



**Department of Pesticide Regulation
Environmental Monitoring Branch
1001 I Street
Sacramento, CA 95812**

Study 310: Surface Water Monitoring for Pesticides in Agricultural Areas of Northern California, 2024

**Mason Zoerner
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1. INTRODUCTION

The California Department of Pesticide Regulation (DPR) has conducted annual monitoring of agricultural pesticides in surface waters throughout California since 2008. (Deng, 2017; Main, 2019; Wagner, 2020; Zoerner, 2021). The Surface Water Protection Program (SWPP) established the long-term monitoring of agricultural regions of the California Central Coast and Imperial Valley in 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 as a part of the continuous evaluation process.

The San Joaquin Valley (SJV) is the most agriculturally productive region in California. Crops grown in the region include almonds, pistachios, grapes, oranges, tomatoes, corn, cotton, and a multitude of other fruits and vegetables (CDFA, 2023). In 2021, of the ten counties that contributed most to California's agricultural economy, seven were within the SJV (CDFA, 2023). As a region of intensive agricultural production, pesticide use is high compared to other parts of the state. In 2021, over 178 million pounds of agricultural pesticides were applied in the San Joaquin Valley (CDPR, 2023). The region is relatively dry, and therefore intensive irrigation is required to enable its high crop output. Between 2001 and 2020, approximately 7.5 to 9 million acre-feet of water has been applied to agriculture in the San Joaquin River Basin, annually (CDWR, 2023). With large volumes of pesticides and water applied, there is greater potential for pesticide transport into surface waters via agricultural runoff, making the SJV region a priority for surface water monitoring.

The Sacramento Valley (SV) is another major agricultural region for California. Like the SJV, it is also a dry region accompanied by high pesticide use and heavy irrigation. In 2021, over 37 million pounds of pesticides were applied for agricultural use in the Sacramento River basin (CDPR, 2023). Additionally, between 2001 and 2020, approximately 7.5 to 10 million acre-feet of water has been applied to agriculture in the Sacramento River Basin, annually (CDWR, 2023). The region's main crop outputs include rice, nuts, grapes, peaches, plums, and tomatoes (CDFA, 2023). 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 which requires 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 also have the potential to 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 DPR since the inception of agricultural surface water monitoring in the SV (Wagner, 2017).

The SWPP will continue to monitor for pesticides in surface waters in the Sacramento and San Joaquin valleys in 2024. The monitoring schedule and site locations were established in previous years of the study (Wagner, 2018; Zoerner, 2021). 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 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 United States Environmental Protection Agency (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;
- Analyze patterns and trends in pesticide concentrations;
- Publish raw data sets on the Surface Water Monitoring Database (SURF) and annual monitoring results in a summary report. Share annual evaluation reports on DPR's SWPP website once they become available.

3. PERSONNEL

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

- Project Leader: Mason Zoerner
- Field Coordinator: KayLynn Newhart
- Reviewing Scientist: Robert Budd, Ph.D.
- Statistician: Xuyang Zhang, Ph.D.
- Laboratory Liaison: Joshua Alvarado

- 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 three sites in the SJV and at five sites in the SV. The SWPP staff 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 1 and 2. Site maps are included in Figures 1 and 2. Study sites were defined in the previous years of the study (Wagner, 2017; Zoerner, 2023). A new sampling location at Hilmar Drain will be introduced in the 2024 monitoring year. The original Hilmar Drain site (TH_HMD), established in 2019 (Wagner, 2019), is no longer a suitable sampling location due to access issues. The new Hilmar Drain site (SJ_Hilmar) is located 0.5 miles east of the former sampling location, where access to the agricultural drain is unrestricted.

4.2. Selection of pesticides

Pesticides to be screened in water were determined using the Surface Water Prioritization Model (SWMP). This model uses toxicity and reported pesticide use to identify active ingredients (AIs) of highest monitoring priority in a given watershed (Luo and Deng, 2015). Monitoring priority was ranked based on the total amount of pesticide use of all the monitored watersheds combined. The model identified 24 high-priority AIs to be included in monitoring. Model outputs are listed in Table 3.

The AIs to be screened for the selected watersheds were designated based on the following criteria:

1. Pesticides with a use score ≥ 2 and/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) or low toxicity (toxicity score < 3).
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.
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 four times in the SJV between June and September, and five times in the SV between May 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 during 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 sampling schedule for both study areas is included in Tables 10 and 11.

4.4. Sample collection.

Surface water samples for chemical analysis 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 sonde, the In-Situ AquaTroll 400 (In-Situ Incorporated, Fort Collins, CO, USA) to measure temperature, specific conductivity, total dissolved solids, salinity, dissolved oxygen, and pH. All field measurements follow closely to those described in the standard operating procedure for the YSI EXO1 multiparameter sonde (Edgerton, 2020).

