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Environmental Monitoring Branch
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Study 310: Surface Water Monitoring for Pesticides in Agricultural Areas of Northern California, 2021

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1. INTRODUCTION

The California Department of Pesticide Regulation (CDPR) routinely monitors agricultural pesticides in surface waters throughout the state (DaSilva, 2016; Deng, 2017; Main, 2019; Wagner, 2020). The Surface Water Protection Program (SWPP) has conducted monitoring in agricultural regions of the California Central Coast and Imperial Valley since 2008 (Main, 2019). Agricultural monitoring expanded in 2017 to include surface waters in the Sacramento Valley (Wagner, 2017) and in 2019 to include the San Joaquin Valley (Wagner, 2019). Study 310 is a continuation of those efforts and contributes to long-term monitoring efforts.

The San Joaquin Valley (SJV) is the most agriculturally productive region in California. In 2019, of the ten counties that contributed most to California's agricultural economy, eight are within the SJV (CDFA, 2020). As a region of intensive agricultural production, pesticide use is high. In 2018, over 76 million pounds of agricultural pesticides were applied in the San Joaquin River Basin (CDPR, 2018), a major watershed within the valley which is a focus for monitoring under Study 310. The region is dry, and therefore intensive irrigation is required to enable its high crop output. In 2014, approximately 7.4 million acre-feet of water was applied for agricultural use in the San Joaquin River Basin, which was approximately 21% of all water applied in the state that year (CDWR, 2018). With large volumes of pesticides and water applied, there is great potential for pesticide transport into surface waters via agricultural runoff, making the SJV a priority area for surface water monitoring. Crops grown in the region include almonds, pistachios, grapes, oranges, tomatoes, corn, cotton, and a multitude of other fruits and vegetables (CDFA, 2020). The wide range of pesticides and application types used in the SJV is a reflection of the diversity of crops grown in this region.

The Sacramento Valley (SV) is another major growing region for California. Like the SJV, it is also a dry region accompanied by high pesticide use and heavy irrigation. In 2018, approximately 36.7 million pounds of pesticides were applied for agricultural use in the Sacramento River basin (CDPR, 2018). Additionally, over 7 million acre-feet of water was applied for agricultural use in the SV in 2014 (CDWR, 2018). The region's main crop outputs include rice, nuts, grapes, peaches, plums, and tomatoes (CDFA, 2020). Rice production in the SV accounts for 97% of the 5 billion pounds yielded in California, annually (Wagner et al., 2019). Rice cultivation is a complex process requiring flood irrigation. Conventional water management systems for rice production are poorly adapted to water-holding requirements for rice pesticides; consequently, tailwater may potentially discharge into adjacent waterways (UCANR, 2018). Seepage and drift may also influence transport of some rice pesticides (Firoved et al., 2019). In contrast, other top commodities in the region, such as nuts and grapes, often utilize drip irrigation to apply water directly to roots, which leads to significant decreases in runoff potential (Hedley, 2014). Thus, monitoring for rice pesticides has been a focus for CDPR since the inception of agricultural surface water monitoring in the SV (Wagner, 2017).

SWPP will continue to monitor for pesticides in surface waters in the Sacramento and San Joaquin valleys in 2021. The monitoring schedule and site locations were established in previous years of the study (Wagner, 2017; 2018; 2019; 2020). Sample collection from long-term sites and adherence to the established annual monitoring schedule allows for collection of data that is spatially and temporally consistent over the years. Long-term monitoring data collected in this study will be used to assess potential impacts to aquatic environments and analyze patterns and/or trends in overall Central Valley pesticide detections.

2. OBJECTIVES

The objectives of the study are to:

- Determine the presence and concentrations of selected pesticides in surface waters and sediments collected from selected sites;
- Assess potential impacts to aquatic organisms by comparing measured pesticide concentrations to USEPA aquatic life benchmarks;
- Determine the toxicity of collected water samples using toxicity tests conducted on representative test organisms, *Hyalella azteca* and *Chironomus dilutus*;
- Evaluate spatial correlations between observed pesticide concentrations/detection frequencies and region-specific pesticide use data; and
- Analyze patterns and trends in pesticide concentrations.

