DEPARTMENT OF PESTICIDE REGULATION

SURFACE WATER AMBIENT MONITORING REPORT

Date: August 24, 2020

1. Study highlights

- DPR Study Number 321
- SURF Study Number 973
- Study Title **Surface Water Monitoring for Pesticides in Agricultural Areas in the Central Coast and Southern California, 2019**
- Project Lead Anson Main, PhD.
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- Protocol url https://www.cdpr.ca.gov/docs/emon/pubs/protocol/study321_monitoring_2019.pdf

  Protocol available online for five years, thereafter, please request a copy from the SWPP list of archived files

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- 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

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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 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 April 2019 to November 2019

- Pesticides monitored

  Abamectin, Acetamiprid, Atrazine, Azoxystrobin, Benfluralin, Bensulide, Bifenthrin, Boscalid, Bromacil, Carbaryl, Chlorantraniliprole, Chlorpyrifos, Clothianidin, Cyfluthrin, Cypermethrin, Cyprodinil, Desulfinyl Fipronil, Desulfinyl Fipronil Amide, Diazinon, Diflubenzuron, Dimethoate, Diuron, Esfenvalerate, Ethalfluralin, Ethoprop, Etofenprox, Fenamidone, Fenhexamid, Fenpropathrin, Fipronil, Fipronil Amide, Fipronil Sulfide, Fipronil Sulfone, Fludioxonil, Hexazinone, Imidacloprid, Indoxacarb, Isoxaben, Kresoxim-methyl, Lambda Cyhalothrin, Malathion, Mefenoxam, Methidathion, Methomyl, Methoxyfenozide, Metribuzin, Norflurazon, Oryzalin, Oxadiazon, Oxyfluorfen, Pendimethalin, Permethrin, Prodiamine, Prometon, Prometryn, Propanil, Propargite, Propiconazole, Pyraclostrobin, Pyriproxyfen, Quinoxyfen, Simazine, S-Metolachlor, Tebuconazole, Tebufenozide, Tebuthiuron, Thiabendazole, Thiacloprid, Thiamethoxam, Thiobencarb, Trifloxystrobin, Trifluralin

- Major findings

INSECTICIDES IN WATER: The most frequently detected insecticidal active ingredients (AIs) were as follows: imidacloprid (98%), chlorantraniliprole (93%), methoxyfenozide (79%), methomyl (74%), thiamethoxam (69%), and clothianidin (67%). Bifenthrin (40%) was the most frequently detected pyrethroid followed by permethrin (34%) and lambda cyhalothrin (30%). There were moderate detections of acetamiprid (56%), mefenoxam (40%), malathion (33%), indoxacarb (28%), and dimethoate (20%). Other insecticides were detected infrequently with cyfluthrin, diazinon, esfenvalerate, fenpropathrin, chlorpyrifos, carbaryl, and cypermethrin ranging between 4 to 13% detections. Other insecticides were not detected in any samples collected during 2019. Several insecticide concentrations frequently surpassed their lowest US EPA aquatic life benchmarks (BMs) including imidacloprid (98%), permethrin (34%), bifenthrin (30%), lambda cyhalothrin (30%), methomyl (28%), and malathion (20%). Seven insecticides infrequently surpassed existing BMs (range: 2% to 14%) whereas concentrations of 22 insecticides did not exceed the lowest US EPA BMs.

HERBICIDES AND FUNGICIDES IN WATER: Bensulide (76%) was the most frequently detected herbicide while boscalid (80%) and propiconazole (80%) were the most frequently detected fungicides. Of the 23 herbicides monitored in 2019, nine were moderately to infrequently detected (range: 2% to 41%). There were moderate detections of prometryn (41%), oxyfluorfen (38%), and pendimethalin (19%). Eight fungicides were also detected in <50% of collected samples including the AIs azoxystrobin (50%), fenamidone (47%), pyraclostrobin (41%), and tebuconazole (20%). Thirteen herbicides and three fungicides were not detected in any surface water samples collected in 2019. There were three herbicides that exceeded aquatic BMs: prometryn (2%), bensulide (9%), and oxyfluorfen (15%).

PYRETHROIDS IN SEDIMENT: Sediment was collected from all 16 monitoring sites in the Central Coast and Imperial Valley. All samples were analyzed for the presence of seven pyrethroids. Detection frequencies were as follows: bifenthrin (44%), lambda cyhalothrin (44%), permethrin (38%), esfenvalerate (19%), cypermethrin (13%), and cyfluthrin (6%). Fenpropathrin was not detected in any sediment samples. To estimate potential toxicity, measured pyrethroid concentrations were converted to toxicity units (TUs) using LC_{50} values established in the scientific literature. TUs ranged from 0.01 to 3.94 with 43% of sediment concentrations (bifenthrin) from the Central Coast >1 TU and 33% of sediment concentrations (esfenvalerate) from Imperial >1 TU. Lambda cyhalothrin (25%) accounted for the greatest percentage of TUs >1 followed by bifenthrin (19%), cypermethrin (6.3%), and esfenvalerate (6.3%).

