Department of Pesticide Regulation
Environmental Monitoring Branch
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Study 310: Surface Water Monitoring for Pesticides in Agricultural Areas of Northern California, 2020

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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 (Burant, 2019; DaSilva, 2016; Deng, 2017; Ensminger, 2016; Wagner, 2019). 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 2018 and 2019, CDPR continued monitoring in the Sacramento Valley and further expanded monitoring coverage into the San Joaquin Valley.

The Sacramento and San Joaquin valleys are regions of high pesticide use. Total agricultural pesticide use in 2017 was 19,236,265 and 39,535,790 pounds in the Sacramento and San Joaquin river basins, respectively (CDPR, Pesticide Use Reports 2017). 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 the San Joaquin Valley in 2020. Three of the four sites in San Joaquin Valley that were part of the study expansion in 2019 will continue to be monitored. Two new sites, one in Butte County and one in Sutter County, will be added to the three in Sacramento Valley from 2019 to provide more comprehensive spatial coverage of the Sacramento Valley and monitor in watersheds of high pesticide use that have not been represented in previous CDPR monitoring efforts.

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 monitoring locations' suitability to serve as long-term monitoring 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 2020, a total of seven sites will be monitored in Butte, Colusa, Merced, Stanislaus, Sutter and Yolo counties (Figures 1 and 2; Table 1). Selected sites include a combination of tributaries, drainage canals, and mainstem waterways. The three sites in San Joaquin Valley were included in 2019 monitoring; the sites in Colusa and Yolo County were included in 2017–2019 monitoring while the sites in Butte and Sutter County are new additions.

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). Pesticides with a use score ≥2 were also considered for monitoring.

2. Low priority pesticides 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 a subset of sites and sent to 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 three toxicity sampling events at each site, one in June, one in September, and one during a storm event (Table 5).

4.5. Sampling schedule

There will be six surface water sampling events at the five Sacramento Valley sites from May through September and four sampling events at the three San Joaquin Valley sites monthly from June through September. The monitoring period was selected to coincide with the peak growing and pesticide application period. There will be an additional sampling event after September at the three San Joaquin Valley sites intended to collect storm water runoff. This storm water sampling event will occur during the first significant rain event during or 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 2020 protocol incorporates some changes from 2019 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 Sacramento Valley*: Two new sites will be monitored this year in the Sacramento 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. *One site in the San Joaquin Valley will no longer be monitored*: Cottonwood Creek will no longer 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 current sampling plan will cover the region represented by Cottonwood Creek.

3. *Add a storm water monitoring event*: We propose to collect samples from the three San Joaquin Valley sites during the first storm event of water year (WY20-21). 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. One storm runoff event was sampled in March 2020 under the 2019 monitoring protocol.

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 QAQC001.01 (Peoples, 2019). 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 and sediment 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; Goodell, 2016). 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 2020 – November 2020 (Table 5)
Chemical Analysis: May 2020 – December 2020
Summary Report: March 2021
SURF Data Upload: April 2021

8. LABORATORY BUDGET

The expected cost for chemical analysis of samples through the CDFA lab is $131,500 (Table 6). This estimate includes laboratory QC samples.

