalition and CRC monitoring are designed to fulfill Irrigated Land Regulatory Program requirements, as directed through the Central Valley Regional Water Quality Control Board (CVRWQCB). The water quality monitoring conducted by growers and their associates are designed to meet the conditions of Waste Discharge Requirements (Orders) by monitoring for a variety of water pollutants including sediment, nutrients, salts, heavy metals, pathogens, and pesticides (ILRP, 2019). Coalition monitoring also focuses on corrective actions following the detection of impairments; thus, the pollutants and sites analyzed every year vary within a given watershed. In contrast, CDPR monitoring focuses on regions with the highest pesticide use and evaluating how pesticide use patterns relate to surface water concentrations. In addition, maintaining long-term sites allows for reporting long-term trends to evaluate the efficacy of mitigation efforts. CDPR proposes to continue monitoring in the Sacramento Valley and to establish new long-term monitoring sites in the San Joaquin Valley. Monitoring at selected sites in the San Joaquin Valley is intended to be exploratory during the first year to satisfy CDPR monitoring objectives. These investigatory sites in the San Joaquin Valley will inform CDPR staff as we establish a long-term agricultural monitoring program in the region.

Monitoring sites were selected using a variety of factors including regional pesticide use, regional crop type, irrigation, accessibility, and likelihood of year-round water flow. Field visits were conducted to select final sites. See section 4.1 below for more details about the site selection process.

2. OBJECTIVES

The objectives of the study are to:

1) Determine the presence and concentrations of selected pesticides in surface waters and sediments of selected monitoring regions;
2) Evaluate potential impacts on aquatic life by comparing concentrations with the U.S. EPA aquatic life benchmarks;
3) Determine the toxicity of water samples using toxicity tests conducted with the amphipod *Hyalella azteca* or the midge *Chironomus*;
4) Analyze spatial correlations between observed pesticide concentrations/detection frequencies and region-specific pesticide uses;
5) Assess trends in pesticide concentrations; and
6) Evaluate how well new San Joaquin Valley monitoring locations satisfy criteria for long-term sites.

3. PERSONNEL

The study will be conducted by SWPP staff under the general direction of Jennifer Teerlink, Ph.D., Senior Environmental Scientist (Supervisor). Key personnel are listed below:

- Project Leader: Scott Wagner
- Field Coordinator: Xin Deng, Ph.D.
- Reviewing Scientist: Robert Budd, 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

In the high pesticide use watersheds of the Sacramento and San Joaquin valleys, candidate watersheds for monitoring were identified using the watershed prioritization method within the Surface Water Monitoring Prioritization (SWMP) model (Luo et al., 2017). The model utilizes pesticide use data in conjunction with pesticide specific fate and transport characteristics to identify key locations. However, CDPR staff used additional resources to consider other factors such as regional hydrography, seasonal flows, and crop irrigation type that are not considered by the model. A list of candidate monitoring sites within watersheds of high pesticide use was created by identifying sites with historical pesticide detections from water quality coalition monitoring; CDPR scientists confirmed that sites could still be accessed by CDPR sampling crews. Further, the historical and projected monitoring frequencies of these sites were assessed to determine whether long-term sampling data from these sites would be beneficial to CDPR. CDPR staff visited each of these coalition sites and assessed them based on probability of year-round flow, accessibility for CDPR sampling crews, and source of agricultural inputs. For each selected site, specific pesticides were then identified for monitoring within its watershed using the pesticide prioritization method within the SWMP model (Luo et al., 2013, 2015). The San Joaquin Valley sites are collocated with either the East San Joaquin Water Quality Coalition or the Westside San Joaquin River Watershed Coalition monitoring program monitoring stations.