4.6. Modifications from Previous Monitoring Year

The 2024 protocol is a continuation of DPR's long-term efforts to monitor agricultural surface waters in the California Central Valley (Wagner, 2017; Wagner, 2019; Zoerner, 2022), with a few notable changes. The new sampling site, SJ_Hilmar, will be monitored in 2024, while the former sampling site, TH_HMD, will no longer be monitored. Reasons for this change are included in section 4.1. Additionally, glyphosate will be monitored in the Sacramento Valley in 2024 due to external stakeholder interest. Samples will be screened for the AI using a recently developed glyphosate screen. Reporting limits and method detection limits for this screen are included in Table 8.

5. LABORATORY ANALYSES

5.1. Chemical Analysis

Chemical analysis for this study will be conducted by the Center for Analytical Chemistry at the CDFA. The laboratory will use multi-residue liquid chromatography tandem mass spectrometry (LC-MS/MS) to screen pesticide AIs in collected water samples. Additional screens will be used to measure concentrations of pyrethroids, dinitroanilines, and glyphosate. Sediment samples will be screened for pyrethroids. Pesticides to be analyzed, as well as their respective reporting limits and method detection limits, are listed in Tables 4 through 9. Extractions will include laboratory blanks and matrix spikes, as per DPR QA/QC guidelines (Peoples, 2019; Segawa, 1995).

5.2. Organic Carbon and Suspended Solid Analyses

The SWPP staff will analyze total organic carbon (TOC) of water and sediment samples, as well as dissolved organic carbon (DOC) of water samples, using a Vario TOC Cube TOC/TNb Analyzer (Elementar Analysensysteme GmbH, Langensfeld, Germany). TOC and DOC analyses will follow methods similar to those outlined by Ensminger (2013) and Goodell (2016). Staff will also measure total suspended solids (TSS) of water samples using a vacuum pump and glass fiber microfilters (Ensminger, 2016). Laboratory 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. During these sampling events, toxicity samples will be collected at each site. The samples will then be transported to the University of California, Davis (UCD), Aquatic Health Program Laboratory, where UCD laboratory will test for mortality of *Hyaella 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 DPR agricultural surface water monitoring studies. Data collected in the study will also be uploaded to the publicly-available SURF. Spatial analysis may be conducted using ArcGIS and R to identify correlations between

reported pesticide use and observed detections. Observed pesticide concentrations in collected water samples will also be compared to USEPA aquatic life benchmarks (USEPA, 2018) to determine potential toxicity. Additionally, concentrations of some rice pesticides will be compared to water quality performance goals established by the Central Valley Regional Water Quality Control Board (CCVRWQCB, 2010).

7. TIMETABLE

Field Sampling: May 2024 – December 2024 (Table 7, 8)

Chemical Analysis: May 2024 – December 2024

Summary Report: March 2025

SURF Data Upload: May 2025

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9. TABLES

Table 1. Description of Study 310 Sacramento Valley sampling sites in 2024.

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 2. Description of Study 310 San Joaquin Valley sampling sites in 2024.

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
SJ_Hilmar	Hilmar Drain at Central Ave	Merced	Town of Hilmar-San Joaquin River	37.390450	-120.941090
IC_INC	Ingram Creek at River Road	Stanislaus	Ingram Creek	37.60022	-121.22506

Table 3. Highest scoring pesticides recommended for monitoring using the SWMP model, based on 2019–2021 pesticide use reports for combined watersheds identified in Table 1.

Chemical Name	Use Score	Toxicity Score	Final Score	Does the model recommend monitoring?
Bifenthrin	3	8	24	Yes
Lambda-cyhalothrin	3	8	24	Yes
Esfenvalerate	3	8	24	Yes
Oxyfluorfen	4	5	20	Yes
Paraquat dichloride	4	5	20	Yes
Halosulfuron-methyl*	3	6	18	No
Chlorothalonil*	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
Permethrin	2	7	14	Yes
Ziram*	4	3	12	No
Glufosinate-ammonium	4	3	12	Yes
Azoxystrobin	4	3	12	Yes
Methoxyfenozide	4	3	12	Yes
Benzobicyclon*	3	4	12	No
Chlorantraniliprole	3	4	12	Yes
Propargite*	3	4	12	No
Malathion	2	6	12	Yes
Diuron	2	5	10	Yes
Imidacloprid	2	5	10	Yes
Flumioxazin	2	5	10	No
Abamectin	2	5	10	Yes
Carbaryl	2	5	10	Yes
Propiconazole	3	3	9	Yes
Captan*	3	3	9	No
Spirodiclofen	3	3	9	Yes
Cyprodinil	3	3	9	Yes
Oryzalin	3	3	9	Yes

Analytes with an asterisk () will not be screened, either due to low historic detections or no analytical methods available.