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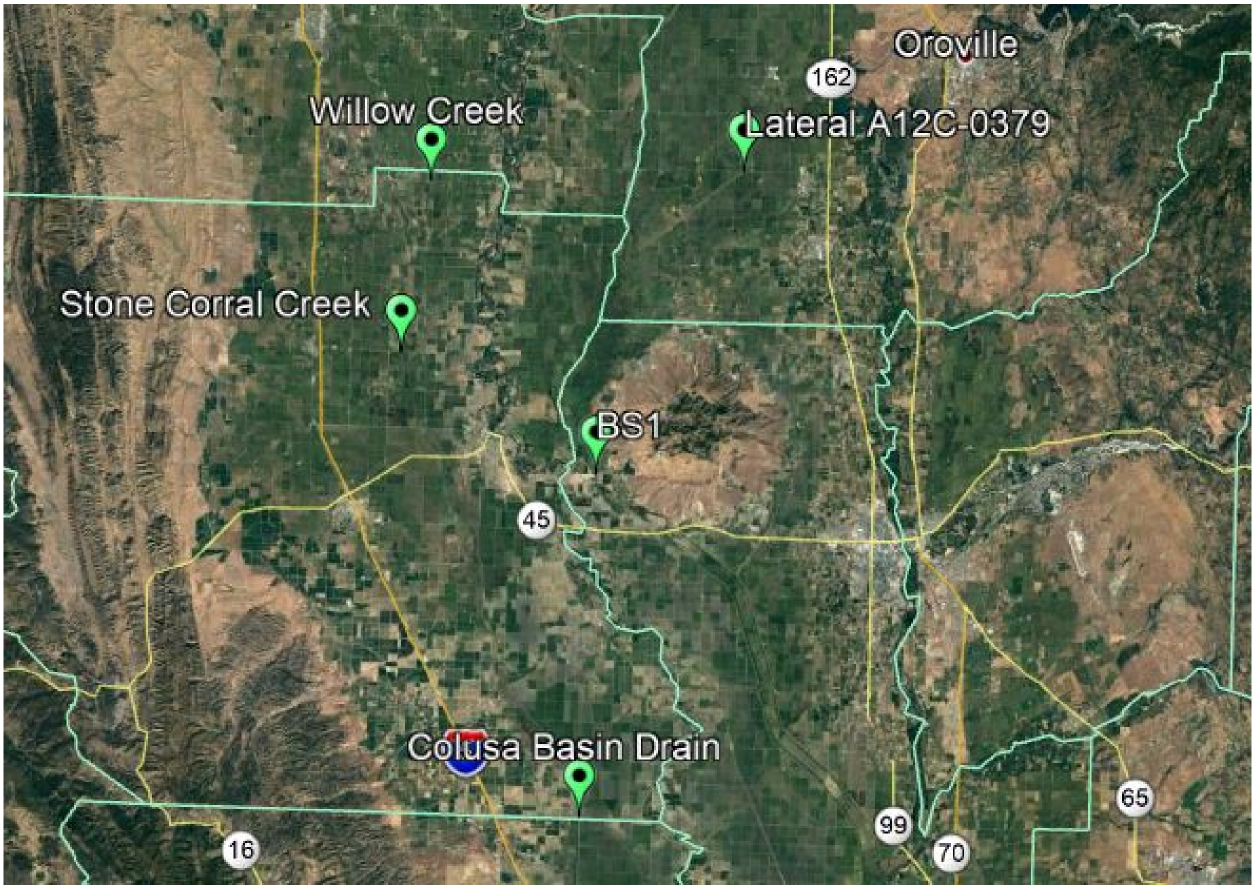

Figure 1. Monitoring sites in Butte, Colusa, Sutter and Yolo counties, Calif.