In 2019, a total of seven sites will be monitored in Colusa, Madera, Merced, Stanislaus, and Yolo counties (Figures 1 and 2; Table 1). Alternate sites will be monitored in the event that samples cannot be collected from any of the primary sites. Selected sites include a combination of tributaries, drainage canals, and mainstem waterways. The selected monitoring sites in the Sacramento Valley were included in the 2017 and 2018 agricultural monitoring studies; all monitoring sites selected in San Joaquin Valley are new sites that have not been monitored in recent CDPR agricultural monitoring studies.

4.2. Selection of pesticides

Results from CDPR's SWMP model were used as a guide in selecting pesticides for monitoring (Luo et al., 2013, 2015). A range of pesticide classes was identified by the model for each watershed and for all watersheds combined. Results from individual watershed prioritizations did not vary significantly from the combined prioritization results. Thus, the prioritized lists for each watershed were combined into one list (Table 2). As a result, selected sites in each region will be monitored for the same suite of pesticides (Tables 3 and 4).

Active ingredients for the 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 multi-residue analytical methods that are being used.
3. Pesticides that were ranked as very low by the model are not included in the final monitoring list (Table 3) but may be monitored as part of a larger analytical screen. 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. Sediment Sampling.
Sediment samples will be collected at four sites (three in the San Joaquin Valley and one in the Sacramento Valley) in July. Sediment from creeks and riverbeds will be collected according to the protocol detailed in Mamola, 2005. Sediment samples will be analyzed for a suite of pyrethroid insecticides at the CDFA lab (Table 4).

4.4. Toxicity.
Water samples will be collected from each site and sent to either the Marine Pollution Studies Laboratory at Granite Canyon or the University of California, Davis, Aquatic Health Program Laboratory, to be tested for 96-hours for mortality/survival of the amphipod *Hyalella azteca* and the midge *Chironomus dilutus* (SWAMP, 2018). There will be two toxicity sampling events at each site, one in June and one in September (Table 5).

4.5. Sampling schedule
There will be six surface water sampling events at the three Sacramento Valley sites from May through July (with an additional event at the end of rice growing season in September) and four sampling events at the four San Joaquin Valley sites monthly from June through September. Monitoring coverage was extended into May to cover the start of rice growing season and the application of pesticides associated with rice. Events will be coordinated with peak irrigation and pesticide applications periods. There will be an additional sampling event after September at the four San Joaquin Valley sites intended to collect storm water runoff. This storm water sampling event will occur during the first significant rain event after September. Sampling during the first storm event will be up to the discretion of the project leader; if the predicted amount of precipitation is too low to likely generate runoff, sampling will not occur. Storm water samples will be analyzed using the LC (full), dinitroaniline, and pyrethroid screens (Table 5). 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.

4.6. Protocol Revisions
The 2019 protocol incorporates some changes from 2018 monitoring based on field staff experience and feedback from stakeholders (Appendix 1). Below, we elaborate on some of those changes and explain the reasoning behind revising the protocol.

1. *New sites will be monitored in the San Joaquin Valley*: Four new sites will be monitored this year in the San Joaquin Valley. These sites will allow CDPR to expand monitoring into regions of high pesticide use that have not recently been monitored by SWPP studies.

2. *Five sites in the Sacramento Valley will no longer be monitored*: Bounde Creek, Ellis Road, Jack Slough, Sycamore Slough, and Sweany Creek at Weber Road will not be monitored. Pesticide concentrations and detection frequencies at these sites were lower in 2017 and 2018 compared to the three sites in the Sacramento Valley that will continue to be monitored. The sites that will no longer be monitored are in regions that will be represented by sites to be monitored in 2019; the status and trends of pesticide surface water concentrations in the Sacramento Valley will continue to be surveyed by SWPP scientists.

3. *More frequent Sacramento Valley monitoring in May, June, and July*: Previous monitoring was conducted in May, July, and September. Detections were highest in May and pesticide use reports suggest that many pesticides of interest in Sacramento Valley are applied in May and June associated with rice cultivation. Thus, to capture surface water concentrations associated with these early summer pesticide application events, monitoring will occur bi-weekly in May, June, and July. There will also be a September monitoring event to capture pesticide concentrations in late summer.