3. PERSONNEL

The study will be conducted by Surface Water Protection Program staff under the general direction of Jennifer Teerlink, Ph.D., Environmental Program Manager. Key personnel are listed below:

- Project Leader: Mason Zoerner, B.Sc.
- Field Coordinator: Xin Deng, Ph.D.
- Reviewing Scientist: Robert Budd, Ph.D.
- Statistician: Xuyang Zhang, Ph.D.
- Laboratory Liaison: Aniela Burant, Ph.D.
- Analytical Chemistry: Center for Analytical Chemistry, California Department of Food and Agriculture (CDFA)

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

4. STUDY PLAN

4.1. Selection of monitoring sites

Monitoring will occur at five sites in the SV and at three sites in the SJV. All study sites were defined in the previous year of the study (Wagner, 2017; 2018; 2020). Sites were selected in watersheds which were determined to be of highest monitoring priority by the Surface Water Monitoring Prioritization (SWMP) model. This model considers pesticide use data and physiochemical properties of applied pesticides to designate watersheds of greatest potential for contamination (Luo et at., 2017). Candidate watersheds for monitoring are listed in Table 1. CDPR staff also considered hydrography, seasonal flows, and crop irrigation type in the selection of sites (Wagner, 2020). Site visits were conducted prior to sampling to verify site suitability and accessibility. Sampling sites are listed in Tables 2 and 3. Site maps are included in Figures 1 and 2.

4.2. Selection of pesticides

Pesticides to be screened in water were determined using SWMP. This model uses toxicity and reported pesticide use to identify active ingredients of highest monitoring priority in a given watershed (Luo and Deng, 2015). Monitoring priority was ranked based on results of watersheds for each site, combined. Model outputs for each site are listed in Table 4.

Active ingredients to be screened for the selected watersheds were designated based on the following criteria:

1. Pesticides with a use score ≥ 2 or a final 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. Low-priority pesticides are not included in the final monitoring list (Table 4) but may be monitored as part of a larger analytical screen.

3. Historical monitoring data 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 schedule

Sampling will occur five times in the SV between May and September, and four times in the SJV between June and September. The monitoring period is intended to coincide with the peak pesticide application and irrigation period. An additional sampling event in each region may occur at the first major storm following the September sampling. Storm samples are intended to check for pesticide concentrations associated with storm runoff. If the first major storm lacks sufficient precipitation to produce runoff, or if weather conditions do not permit safe travel, then the storm sampling will not take place. The full sampling schedule is listed in Tables 7 and 8.

4.4. Sample collection.

Water samples will be collected during each sampling event. Samples will be collected using 1 L amber glass bottles, by hand or by sampling pole. Bottles will be submerged into waterways at a depth of approximately 10 cm below the surface and sealed once full (Bennett, 1997; Deng and Ensminger, 2021). Sediment samples will be collected in July, at three sites in the SJV and at two sites in the SV. Composite sediment samples will be collected from waterway banks using a stainless steel scoop, sieved with a 2 mm sieve, and sealed in half-pint glass Mason jars (Deng and Ensminger, 2021; Mamola, 2005). All sample containers will be rinsed prior to placement in an ice chest, maintaining samples in a 4°C environment for the duration of transport (Deng and Ensminger, 2021; Jones, 1999).

4.5. Field measurements

Field measurements will be taken concurrently with sample collection at each site. Staff will use a multiparameter YSI EXO1 Sonde (YSI Incorporated, Yellow Springs, OH, USA) to measure temperature, specific conductivity, total dissolved solids, salinity, dissolved oxygen, and pH (Doo and He, 2008).