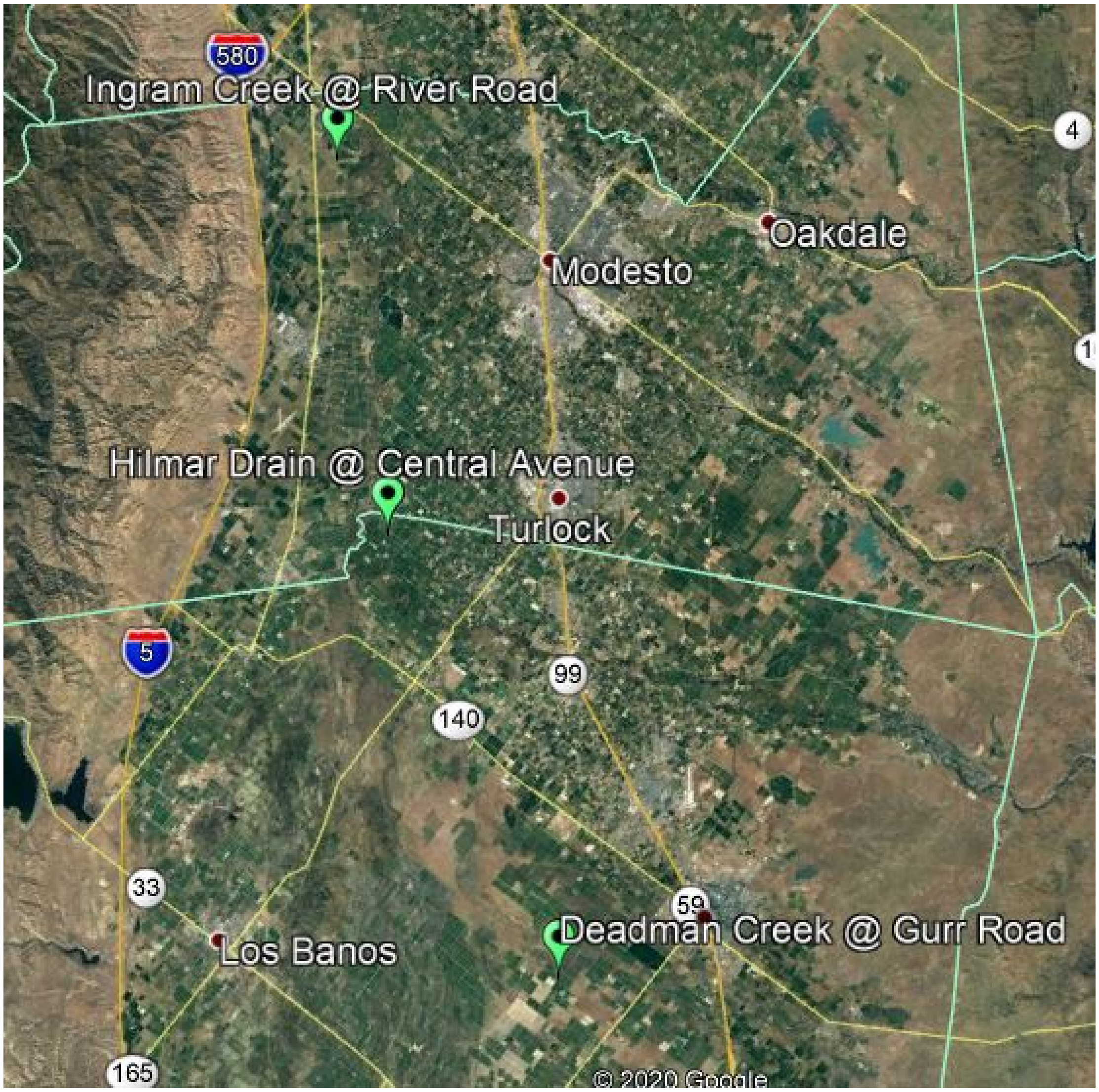

Figure 2. Monitoring sites in Merced and Stanislaus counties, Calif.

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
LA12	Lateral A12C-0379 at Biggs-Princeton Rd	Butte	Drumheller Slough-Butte Creek	39.421061	-121.772073
BS1	Butte Slough at Pass Rd	Sutter	Gilsizer Slough-Snake River	39.187300	-121.908955
San Joaquin Valley sites					
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

Table 2. Highest scoring pesticides recommended for monitoring using the SWMP model, based on 2015–2017 pesticide use reports for combined watersheds identified in Table 1.