STORMWATER SAMPLING: In 2019, six sites were further monitored during a late-November storm event. Compared to monitoring conducted during the irrigation season, pesticide concentrations in water were greater during stormwater monitoring for several active ingredients including bifenthrin, chlorpyrifos, cyfluthrin, and lambda cyhalothrin.

TOXICITY: UC Davis Granite Canyon Marine Pollution Laboratory conducted 96-hr *Hyalella azteca* and 10-d *Chironomus dilutus* toxicity tests from 28 water samples collected from 10 monitoring locations. All samples were collected during the irrigation season. Toxicity endpoints included survival (*Hyalella*, *Chironomus*) and growth (*Chironomus* only). Compared to laboratory controls, *Chironomus* survival was significantly reduced in 71% of surface water samples and *Hyalella* survival was significantly reduced in 39% of samples. In contrast, *Chironomus* growth was reduced in only 21% of field-collected water.

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

Linuron, PCNB

2. Pesticide detection frequency

Data available in SURF (https://www.cdpr.ca.gov/docs/emon/surfwtr/surfdata.htm) 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 detected in water

Pesticide	Sample Number	Detection Number	Detection frequency (%)	Reporting Limit (µg/L)	Lowest USEPA benchmark (BM) (µg/L)[1]	BM Type[2]	Number of BM exceed-ances	BM exceedance frequency (%)
Abamectin	5	0	0	0.02	0.17	IA	0	0
Acetamiprid	36	20	56	0.02	2.1	IC	0	0
Atrazine	54	6	11	0.02	1	NVA	0	0
Azoxystrobin	54	27	50	0.02	44	IC	0	0
Benfluralin	52	0	0	0.05	1.9	FC	0	0
Bensulide	54	41	76	0.02	11	IC	5	9
Bifenthrin	53	21	40	0.001	0.0013	IC	16	30
Boscalid	5	4	80	0.02	116	FC	0	0
Bromacil	5	0	0	0.02	6.8	NVA	0	0
Carbaryl	22	1	5	0.02	0.5	IC	0	0
Chlorantraniliprole	54	50	93	0.02	4.47	IC	2	4
Chlorpyrifos	54	3	6	0.02	0.04	IC	1	2
Clothianidin[3]	36	24	67	0.02	0.05	IC	17	57
Cyfluthrin	52	7	13	0.002	0.0074	IC	2	4
Cypermethrin	53	2	4	0.005	0.069	IC	0	0
Cyprodinil	54	9	17	0.02	8.2	IC	0	0
Desulfinyl Fipronil	5	0	0	0.01	0.54	FC	0	0
Diazinon	23	3	13	0.02	0.105	IA	0	0
Diflubenzuron	23	0	0	0.02	0.00025	IC	0	0
Dimethoate	54	11	20	0.02	0.5	IC	1	2
Diuron	54	6	11	0.02	2.4	NVA	0	0
Esfenvalerate	53	4	8	0.005	0.017	IC	2	4
Ethalfluralin	52	0	0	0.05	0.4	FA	0	0
Ethoprop	5	0	0	0.02	0.8	IC	0	0
Etofenprox	5	0	0	0.02	0.17	IC	0	0
Fenamidone	36	17	47	0.02	4.7	FC	0	0
Fenhexamid	36	0	0	0.02	101	FC	0	0
Fenpropathrin	52	3	6	0.005	0.06	FC	1	2