4. *Add a storm water monitoring event*: We propose to collect samples from the four San Joaquin Valley sites during the first storm event after September. CDPR sampling crews will learn from these initial storm water monitoring events to better understand the relationship between runoff from agriculture fields and predicted precipitation amounts. The first flush rain event of the season in California has the potential to carry pesticides that have accumulated on land over the dry season into surface waters. Historically, agriculturally impacted surface waters have not been the focus of storm sampling efforts.

5. LABORATORY ANALYSES

5.1. Chemical Analysis

The Center for Analytical Chemistry, at the California Department of Food and Agriculture (CDFA) will conduct the chemical analyses for this study. The lab will utilize four pesticide screens, which includes 60 chemical compounds in surface water and 7 compounds in sediment (Table 3). The multi-residue liquid chromatography tandem mass spectrometry (LC-MS/MS) method used by the CDFA analytical laboratory has the ability to analyze for a variety of compounds from different pesticide classes (Table 3). The method detection limit and reporting limit for each analyte are listed as well (Table 3). 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, QA/QC results and detected compounds will be reported by the lab for each sample set.

5.2. Organic Carbon and Suspended Solid Analyses

All water samples will be analyzed for total organic carbon (TOC) and dissolved organic carbon (DOC) 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 ran before every sample set to ensure high quality of the data.

6. DATA ANALYSIS

Data from this study will be stored in a Microsoft Office Access database that holds all field measurements and lab data. Ultimately, the data will be uploaded to CDPR's publicly-available Surface Water Database (SURF). Pesticide concentrations will be evaluated against aquatic life toxicity benchmarks, water quality limits and/or other toxicity thresholds (US EPA, 2018; 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: May 2019 – September 2019 (Table 5)
Chemical Analysis: May 2019 – October 2019
Summary Report: March 2020
SURF Data Upload: April 2020

8. LABORATORY BUDGET

The expected cost for chemical analysis of samples through the CDFA lab is $112,200 (Table 6). This estimate includes laboratory QC samples.

