DEPARTMENT OF PESTICIDE REGULATION (DPR) Date: March 6, 2023

SURFACE WATER AMBIENT MONITORING REPORT

1. Study highlights

- DPR Study Number 321
- SURF (Surface Water Database) Study Number 91
- Study Title **Surface Water Monitoring for Pesticides in Agricultural Areas in the Central Coast and Southern California, 2021**
- Project Lead Xin Deng, PhD.
- Email Xin.Deng@cdpr.ca.gov
- Protocol Source (*protocol available online for five years, thereafter, request a copy from the SWPP list of archived files)* Environmental Monitoring Protocol Page

- Study Area

  County: Imperial, Monterey, Santa Barbara, San Luis Obispo

  Waterbody/Watershed: Alamo River, New River, Oso Flaco Creek, Salinas River, Santa Maria River, Tembladero Slough

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

- Water body type

  ☒ Creek ☒ River ☐ Pond ☐ Lake

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

- Objectives

  1. Determine occurrences (% detections) and measured chemical concentrations of pesticides in surface water and sediment collected from agricultural areas; 2. Compare environmental concentrations to the lowest US EPA aquatic life benchmarks; 3. Determine the toxicity of a subset of collected water samples to surrogate aquatic species in 96-hour (acute) or 10-day (chronic) water column testing.

- Sampling period January 2021 to December 2021

- Major findings

  INSECTICIDES IN WATER: Insecticides with detection frequencies (DF) > 50% were as follows: imidacloprid (96%), chlorantraniliprole (95%), thiamethoxam (84%), methoxyfenozide (79%), clothianidin (78%), bifenthrin (74%), permethrin (63%), and methomyl (58%). Insecticides with DFs between 15 and 50% include lambda cyhalothrin (48%), acetamiprid (46%), malathion (34%), carbaryl (21%), fenpropathrin (15%). Insecticides detected infrequently with DFs ranging between 3 to 9% include

indoxacarb, cyfluthrin, esfenvalerate/fenvalerate, cypermethrin, dimethoate, diflubenzuron, diazinon, abamectin and fipronil. Other insecticides were not detected in any samples collected during 2021.

Seven insecticides were detected with concentrations that surpassed their associated lowest US EPA aquatic life benchmarks (BMs) with exceedance frequencies (EF) higher than10%. These insecticides were imidacloprid (96% EF), bifenthrin (74% EF), permethrin (49% EF), lambda cyhalothrin (48% EF), malathion (24% EF), methomyl (18% EF), and fenpropathrin (15% EF). The BM exceedance frequencies for other insecticides ranged from 0 to 9%.

HERBICIDES AND FUNGICIDES IN WATER: Herbicides with DFs ≥ 10% were bensulide (71%), prometryn (54%), oxyfluorfen (53%), diuron (33%), and pendimethalin (19%). Other herbicides were detected infrequently with DFs <5%. Fungicides with DFs ≥ 10% were boscalid (90%), azoxystrobin (65%), propiconazole (61%), mefenoxam (50%), pyraclostrobin (46%), cyprodinil (30%), and fenamidone (28%), fludioxonil (24%), fenhexamid (13%), tebuconazole (11%). Other fungicides were detected infrequently with DFs < 8%. There were three herbicides and no fungicides with concentrations exceeding their lowest US EPA BMs; these included oxyfluorfen (25% EF), duiron (15% EF), and bensulide (8% EF).

PYRETHROIDS IN SEDIMENT: Sediment was collected from all 18 monitoring sites in the Central Coast and Imperial County. All samples were analyzed for the presence of seven pyrethroids. Detection frequencies were as follows: lambda cyhalothrin (61%), bifenthrin (56%), permethrin (56%), cyfluthrin (17%), esfenvalerate (17%), fenpropathrin (11%), and cypermethrin (11%).

STORMWATER SAMPLING: In 2021, twelve sites were further monitored during two storm events in the Central Coast in January and October. The DFs and EFs of all the pesticides analyzed in storm samples were significantly higher than those analyzed during the irrigation season. The overall DFs were 32% for storm samples and 17% for non-storm samples, respectively. Overall BM exceedance frequencies were 11% in storm samples and 5% in non-storm samples.