5. LABORATORY ANALYSES

5.1. Chemical Analysis

Chemical analysis for this study will be conducted by the Center for Analytical Chemistry at the California Department of Food and Agriculture (CDFA). The laboratory will use multi-residue liquid chromatography tandem mass spectrometry (LC-MS/MS) to screen pesticide active ingredients in collected samples. Additional screens will measure concentrations of pyrethroids and dinitroanilines. Pesticides to be analyzed, as well as their respective reporting limits, are listed in Tables 4 and 5. Extractions will include laboratory blanks and matrix spikes, as per CDPR QA/QC guidelines (Peoples, 2019; Segawa, 1995).

5.2. Organic Carbon and Suspended Solid Analyses

CDPR staff will use a TOC-V CSH/CNS analyzer (Shimadzu Corporation, Kyoto, Japan) to analyze total organic carbon (TOC) of water and sediment samples, as well as dissolved organic carbon (DOC) of water samples (Ensminger, 2013; Goodell, 2016). Staff will also measure total suspended solids (TSS) of water samples using a vacuum pump and glass fiber microfilters (Ensminger, 2016). Lab blanks and calibration standards will be run prior to each sample set to ensure high data quality.

5.3. Toxicity.

Samples for toxicity testing will be collected in each region in June and September, as well as during the storm sampling event. At least three water samples for toxicity testing will be collected from the SV, while at least one water sample will be collected from the SJV. Additional toxicity samples may be collected in both regions, if budget allows. Toxicity samples will be transported to the University of California, Davis, Aquatic Health Program Laboratory. The lab will test for mortality of *Hyalella azteca* and *Chironomus dilutus* on a 96-hour acute exposure basis.

6. DATA ANALYSIS

Data from this study will be entered into a Microsoft Office Access database which contains field measurements and laboratory results for all of CDPR's agricultural surface water monitoring studies. Data collected in the study will also be uploaded to the publicly-available Surface Water Database (SURF). Spatial analysis may be conducted using ArcGIS and R to identify correlations between reported pesticide use and observed detections. Observed concentrations will also be compared to USEPA aquatic life benchmarks (USEPA, 2018), as well as water quality limits established by the Central Valley Regional Water Quality Control Board (CCVRWQCB, 2012).

7. PROTOCOL REVISIONS

Sampling sites, as well as sampling and laboratory methods, have been adopted from the 2020 protocol (Wagner, 2020). However, the current 2021 protocol will incorporate some changes from the previous year. In 2020, some water samples were screened for only a subset of pesticides in the LC-MS/MS analysis (Wagner, 2020). In 2021, all sites will be screened for all pesticides identified in the prioritization model, except for those with no available analytical method or low historic detections. Additionally, a historical monitoring site will be reintroduced. Bounde Creek at Norman Rd was sampled in 2017 and 2018 (Wagner, 2017; 2018), but sampling at this site was discontinued in 2019 due to low detections (Wagner, 2019). Sampling will resume at this site in 2021 to assist in evaluating the success of rice pesticide mitigation efforts.

8. TIMETABLE

Field Sampling: May 2021 – November 2021 (Table 6)
Chemical Analysis: May 2021 – December 2021
Summary Report: March 2022
SURF Data Upload: Fall 2022

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Table 1. Candidate watersheds for monitoring, as identified by the watershed prioritization model. Hydrologic Unit (HU) refers to watershed boundaries defined by United States Geological Survey (USGS).

HU	HU Name	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

Table 2. Description of Study 310 Sacramento Valley sampling sites in 2021.

Site ID	Site Location	County	HU-12 Watershed	Latitude	Longitude
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_Bounde Creek	Bounde Creek at Norman Rd	Colusa	Colusa Drain	39.406297	-122.055885
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

Table 3. Description of Study 310 San Joaquin Valley sampling sites in 2021.

Site ID	Site Location	County	HU-12 Watershed	Latitude	Longitude
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

Figure 1: Map of Sacramento Valley (SV) monitoring sites.