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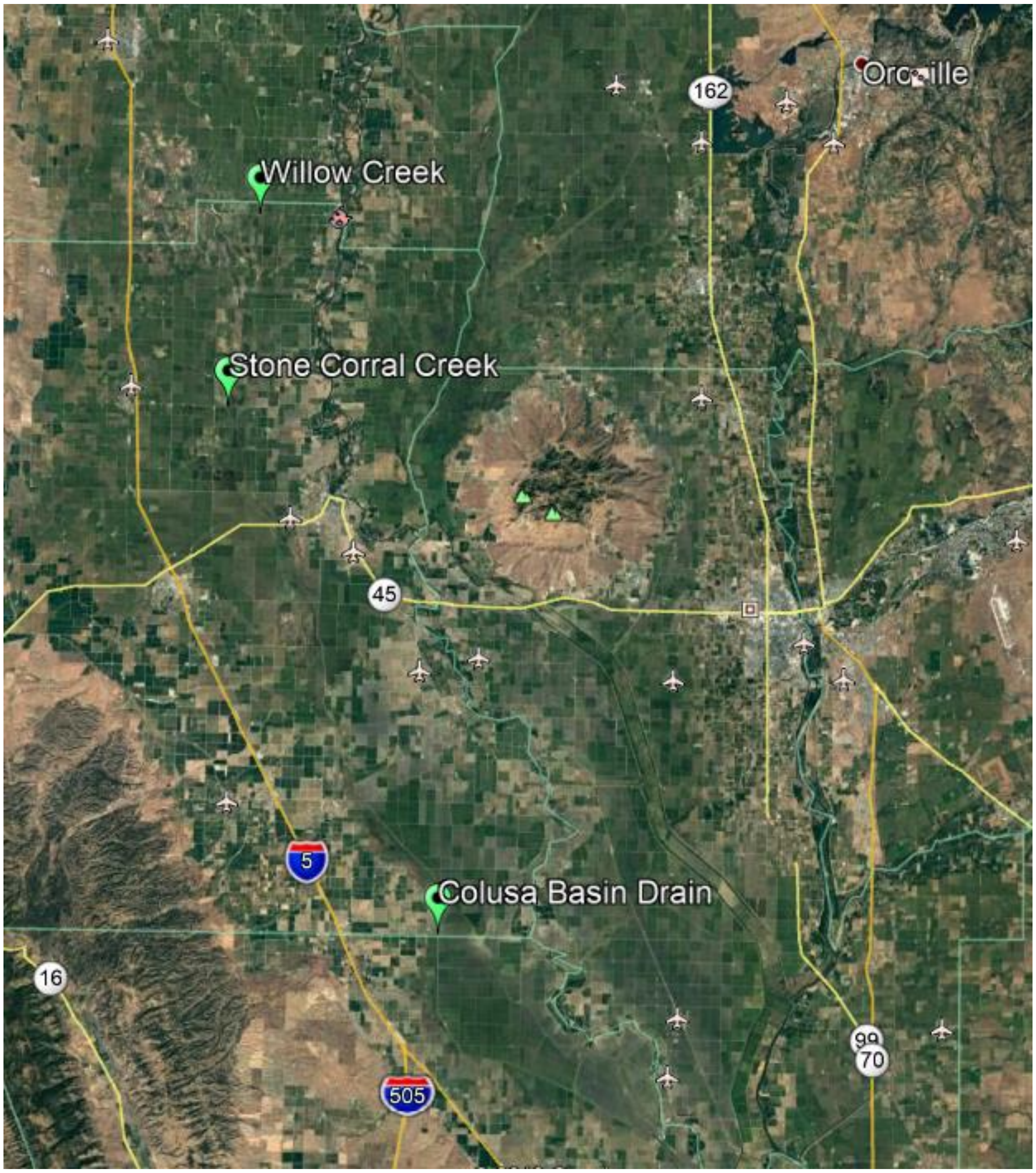

Figure 1. Monitoring sites in Colusa and Yolo counties, Calif.