Table 4. Reporting limits and method detection limits for pesticides in whole water using the LC* screen.

Analyte	Method Detection Limit (ng/L)	Reporting Limit (ng/L)
2,4-D	4	20
Abamectin	4	20
Atrazine	4	20
Azoxystrobin	4	20
Bensulide	4	20
Bromacil	4	20
Carbaryl	4	20
Chlorantraniliprole	4	20
Chlorpyrifos	4	20
Cyprodinil	4	20
Diazinon	4	20
Diffubenzuron	4	20
Dimethoate	4	20
Diuron	4	20
Ethoprop	4	20
Etofenprox	4	20
Hexazinone	4	20
Indoxacarb	4	20
Isoxaben	4	20
Kresoxim-methyl	4	20
Malathion	4	20
Methidathion	4	20
Methomyl	4	20
Methoxyfenozide	4	20
Metribuzin	4	20
Norflurazon	4	20
Oryzalin	4	20
Oxadiazon	4	20
Prometon	4	20
Prometryn	4	20
Propanil	4	20
Propargite	4	20
Propiconazole	4	20
Pyraclostrobin	4	20
Pyriproxyfen	4	15
Quinoxifen	4	20
Simazine	4	20
S-Metolachlor	4	20
Tebufenozide	4	20
Thiobencarb	4	20
Trifloxystrobin	4	20

Fipronil	4	10
Fipronil Amide	4	10
Fipronil Sulfide	4	10
Fipronil Sulfone	4	10
Desulfinyl Fipronil	4	10
Desulfinyl Fipronil Amide	4	10

*LC = Liquid chromatograph multi-analyte screen (47 AIs).

Table 5. Reporting limits and method detection limits for pesticides in whole water using the pyrethroid screen.

Analyte	Method Detection Limit (ng/L)	Reporting Limit (ng/L)
Bifenthrin	0.91	1
Cyfluthrin	1.46	2
Cypermethrin	1.54	5
Esfenvalerate/fenvalerate	1.66	5
Fenpropathrin	1.32	5
Lambda-cyhalothrin	1.74	2
Permethrin	1.05	2

Table 6. Reporting limits and method detection limits for pesticides in whole water using the dinitroaniline screen.

Analyte	Method Detection Limit (ng/L)	Reporting Limit (ng/L)
Benfluralin	14	50
Ethalfuralin	15	50
Oxyfluorfen	10	50
Pendimethalin	12	50
Prodiamine	12	50
Trifluralin	14	50

Table 7. Reporting limits and method detection limits for pesticides in whole water using the neonicotinoid screen.

Analyte	Method Detection Limit (ng/L)	Reporting Limit (ng/L)
Acetamiprid	4	20
Clothianidin	4	20
Dinotefuran	4	20
Imidacloprid	4	10
Sulfoxaflor	4	20
Thiacloprid	4	20
Thiamethoxam	4	20

Table 8. Reporting limits and method detection limits for pesticides in whole water using the glyphosate screen.

Analyte	Method Detection Limit (ng/L)	Reporting Limit (ng/L)
Glyphosate	0.00495	70
Glufosinate-ammonium	0.01154	70
Aminomethylphosphonic Acid (AMPA)	0.02786	200

Table 9. Reporting limits and method detection limits for pesticides in sediment using the pyrethroid screen.

Analyte	Method Detection Limit (ng/g dry weight)	Reporting Limit (ng/g dry weight)
Bifenthrin	0.1083	1
Cyfluthrin	0.1830	1
Cypermethrin	0.107	1
Esfenvalerate/fenvalerate	0.143	1
Lambda-cyhalothrin	0.1154	1
Permethrin cis	0.1159	1
Permethrin trans	0.1352	1

Table 10. Monitoring schedule for sites in the Sacramento Valley, 2024. 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	6	6	6	6	0	6	6
Pyrethroid screen	6	6	6	6	0	6	6
Neonicotinoid screen	6	6	6	6	0	6	6
Glyphosate screen	0	0	6	6	0	6	6
Sediment pyrethroid screen	0	0	0	0	0	3	0
Toxicity testing (Hyalella)	0	0	6	0	0	6	6
Toxicity testing (Chironomus)	0	0	6	0	0	6	6

Table 11. Monitoring schedule for sites in the San Joaquin Valley, 2024. Numbers listed indicate the amount of each type of sample collected.

	May	June	July	August	September	Storm Event
LC screen	0	3	3	3	3	3
Pyrethroid screen	0	3	3	3	3	3
Neonicotinoid screen	0	3	3	3	3	3
Dinitroaniline screen	0	3	3	3	3	3
Sediment pyrethroid screen	0	0	0	0	2	0
Toxicity testing (Hyaella)	0	3	0	0	3	3
Toxicity testing (Chironomus)	0	3	0	0	3	3

10. FIGURES

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



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