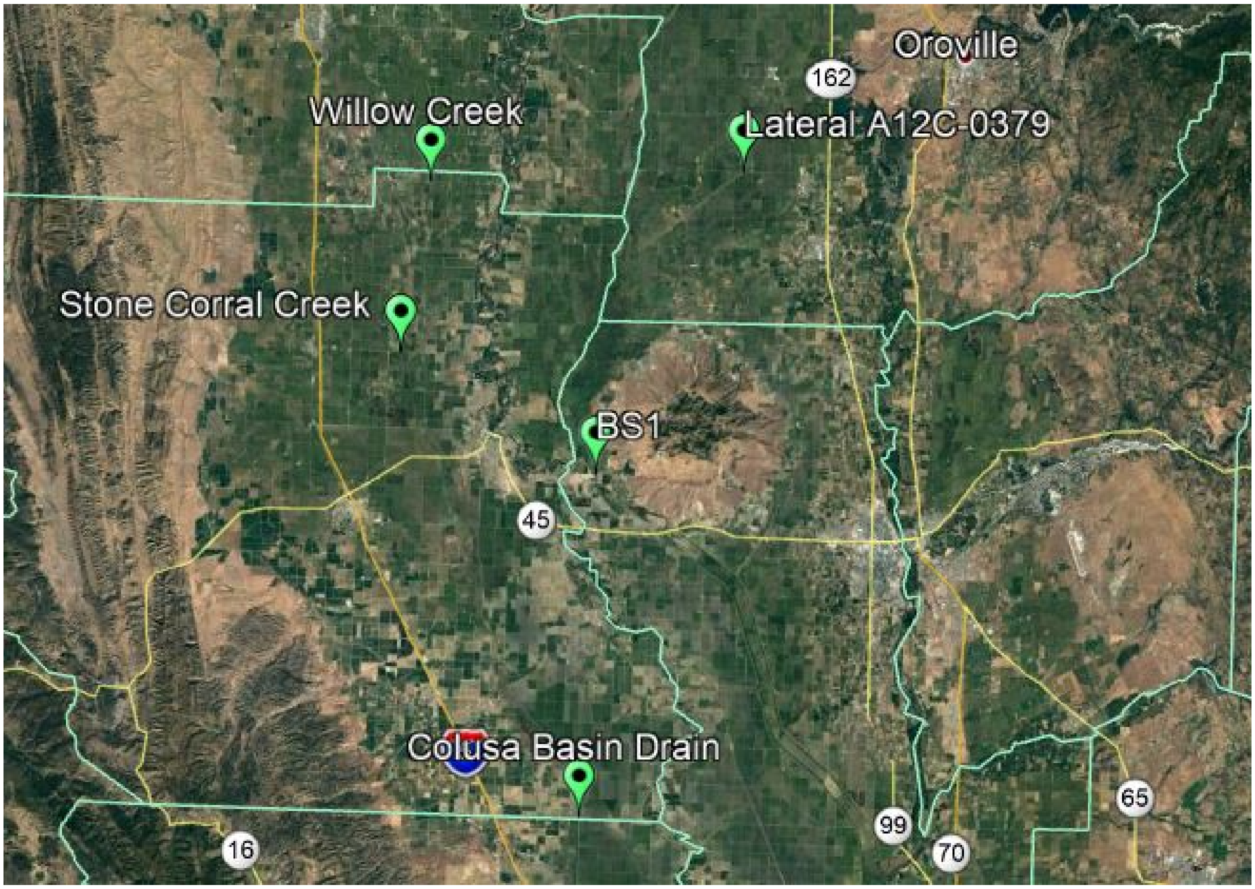

Figure 2: Map of San Joaquin Valley (SJV) monitoring sites.