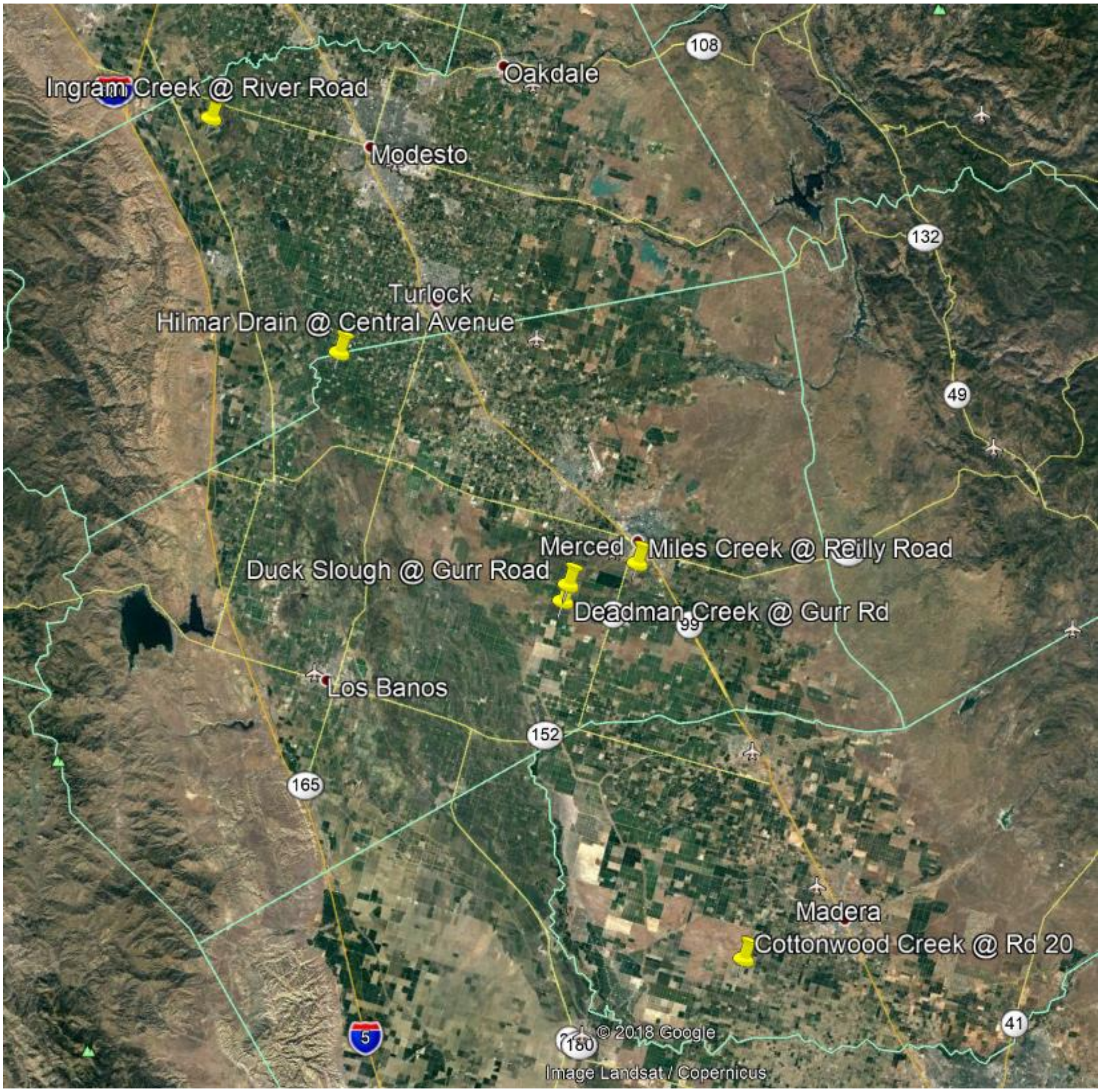

Figure 2. Monitoring sites in Madera, Merced, and Stanislaus counties, Calif.

Table 1. Description of sampling sites for Northern California in 2019.

Site ID	Site Location	County	Watershed	Latitude	Longitude
Sacramento Valley sites					
LLC_SCC	Stone Corral Creek near Maxwell Rd	Colusa	Lower Logan Creek	39.2751	-122.1043
WC_Willow	Willow Creek at Norman Rd	Colusa	Willow Creek	39.406432	-122.080504
CD_CBD	Colusa Basin Drain at County Line Rd	Yolo	Clarks Ditch-Colusa Basin Drain	38.924458	-121.913986
San Joaquin Valley sites					
LCC_CWC	Cottonwood Creek at Road 20	Madera	Lower Cottonwood Creek	36.8686	-120.1818
SS_DMC	Deadman Creek at Gurr Road	Merced	South Slough-Deadman Creek	37.19514	-120.56147
TH_HMD	Hilmar Drain at Central Avenue	Merced	Town of Hilmar-San Joaquin River	37.39058	-120.9582
IC_INC	Ingram Creek at River Road	Stanislaus	Ingram Creek	37.60022	-121.22506
Alternate sites for San Joaquin Valley					
MCD_DS	Duck Slough at Gurr Road	Merced	Mariposa Creek-Duck Slough	37.21408	-120.56126
LOC_MC	Miles Creek at Reilly Road	Merced	Lower Owens Creek	37.2583	-120.47524

Table 2. Highest scoring pesticides recommended for monitoring using the SWMP model, based on 2014–2016 pesticide use reports for combined watersheds identified in Table 1.