HUC12 Watershed of interest: 180201040504,180201040303,180201041003,180201580404,180201590400,180400011604,180400020202,180400020502, with estimated drainage area of 2226 km^2				
Pesticide Name	**Use Score**	**Toxicity score**	**Final Score**	**Does model recommend monitoring?**
CHLORPYRIFOS	4	6	24	Yes
LAMBDA-CYHALOTHRIN	3	7	21	Yes
PARAQUAT DICHLORIDE	4	5	20	Yes
OXYFLUORFEN	4	5	20	Yes
BIFENTHRIN	3	6	18	Yes
CHLOROTHALONIL	4	4	16	No
ZIRAM	4	4	16	No
PENDIMETHALIN	4	4	16	Yes
S-METOLACHLOR	4	4	16	Yes
PROPANIL	5	3	15	Yes
THIOBENCARB	5	3	15	Yes
MANCOZEB	5	3	15	No
DIAZINON	3	5	15	Yes
CARBARYL	3	5	15	Yes
AZOXYSTROBIN	4	3	12	Yes
TRIFLURALIN	3	4	12	Yes
DIURON	3	4	12	Yes
ETHALFLURALIN	3	4	12	Yes
SIMAZINE	3	4	12	Yes
CHLORANTRANILIPROLE	3	4	12	Yes
PYRACLOSTROBIN	3	4	12	Yes
PROPARGITE	3	4	12	Yes
ESFENVALERATE	2	6	12	Yes
MALATHION	2	6	12	Yes
PERMETHRIN	2	6	12	Yes
IMIDACLOPRID	2	5	10	Yes
ABAMECTIN	2	5	10	Yes
FLUMIOXAZIN	2	5	10	No
GLUFOSINATE-AMMONIUM	3	3	9	Yes
CAPTAN	3	3	9	No
METHOXYFENOZIDE	3	3	9	Yes
PROPICONAZOLE	3	3	9	Yes
ORYZALIN	3	3	9	Yes
CYPRODINIL	3	3	9	Yes
DIMETHOATE	3	3	9	Yes
CLOMAZONE	4	2	8	No

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
	Acetamiprid	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
	Clothianidin	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
	Thiamethoxam	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	0.00099	0.001
	Permethrin (cis)	0.00074	0.001
	Permethrin (trans)	0.00087	0.001
	Cypermethrin	0.00183	0.005
	Lambda-cyhalothrin	0.00137	0.002
	Esfenvalerate/fenvalerate	0.00238	0.005
Dinitroaniline Screen (DN)	Benfluralin	0.012	0.05
	Ethalfluralin	0.015	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, 2020.

Sacramento Valley

	May (Event 1)	May (Event 2)	June	July (Event 1)	July (Event 2)	August	September	Storm Event
LC screen (short)	5	5	5	0	5	0	5	0
LC screen (full)	0	0	0	5	0	0	0	0
Pyrethroid screen	5	5	5	5	5	0	5	0
Dinitroaniline screen	5	0	0	5	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	3	0	3	3	0
LC screen (full)	0	0	3	0	0	3
Pyrethroid screen	0	3	3	3	3	3
Dinitroaniline screen	0	3	3	3	3	3
Sediment pyrethroid screen	0	0	3	0	0	0
Toxicity testing (Hyalella)	0	3	0	0	3	3
Toxicity testing (Chironomus)	0	3	0	0	3	3

Table 6. Analytical cost estimate for agricultural area samples for Northern California, 2020.

Analytical Screen	Total Samples*	Cost per sample	Cost estimate

LC screen (short)	34	$1,700	$57,800
LC screen (full)	11	$2,500	$27,500
Pyrethroid screen	45	$600	$27,000
Dinitroaniline screen	20	$840	$16,800
Sediment Pyrethroid screen	4	$600	$2,400
Total cost			$131,500

*QC samples included in the total number of samples

Appendix 1. Listed below are modifications for the 2020 protocol (from 2019 Study 310 protocol, https://www.cdpr.ca.gov/docs/emon/pubs/protocol/study310_wagner_2019.pdf).

Change from 2019 protocol	Justification
Discontinue sampling at Cottonwood Creek in San Joaquin Valley	The three remaining sites in the San Joaquin Valley represent well the pesticide uses and water discharges in areas on interest. Sampling at this sites was discontinued in order to move the sampling budget to new sites in the Sacramento Valley.
Add sampling at 2 sites (Butte Slough at Pass Road, Lateral A12C-0379 at Biggs-Princeton Road) in the Sacramento Valley	Reported pesticide use is high in the regions and watersheds (identified by the CDPR model) where these sites are located. CDPR has not recently conducted monitoring in Sutter or Butte County, despite significant agricultural pesticide use in these counties.
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. CDPR sampled during a late-season storm event (March 2020) under the 2019 protocol, but hopes to sample during a rain event earlier in the 2020 water season.