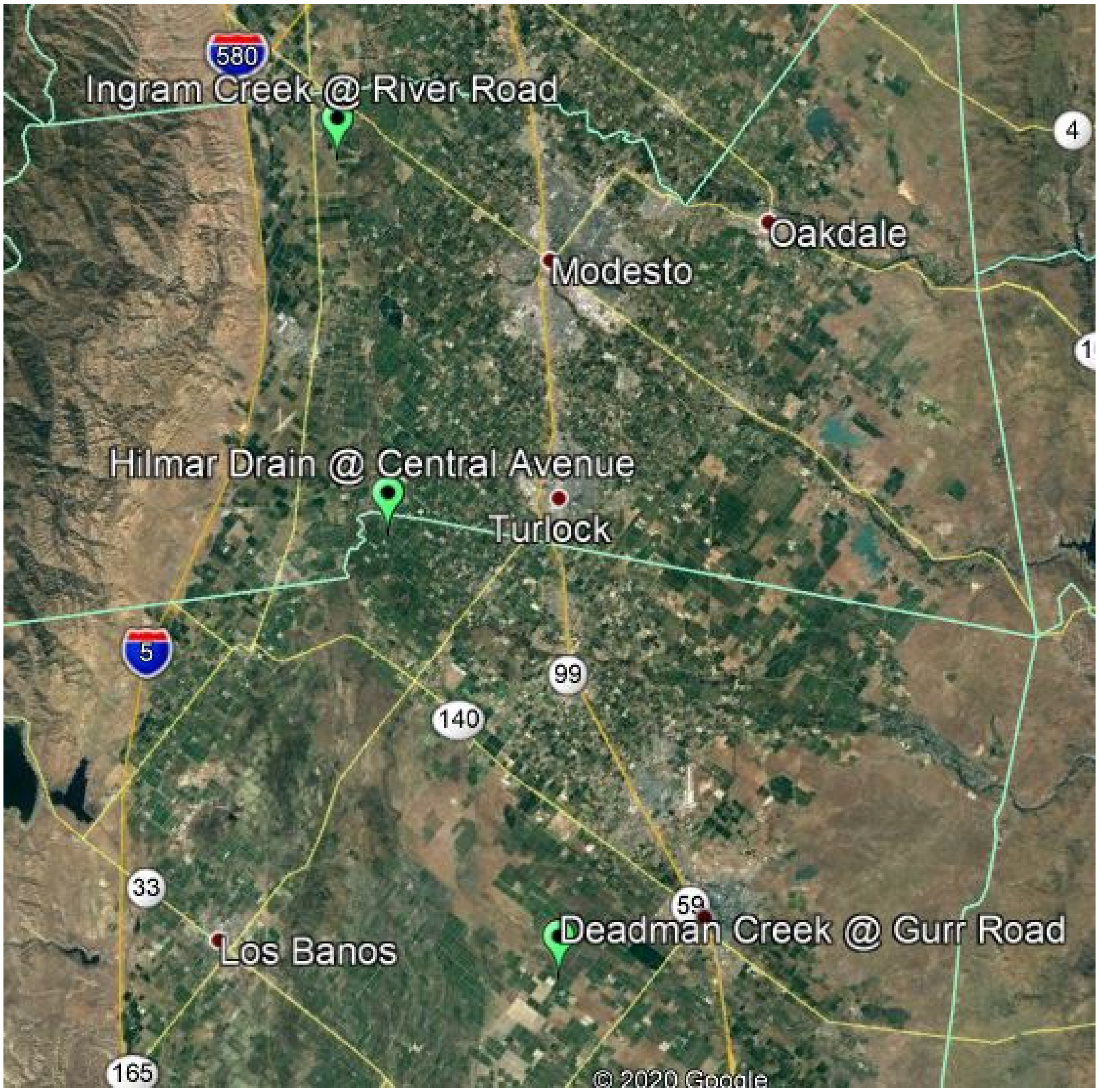

Table 4. Highest scoring pesticides recommended for monitoring using the SWMP model, based on 2016–2018 pesticide use reports for combined watersheds identified in Table 1.

Chemical Name	**Use Score**	**Toxicity Score**	**Final Score**	**Does the 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
Chlorothanlonil	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
Azoxystrobin	4	3	12	Yes
Glufosinate ammonium*	4	3	12	Yes
Trifluralin	3	4	12	Yes
Ethalfluraline	3	4	12	Yes
Chlorantraniliprole	3	4	12	Yes
Benzobicyclon	3	4	12	No
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
Carbaryl	2	5	10	Yes
Flumioxazine	2	5	10	No
Methozyfenozide	3	3	9	Yes
Captan	3	3	9	No
Propiconazole	3	3	9	Yes
Cyprodinil	3	3	9	Yes
Oryzalin	3	3	9	Yes
Dimethoate	3	3	9	Yes

*Analytes with an asterisk (*) will not be screened, either due to low historic detections or unavailable analytical methods.