Combined watersheds, Drainage area= 1218 km^2 HUC12: 180201040504, 180201040303, 180201041003, 180400010204, 180400011604, 180400020202, 180400020502, 180400011504, 180400011703				
Active Ingredient	**Use score**	**Toxicity score**	**Final score**	**Does model recommend monitoring?**
PARAQUAT DICHLORIDE	4	5	20	True
OXYFLUORFEN	4	5	20	True
CHLORPYRIFOS	3	6	18	True
MALATHION	3	6	18	True
BIFENTHRIN	3	6	18	True
PENDIMETHALIN	4	4	16	True
CHLOROTHALONIL	4	4	16	False
S-METOLACHLOR	4	4	16	True
ZIRAM	4	4	16	False
PROPANIL	5	3	15	True
THIOBENCARB	5	3	15	True
IMIDACLOPRID	3	5	15	True
LAMBDA-CYHALOTHRIN	2	7	14	True
MANCOZEB	4	3	12	False
GLUFOSINATE-AMMONIUM	4	3	12	True
METHOXYFENOZIDE	4	3	12	True
ORYZALIN	4	3	12	True
TRIFLURALIN	3	4	12	True
PROPARGITE	3	4	12	True
ETOXAZOLE	3	4	12	True
DIURON	3	4	12	True
SIMAZINE	3	4	12	True
PERMETHRIN	2	6	12	True
CARBARYL	2	5	10	True
FLUBENDIAMIDE	2	5	10	True
FLUMIOXAZIN	2	5	10	False
ABAMECTIN	2	5	10	True
AZOXYSTROBIN	3	3	9	True
DIMETHOATE	3	3	9	True
PROPICONAZOLE	3	3	9	True
CAPTAN	3	3	9	False
CYPRODINIL	3	3	9	True
PYRACLOSTROBIN	2	4	8	True

Table 3. Reporting limit and method detection limit for pesticides monitored in 2019

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
	Bensulide	0.004	0.02
	Bromacil	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
	Ethoprop	0.004	0.02
	Etofenprox	0.004	0.02
	Hexazinone	0.004	0.02
	Imidacloprid*	0.004	0.01
	Indoxacarb	0.004	0.02
	Isoxaben	0.004	0.02
	Kresoxim-methyl	0.004	0.02
	Malathion*	0.004	0.02
	Methidathion	0.004	0.02
	Methomyl	0.004	0.02
	Methoxyfenozide*	0.004	0.02
	Metribuzin	0.004	0.02
	Norflurazon	0.004	0.02
	Oryzalin*	0.004	0.02
	Oxadiazon	0.004	0.02
	Prometon	0.004	0.02
	Prometryn	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	0.015
	Quinoxyfen	0.004	0.02
	Simazine*	0.004	0.02
	S-Metolachlor*	0.004	0.02
	Tebufenozide	0.004	0.02
	Thiobencarb*	0.004	0.02

	Trifloxystrobin*	0.004	0.02
	Fipronil	0.004	0.01
	Fipronil Amide	0.004	0.01
	Fipronil Sulfide	0.004	0.01
	Fipronil Sulfone	0.004	0.01
	Desulfinyl Fipronil	0.004	0.01
	Desulfinyl Fipronil Amide	0.004	0.01
Pyrethroid Screen (PYR)	Bifenthrin	0.00091	0.001
	Permethrin (cis)	0.00105	0.002
	Permethrin (trans)	0.00106	0.005
	Cypermethrin	0.00154	0.005
	Lambda-cyhalothrin	0.00174	0.002
	Esfenvalerate/fenvalerate	0.00166	0.005
Dinitroaniline Screen (DN)	Benfluralin	0.012	0.05
	Ethalfluralin	0.015	0.05
	Oryzalin	0.021	0.05
	Oxyfluorfen	0.01	0.05
	Pendimethalin	0.012	0.05
	Prodiamine	0.012	0.05
	Trifluralin	0.014	0.05

*Analytes with an asterisk (*) will be included in the LC short and full screens, those without an asterisk will only be in the LC full screen.

