DEPARTMENT OF PESTICIDE REGULATION (DPR) Date: March 24, 2023

SURFACE WATER AMBIENT MONITORING REPORT

1. Study highlights

- DPR Study Number 310
- SURF (Surface Water Database) Study Number 658
- Study Title **Surface Water Monitoring for Pesticides in Agricultural Areas of Northern California, 2021**
- Project Lead Mason Zoerner
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- Protocol Source (*protocol available online for five years, thereafter, request a copy from the SWPP list of archived files)* Environmental Monitoring Protocol Page

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- Study Area

  County: Butte, Colusa, Merced, Stanislaus, Sutter, Yolo

  Waterbody/Watershed: Lower Logan Creek, Willow Creek, Clarks Ditch-Colusa Basin Drain, Lower Cottonwood Creek, South Slough-Deadman Creek, Town of Hilmar-San Joaquin River, Ingram Creek

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- Land use type ☒ Ag ☐ Urban ☐ Forested ☐ Mixed ☐ Other

- Water body type

  ☒ Creek ☐ River ☐ Pond ☐ Lake

  ☒ Drainage Ditch ☐ Storm drain outfall ☐ Other Enter other type

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- Objectives

1) Determine the presence and concentrations of selected pesticides in surface waters and sediments collected from selected sites; 2) Assess potential impacts to aquatic organisms by comparing measured pesticide concentrations to USEPA (United States Environmental Protection Agency) aquatic life benchmarks; 3) Determine the toxicity of collected water samples using toxicity tests conducted on representative test organisms.

- Sampling period May 2021 to December 2021

- Major findings

INSECTICIDES IN WATER: Overall, the most frequently detected insecticidal active ingredients (AIs) were as follows: methoxyfenozide (84%), bifenthrin (32%), chlorantraniliprole (24%), and imidacloprid (11%), and permethrin (11%). AIs with detection frequencies (DFs) between 2% and 10% included

acetamiprid, diflubenzuron, carbaryl, clothianidin, dimethoate, and lambda cyhalothrin. Other monitored insecticides were not detected in any samples collected during 2022. Insecticides with the greatest exceedances (=exceedance frequency (EF)) of their lowest USEPA aquatic life benchmarks (BMs) included bifenthrin (32% EF), imidacloprid (11% EF), permethrin (11% EF), diflubenzuron (8% EF), methoxyfenozide (5% EF), dimethoate (3% EF), lambda cyhalothrin (3% EF), and fenpropathrin (3% EF).

HERBICIDES AND FUNGICIDES IN WATER: Listed by greatest DF, herbicides that were detected included thiobencarb (65%), diuron (35%), propanil (27%), s-metolachlor (27%), oxyfluorfen (22%), pendimethalin (22%), oryzalin (5%), simazine (5%), and hexazinone (3%). Herbicides that exceeded aquatic life BMs included oxyfluorfen (11% EF), diuron (8% EF), and thiobencarb (5% EF). Fungicides detected in 2021 included azoxystrobin (78% DF), propiconazole (49% DF), thiabendazole (14% DF), tebuconazole (8% DF), boscalid (5% DF), cyprodinil (5% DF), pyraclostrobin (3% DF), and trifloxystrobin (3% DF). There were no fungicide concentrations that exceeded aquatic life BMs. Other monitored herbicides and fungicides were not detected in any sample collected in 2021.

PYRETHROIDS IN SEDIMENT: Five sediment samples were collected in September 2021 from the Sacramento and San Joaquin Valleys. Samples were screened for bifenthrin, cyfluthrin, cypermethrin, esfenvalerate/fenvalerate, lambda cyhalothrin, and permethrin. The DF of bifenthrin was 80%, while the DFs of cypermethrin and lambda cyhalothrin were 20%. Other pyrethroids were not detected in sediment samples collected during the sampling year.

TOXICITY: Twenty-five samples were used for toxicity testing. The 96-hour toxicity tests were conducted on an acute exposure basis, measuring survival of test organisms, *Hyalella azteca* and *Chrionomus dilutus*. Survival significantly decreased in 36% of tests on *H. azteca*, and in 16% of tests on *C. dilutus*.

- Recommendations for pesticides that need a CDFA analytical method (from SWMP):

  Paraquat dichloride, glufosinate ammonium

2. Pesticide detection frequency

Data available in SURF upon yearly update. Contact Project Lead for data not yet uploaded. In SURF, use "SURF Study Number" (Section 1) for obtaining the data.