Table 5. Reporting limits and method detection limits for pesticides monitored in 2021.

Analytical Screen	Analyte	Method Detection Limit (µg/L)	Reporting Limit (µg/L)
LC	Abamectin	0.004	0.02
LC	Acetamiprid	0.004	0.02
LC	Atrazine	0.004	0.02
LC	Azoxystrobin	0.004	0.02
LC	Bensulide	0.004	0.02
LC	Bromacil	0.004	0.02
LC	Carbaryl	0.004	0.02
LC	Chlorantraniliprole	0.004	0.02
LC	Chlorpyrifos	0.004	0.02
LC	Clothianidin	0.004	0.02
LC	Cyprodinil	0.004	0.02
LC	Diazinon	0.004	0.02
LC	Diflubenzuron	0.004	0.02
LC	Dimethoate	0.004	0.02
LC	Diuron	0.004	0.02
LC	Ethoprop	0.004	0.02
LC	Etofenprox	0.004	0.02
LC	Hexazinone	0.004	0.02
LC	Imidacloprid	0.004	0.01
LC	Indoxacarb	0.004	0.02
LC	Isoxaben	0.004	0.02
LC	Kresoxim-methyl	0.004	0.02
LC	Malathion	0.004	0.02
LC	Methidathion	0.004	0.02
LC	Methomyl	0.004	0.02
LC	Methoxyfenozide	0.004	0.02
LC	Metribuzin	0.004	0.02
LC	Norflurazon	0.004	0.02
LC	Oryzalin	0.004	0.02
LC	Oxadiazon	0.004	0.02
LC	Prometon	0.004	0.02
LC	Prometryn	0.004	0.02
LC	Propanil	0.004	0.02
LC	Propargite	0.004	0.02
LC	Propiconazole	0.004	0.02
LC	Pyraclostrobin	0.004	0.02
LC	Pyriproxyfen	0.004	0.015
LC	Quinoxyfen	0.004	0.02
LC	Simazine	0.004	0.02
LC	S-Metolachlor	0.004	0.02
LC	Tebufenozide	0.004	0.02

LC	Thiamethoxam	0.004	0.02
LC	Thiobencarb	0.004	0.02
LC	Trifloxystrobin	0.004	0.02
LC	Fipronil	0.004	0.01
LC	Fipronil Amide	0.004	0.01
LC	Fipronil Sulfide	0.004	0.01
LC	Fipronil Sulfone	0.004	0.01
LC	Desulfinyl Fipronil	0.004	0.01
LC	Desulfinyl Fipronil Amide	0.004	0.01
PY	Bifenthrin	0.00099	0.001
PY	Permethrin (cis)	0.00074	0.001
PY	Permethrin (trans)	0.00087	0.001
PY	Cypermethrin	0.00183	0.005
PY	Lambda-cyhalothrin	0.00137	0.002
PY	Esfenvalerate/fenvalerate	0.00238	0.005
DN	Benfluralin	0.012	0.05
DN	Ethalfluralin	0.015	0.05
DN	Oxyfluorfen	0.01	0.05
DN	Pendimethalin	0.012	0.05
DN	Prodiamine	0.012	0.05
DN	Trifluralin	0.014	0.05

Table 6. Pyrethroid chemicals included in the sediment analysis in Study 310. Sediment analysis will be conducted by the CDFA Center for Analytical Chemistry laboratory.

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 7. Monitoring schedule for sites in the Sacramento Valley, 2021. Numbers listed indicate the amount of each type of sample collected.

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

Table 8: Monitoring schedule for sites in the San Joaquin Valley, 2021.

	May	June	July	August	September	Storm Event
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