Table 4. Chemical analysis of pyrethroids in Northern California agricultural monitoring Study 310. The Department of Food and Agriculture will analyze sediment samples.

Pesticide	Method Detection Limit (ng g^{-1} dry weight)	Reporting Limit (ng g^{-1} dry weight)
Bifenthrin	0.1083	1.0
Cypermethrin	0.107	1.0
Esfenvalerate/fenvalerate	0.143	1.0
Lambda-cyhalothrin	0.1154	1.0
Permethrin cis	0.1159	1.0
Permethrin trans	0.1352	1.0

Table 5. Monitoring schedule for sites in the Sacramento and San Joaquin valleys, 2019.

Sacramento Valley								
	May (Event 1)	May (Event 2)	June	July (Event 1)	July (Event 2)	August	September	Storm Event
LC screen (short)	3	3	3	0	3	0	3	0
LC screen (full)	0	0	0	3	0	0	0	0
Pyrethroid screen	3	3	3	3	3	0	3	0
Dinitroaniline screen	0	0	0	0	0	0	0	0
Sediment pyrethroid screen	0	0	0	1	0	0	0	0
Toxicity testing (Hyalella)	0	0	3	0	0	0	3	0
Toxicity testing (Chironomus)	0	0	3	0	0	0	3	0

San Joaquin Valley						
	May	June	July	August	September	Storm Event
LC screen (short)	0	4	0	4	4	0
LC screen (full)	0	0	4	0	0	4
Pyrethroid screen	0	4	4	4	4	4
Dinitroaniline screen	0	4	4	4	4	4
Sediment pyrethroid screen	0	0	3	0	0	0
Toxicity testing (Hyalella)	0	4	0	0	4	0
Toxicity testing (Chironomus)	0	4	0	0	4	0

Table 6. Analytical cost estimate for agricultural area samples for Northern California, 2019.

Analytical Screen	Total Samples*	Cost per sample	Cost estimate
LC screen (short)	27	$1,700	$45,900
LC screen (full)	11	$2,500	$27,500
Pyrethroid screen	38	$600	$22,800
Dinitroaniline screen	20	$840	$16,800
Sediment Pyrethroid screen	4	$600	$2,400
Total cost			$115,400

*QC samples included in the total number of samples

Appendix 1. Listed below are modifications for the 2019 protocol (from 2018 Study 310 protocol, https://www.cdpr.ca.gov/docs/emon/pubs/protocol/study310_wagner_2018.pdf).

Change from 2018 protocol	Justification
Discontinue sampling at Bounde Creek, Ellis Road, Jack Slough, Sycamore Slough, and Sweany Creek at Weber Rd	The three remaining sites in the Sacramento Valley represent well the pesticide uses and water discharges in areas on interest. Sampling at these sites was discontinued in order to move the sampling budget to new sites in the San Joaquin Valley.
Add sampling at 4 sites (Cottonwood Creek, Hilmar Drain, Deadman Creek, and Ingram Creek) in the San Joaquin Valley	Reported pesticide use is high in the regions where these sites are located. For years, DPR has not monitored at sites in the San Joaquin Valley for long-term monitoring purposes. By adding these monitoring sites, we hope to begin long-term monitoring in the San Joaquin Valley.
Utilize full LC screen analytical suite at least once at all monitoring sites	By screening for all of the analytes in the full LC screen, we will be able to monitor for pesticides that we previously did not monitor for; the full LC screen will help improve modeling capabilities by identifying constituents in water that were not prioritized by our model.
Add a storm water monitoring event in the San Joaquin Valley	We plan on monitoring during the first storm event after September that generates enough rainfall to generate significant runoff from agriculture fields. First flush storm events have the potential to carry accumulated pesticides from local fields to waterways.