TOXICITY: UC Davis Granite Canyon Marine Pollution Laboratory conducted 96-hr *Hyalella azteca* and 10-d *Chironomus dilutus* toxicity tests from 54 water samples collected from 12 monitoring locations. Samples were collected during the irrigation season and one storm event. Toxicity endpoints included survival (*Hyalella* and*Chironomus*) and growth (*Chironomus* only). Compared to laboratory controls, *Chironomus* survival was significantly reduced in 57% of surface water samples and *Hyalella* survival was significantly reduced in 52% of samples. In contrast, *Chironomus* growth was significantly reduced in one of 42 field water samples with survived organisms.

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

  Linuron, PCNB

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	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	80	4	5	0.02	0.17	IA	0	0
Acetamiprid	80	37	46	0.02	2.1	IC	3	4
Atrazine	80	2	3	0.02	1	NA	0	0
Azoxystrobin	80	52	65	0.02	44	IC	0	0
Benfluralin	80	1	1	0.05	1.9	FC	0	0
Bensulide	80	57	71	0.02	11	IC	6	8
Bifenthrin	80	59	74	0.001	0.00005	IC	59	74
Boscalid	80	72	90	0.02	116	FC	0	0
Bromacil	80	3	4	0.02	6.8	NA	0	0
Carbaryl	80	17	21	0.02	0.5	IC	3	4
Chlorantraniliprole	80	76	95	0.02	3.02	IC	3	4
Chlorfenapyr	49	0	0	0.1	2.915	IA	0	0
Chlorpyrifos	80	0	0	0.02	0.04	IC	0	0
Clothianidin[3]	80	62	78	0.02	0.05	IC	-	-
Cyfluthrin	80	7	9	0.002	0.00012	IC	7	9
Cypermethrin	80	5	6	0.005	0.00005	IC	5	6
Cyprodinil	80	24	30	0.02	8.2	IC	0	0
Deltamethrin	23	0	0	0.004	0.000026	IC	0	0
Desulfinyl Fipronil	80	7	9	0.01	0.53	FC	0	0
Desulfinyl Fipronil Amide	80	2	3	0.01		(no BM)	-	-
Diazinon	80	3	4	0.02	0.105	IA	1	1
Diflubenzuron	80	4	5	0.02	0.00025	IC	4	5
Dimethoate	80	5	6	0.02	0.5	IC	0	0
Diuron	80	26	33	0.02	0.13	VA	12	15
Esfenvalerate/Fenvalerate	80	6	8	0.005	0.0000309	IC	6	8
Ethalfluralin	80	0	0	0.05	0.4	FC	0	0
Ethoprop	80	0	0	0.02	0.8	IC	0	0
Etofenprox	80	0	0	0.02	0.17	IC	0	0
Fenamidone	80	22	28	0.02	4.7	FC	0	0
Fenhexamid	80	10	13	0.02	101	FC	0	0
Fenpropathrin	80	12	15	0.005	0.0015	IC	12	15
Fipronil	80	2	3	0.01	0.011	IC	2	3
Fipronil Amide	80	5	6	0.01		(no BM)	-	-
Fipronil Sulfide	80	0	0	0.01	0.83	FC	0	0
Fipronil Sulfone	80	1	1	0.01	0.22	IC	0	0
Fludioxonil	80	19	24	0.02	14	IC	0	0
Hexazinone	80	0	0	0.02	7	NA	0	0
Imidacloprid	80	77	96	0.01	0.01	IC	77	96
Indoxacarb	80	7	9	0.02	75	IC	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 (%)
Isoxaben	80	1	1	0.02	10	VA	0	0
Kresoxim-methyl	80	2	3	0.02	30.3	NA	0	0
Lambda Cyhalothrin	80	38	48	0.002	0.00004	IA	38	48
Malathion	80	27	34	0.02	0.049	IA	19	24
Mefenoxam	80	40	50	0.02	1200	IC	0	0
Methidathion	80	0	0	0.02	0.66	IC	0	0
Methomyl	80	46	58	0.02	0.6	IC	14	18
Methoxyfenozide	80	63	79	0.02	3.1	IC	1	1
Metribuzin	80	0	0	0.02	8.1	NA	0	0
Norflurazon	80	0	0	0.02	9.7	NA	0	0
Oryzalin	80	0	0	0.02	13	VA	0	0
Oxadiazon	80	1	1	0.02	0.88	FC	0	0
Oxyfluorfen	80	42	53	0.05	0.29	NA	20	25
Pendimethalin	80	15	19	0.05	5.2	NA	0	0
Permethrin	80	50	63	0.001	0.0033	IA	39	49
Prodiamine	80	0	0	0.05	1.5	IC	0	0
Prometon	80	1	1	0.02	98	NA	0	0
Prometryn	80	43	54	0.02	1.04	NA	0	0
Propanil	80	0	0	0.02	9.1	FC	0	0
Propargite	80	0	0	0.02	7	IA	0	0
Propiconazole	80	49	61	0.02	15	FC	0	0
Pyraclostrobin	80	37	46	0.02	1.5	NA	0	0
Pyriproxyfen	80	0	0	0.015	0.015	IC	0	0
Quinoxyfen	80	3	4	0.02	13	FC	0	0
Simazine	80	1	1	0.02	6	NA	0	0
S-Metolachlor	80	2	3	0.02	8	NA	0	0
Tebuconazole	80	9	11	0.02	11	FC	0	0
Tebufenozide	80	0	0	0.02	29	IC	0	0
Tebuthiuron	80	0	0	0.02	50	NA	0	0
Thiabendazole	80	0	0	0.02	42	IC	0	0
Thiacloprid	80	0	0	0.02	0.97	IC	0	0
Thiamethoxam	80	67	84	0.02	0.74	IC	7	9
Thiobencarb	80	0	0	0.02	1	IC	0	0
Trifloxystrobin	80	6	8	0.02	2.76	IC	0	0
Trifluralin	80	1	1	0.05	1.9	FC	0	0