Table 1. Pesticides detection in water

Pesticide	Number of samples	Number of detections[1]	Detection frequency (%)	Minimum Reporting Limit (µg/L)	Lowest USEPA benchmark (BM) (µg/L)[1]	BM Type[2]	Number of BM exceed-ances	BM exceedance frequency (%)
Abamectin	37	0	0	0.02	0.17	IA	0	0
Acetamiprid	36	3	8	0.02	2.1	IC	0	0
Atrazine	37	0	0	0.02	1	NVA	0	0
Atrazine-d5	9	9	100	0.02		(no BM)	0	0
Azoxystrobin	37	29	78	0.02	44	IC	0	0
Benfluralin	9	0	0	0.05	1.9	FC	0	0

Pesticide	Number of samples	Number of detections[1]	Detection frequency (%)	Minimum Reporting Limit (µg/L)	Lowest USEPA benchmark (BM) (µg/L)[1]	BM Type[2]	Number of BM exceed-ances	BM exceedance frequency (%)
Bensulide	37	0	0	0.02	11	IC	0	0
Bifenthrin	38	12	32	0.001	0.00005	IC	12	32
Boscalid	37	2	5	0.02	116	FC	0	0
Bromacil	37	0	0	0.02	6.8	NVA	0	0
Carbaryl	37	3	8	0.02	0.5	IC	0	0
Chlorantraniliprole	37	9	24	0.02	3.02	IC	0	0
Chlorfenapyr	9	0	0	0.1	2.915	IA	0	0
Chlorpyrifos	36	0	0	0.02	0.04	IC	0	0
Clothianidin[3]	37	2	5	0.02	0.05	IC	1	3
Cyfluthrin	38	0	0	0.002	0.00012	IC	0	0
Cypermethrin	38	0	0	0.005	0.00005	IC	0	0
Cyprodinil	37	2	5	0.02	8.2	IC	0	0
Desulfinyl Fipronil	37	0	0	0.01	0.53	FC	0	0
Desulfinyl Fipronil Amide	37	0	0	0.01		(no BM)	0	0
Diazinon	37	0	0	0.02	0.105	IA	0	0
Diflubenzuron	37	3	8	0.02	0.00025	IC	3	8
Dimethoate	37	2	5	0.02	0.5	IC	1	3
Diuron	37	13	35	0.02	0.13	VA	3	8
Esfenvalerate/Fenvalerate	38	0	0	0.005	0.0000309	IC	0	0
Ethalfluralin	9	0	0	0.05	0.4	FC	0	0
Ethoprop	37	0	0	0.02	0.8	IC	0	0
Etofenprox	37	0	0	0.02	0.17	IC	0	0
Fenamidone	37	0	0	0.02	4.7	FC	0	0
Fenhexamid	37	0	0	0.02	101	FC	0	0
Fenpropathrin	39	0	0	0.005	0.0015	IC	1	3
Fipronil	37	0	0	0.01	0.011	IC	0	0
Fipronil Amide	37	1	3	0.01		(no BM)	0	0
Fipronil Sulfide	37	0	0	0.01	0.83	FC	0	0
Fipronil Sulfone	37	0	0	0.01	0.22	IC	0	0
Fludioxonil	37	0	0	0.02	14	IC	0	0
Hexazinone	37	1	3	0.02	7	NVA	0	0
Imidacloprid	37	4	11	0.01	0.01	IC	4	11
Imidacloprid-d4	7	7	100	0.02		(no BM)	0	0
Indoxacarb	37	0	0	0.02	75	IC	0	0
Isoxaben	37	0	0	0.02	10	VA	0	0
Kresoxim-methyl	37	0	0	0.02	30.3	NVA	0	0

Pesticide	Number of samples	Number of detections[1]	Detection frequency (%)	Minimum Reporting Limit (µg/L)	Lowest USEPA benchmark (BM) (µg/L)[1]	BM Type[2]	Number of BM exceed-ances	BM exceedance frequency (%)
Lambda Cyhalothrin	38	1	3	0.002	0.00004	IA	1	3
Malathion	37	0	0	0.02	0.049	IA	0	0
Mefenoxam	37	0	0	0.02	1200	IC	0	0
Methidathion	37	0	0	0.02	0.66	IC	0	0
Methomyl	37	0	0	0.02	0.6	IC	0	0
Methoxyfenozide	37	31	84	0.02	3.1	IC	2	5
Metribuzin	37	0	0	0.02	8.1	NVA	0	0
Norflurazon	37	0	0	0.02	9.7	NVA	0	0
Oryzalin	37	2	5	0.02	13	VA	0	0
Oxadiazon	37	0	0	0.02	0.88	FC	0	0
Oxyfluorfen	9	2	22	0.05	0.29	NVA	1	11
Pendimethalin	9	2	22	0.05	5.2	NVA	0	0
Permethrin Total	38	4	11	0.002	0.0033	IA	4	11
Prodiamine	9	0	0	0.05	1.5	IC	0	0
Prometon	37	0	0	0.02	98	NVA	0	0
Prometryn	37	0	0	0.02	1.04	NVA	0	0
Propanil	37	10	27	0.02	9.1	FC	0	0
Propargite	37	0	0	0.02	7	IA	0	0
Propiconazole	37	18	49	0.02	15	FC	0	0
Pyraclostrobin	37	1	3	0.02	1.5	NVA	0	0
Pyriproxyfen	37	0	0	0.015	0.015	IC	0	0
Quinoxyfen	37	0	0	0.02	13	FC	0	0
Simazine	37	2	5	0.02	6	NVA	0	0
S-Metolachlor	37	10	27	0.02	8	NVA	0	0
Tebuconazole	37	3	8	0.02	11	FC	0	0
Tebufenozide	36	0	0	0.02	29	IC	0	0
Tebuthiuron	37	0	0	0.02	50	NVA	0	0
Thiabendazole	37	5	14	0.02	42	IC	0	0
Thiacloprid	37	0	0	0.02	0.97	IC	0	0
Thiamethoxam	37	0	0	0.02	0.74	IC	0	0
Thiobencarb	37	24	65	0.02	1	IC	2	5
Trifloxystrobin	37	1	3	0.02	2.76	IC	0	0
Trifluralin	9	0	0	0.05	1.9	FC	0	0

[1] Benchmarks are used as a screening tool for risk analysis

[2] FA, fish acute; FC, fish chronic; IA, invertebrate acute; IC, invertebrate chronic; NA, non-vascular acute; VA, vascular acute

[3] Clothianidin detections are qualitative only

Table 2. Pesticide detection in sediment

Pesticide	Number of samples	Number of detections	Detection frequency (%)	LC_{50} (µg/kg OC)*	Detection frequency > LC_{50} (%) **
Bifenthrin	5	4	80	520	NA
Cyfluthrin	5	0	0	1080	NA
Cypermethrin	5	1	20	380	NA
Esfenvalerate/Fenvalerate	5	0	0	1540	NA
Lambda Cyhalothrin	5	1	20	450	NA
Permethrin	5	0	0	10830	NA

*LC50 is derived from published values (from Amweg et al. 2005, Toxicol. Chem. 24:966-972; Amweg and D.P. Weston 2007, Environ. Toxicol. Chem. 26:2389-2396; Maund et al. 2002, Environ. Toxicol. Chem., 21:9-15)

**Due to technical issues with the TOC/DOC instrument, organic content (OC) in sediment samples were unavailable at this time. The data will be updated once OC values become available.

3. Tracking Exceedances of Aquatic Benchmarks or Sediment LC50 values

For further data analysis: pesticides that have ≥ 10% BM exceedance rate or exceed their OC normalized sediment LC_{50} for three consecutive years are recommended for further detailed data analysis if no analysis has been complete in the past five years (Ambient Urban Monitoring Methodology SOP METH014).

Table 3. Pesticides with three consecutive years of either 1) ≥ 10% of their detections exceeding their lowest BMs or 2) percentage of sediment detections exceeding their sediment LC_{50} (normalized to OC).

Pesticide	Matrix	Current year (2021)	2020	2019	Last written evaluation (reference)	Further data analysis (Y/N)
Bifenthrin	Water	32	24	23	Budd et al. (2020)	Y
Imidacloprid	Water	11	14	9	Deng et al. (2019)	Y
Oxyfluorfen	Water	11	13	7	Deng et al. (2019)	Y
Permethrin	Water	11	3	0	Budd et al. (2020)	Y

4. Quality Control

Table 4. Laboratory Quality Control (QC) summary

QC Type	Sample Matrix	Total Number	Number of QC Out of Control
Blind Spike	Water	-	-
Lab Blank	Water	521	2
Matrix Spike	Water	521	41
Surrogate Spike	Water	80	0
Lab Blank	Sediment	9	0
Matrix Spike	Sediment	9	0

For this project, recoveries of the QC limits were set to be acceptable at a range of 70% to 120%. One lab blank for each of fipronil sulfone and lambda cyhalothrin fell outside of control limits due to high matrix recoveries, and as a result, one detection of lambda cyhalothrin may have been a false positive. Out of 521 matrix spikes, 41 were outside of QC limits. 39 of these lab blanks exceeded control limits due to human error in one LC screen. Due to the exceedances of the control limit, analytical results associated with these samples should be evaluated using sample-specific surrogate spikes. Additionally, one lab blank each fell outside of QC limits for thiabendazole (24.6%) and fipronil sulfone (121.1%). These analytes were associated with six and three samples, respectively. All surrogate spikes, as well as lab blanks and matrix spikes for sediment, were within QC limits.

5. Data: water quality, aquatic toxicity, and analytical chemistry results

Water quality data, aquatic toxicity data, and monitoring results are available upon request. Please contact the Project Lead or SURF database administrator for the data.