[1] Benchmarks (BM) 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	18	10	56	520	NA
Cyfluthrin	18	3	17	1080	NA
Cypermethrin	18	2	11	380	NA
Esfenvalerate/Fenvalerate	18	3	17	1540	NA
Fenpropathrin	18	2	11	No Data	NA
Lambda Cyhalothrin	18	11	61	450	NA
Permethrin	18	10	56	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% aquatic benchmark 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 USEPA aquatic life water benchmark or 2) percentage of sediment detections exceeding their sediment LC_{50} (normalized to OC) (data unavailable)

Pesticide	Matrix	Current year (2021)	2020	2019	Last written evaluation (reference)	Further data analysis (Y/N)
Bifenthrin	Water	74	66	31	Deng et al. 2019	Y
Diuron	Water	15	13	0	Deng et al. 2019	N
Fenpropathrin	Water	15	0	2	Deng et al. 2019	N
Imidacloprid	Water	96	97	98	Deng et al. 2019	Y
Lambda Cyhalothrin	Water	48	25	31	Deng et al. 2019	Y
Malathion	Water	25	13	21	Deng et al. 2019	Y
Methomyl	Water	19	41	31	Deng et al. 2019	Y
Oxyfluorfen	Water	25	9	15	Deng et al. 2019	N
Permethrin	Water	49	31	34	Deng et al. 2019	Y
Thiamethoxam	Water	10	22	14	None	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	783	0
Matrix Spike	Water	783	2
Surrogate Spike	Water	168	0
Lab Blank	Sediment	27	0
Matrix Spike	Sediment	27	1

Recoveries of the QC limits were set to be acceptable at a range from 70% to 120% for this project. All lab blanks and surrogate spikes were within the QC limits. Two water matrix spikes for thiabendazole had recoveries out of QC limits (26.6% and 35.2%, respectively). These matrix spikes were associated with 17 samples for thiabendazole (Table 1). One sediment matrix spike for fenpropathrin had a recovery of 57.6% that was below the QC limits. This matrix spike was associated with six samples for fenpropathrin (Table 2). The concentrations of all those samples could be underestimated due to low recovery rates, and the concentrations were all below their reporting limits. Matrix spikes for other analytes in water and sediment samples were within the 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.