Pesticide	Sample Number	Detection Number	Detection frequency (%)	Reporting Limit (µg/L)	Lowest USEPA benchmark (BM) (µg/L)[1]	BM Type[2]	Number of BM exceed-ances	BM exceedance frequency (%)
Fipronil	5	0	0	0.01	0.011	IC	0	0
Fipronil Amide	5	0	0	0.01	NA	--	0	0
Fipronil Sulfide	5	0	0	0.01	0.11	IC	0	0
Fipronil Sulfone	5	0	0	0.01	0.037	IC	0	0
Fludioxonil	36	7	19	0.02	14	IC	0	0
Hexazinone	23	0	0	0.02	7	NVA	0	0
Imidacloprid	53	52	98	0.01	0.01	IC	52	98
Indoxacarb	54	15	28	0.02	75	IC	0	0
Isoxaben	5	0	0	0.02	10	NVA	0	0
Kresoxim-methyl	5	0	0	0.02	30.3	NVA	0	0
Lambda Cyhalothrin	53	16	30	0.002	0.002	IC	16	30
Malathion	54	18	33	0.02	0.049	IA	11	20
Mefenoxam	5	2	40	0.02	1200	IC	0	0
Methidathion	5	0	0	0.02	0.66	IC	0	0
Methomyl	54	40	74	0.02	0.7	IC	15	28
Methoxyfenozide	53	42	79	0.02	3.1	IC	0	0
Metribuzin	5	0	0	0.02	8.1	NVA	0	0
Norflurazon	5	0	0	0.02	9.7	NVA	0	0
Oryzalin	21	3	14	0.02	13	VA	0	0
Oxadiazon	5	0	0	0.02	5.2	NVA	0	0
Oxyfluorfen	53	20	38	0.05	0.29	NVA	8	15
Pendimethalin	53	10	19	0.05	5.2	NVA	0	0
Permethrin	53	18	34	0.002	0.0014	IC	18	34
Prodiamine	52	0	0	0.05	1.5	IC	0	0
Prometon	5	0	0	0.02	98	NVA	0	0
Prometryn	54	22	41	0.02	1.04	NVA	1	2
Propanil	5	0	0	0.02	9.1	FC	0	0
Propargite	5	0	0	0.02	7	IA	0	0
Propiconazole	5	4	80	0.02	21	NVA	0	0
Pyraclostrobin	54	22	41	0.02	1.5	NVA	0	0
Pyriproxyfen	5	0	0	0.015	0.015	IC	0	0
Quinoxyfen	53	1	2	0.02	13	FC	0	0
Simazine	54	1	2	0.02	6	NVA	0	0
S-Metolachlor	54	1	2	0.02	8	NVA	0	0
Tebuconazole	5	1	20	0.02	11	FC	0	0
Tebufenozide	5	0	0	0.02	29	IC	0	0
Tebuthiuron	5	0	0	0.02	50	NVA	0	0
Thiabendazole	5	0	0	0.02	42	IC	0	0
Thiacloprid	5	0	0	0.02	0.97	IC	0	0
Thiamethoxam	36	25	69	0.02	0.74	IC	5	14
Thiobencarb	5	0	0	0.02	1	IC	0	0

Pesticide	Sample Number	Detection Number	Detection frequency (%)	Reporting Limit (µg/L)	Lowest USEPA benchmark (BM) (µg/L)[1]	BM Type[2]	Number of BM exceed-ances	BM exceedance frequency (%)
Trifloxystrobin	54	5	9	0.02	2.76	IC	0	0
Trifluralin	53	5	9	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; NVA, non-vascular acute; VA, vascular acute
[3] Clothianidin detections are qualitative only

Table 2. Pesticides detected in sediment

Pesticide	Sample Number	Detection Number	Detection frequency (%)	LC_{50} (µg/g OC)*	Detection frequency (%) of sediments ≥ 1 TU *	Median TUs*
Bifenthrin	16	7	44	0.52	19	0.77
Cyfluthrin	16	1	6	1.08	0	0.31
Cypermethrin	16	2	13	0.38	6.3	1.07
Esfenvalerate	16	3	19	1.54	6.3	0.32
Fenpropathrin	16	0	0	1.60	0	--
Lambda Cyhalothrin	16	7	44	0.45	25	1.94
Permethrin	16	6	38	10.83	0	0.20

*Sediment Toxicity Units (TUs) are calculated using the formula, use TU = C/1000/LC50 / % TOC, where C = concentration (µg/kg dry weight), LC50 (µg/kg) is derived from accepted 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), % TOC is stated in the sediment results Appendix III. One TU is equal to the LC50. If using other LC50 values, list value and reference

3. Tracking Benchmark Exceedances (BME) or Sediment Toxicity (TU)

For further data analysis: pesticides that have ≥ 10% aquatic benchmark exceedances [BME] or ≥ 1 sediment toxicity units [TU] for 3 consecutive years are recommended for further detailed data analysis (Ambient Urban Monitoring Methodology SOP METH014).

Table 3. BME (for pesticides with ≥ 10% BME) or median sediment TUs (for pesticides with ≥ 1 sediment TU) (all sites) for the past 3 years

Pesticide	Water	Sedi-ment	Current year (i)	i - 1	i - 2	Last written evaluation (reference)	Further data analysis (Y/N)
Bifenthrin	X		30	28	38	None	Y
Imidacloprid	X		98	94	95	In progress	N
Lambda Cyhalothrin	X		30	28	28	None	Y
Malathion	X		20	18	13	None	Y

Pesticide	Water	Sedi-ment	Current year (i)	i - 1	i - 2	Last written evaluation (reference)	Further data analysis (Y/N)
Methomyl	X		28	16	20	None	Y
Oxyfluorfen	X		15	6	9	None	N
Permethrin	X		34	20	38	None	Y
Thiamethoxam	X		14	NA	NA	None	N
Bifenthrin		X	19	12.5	NA	None	N
Lambda Cyhalothrin		X	25	12.5	NA	None	N

4. QC

Table 4. Laboratory Quality Control (QC) summary

QC Type	Water Samples		Sediment Samples	
	Total Number	Number of QC out of control	Total Number	Number of QC out of control
Lab Blanks	267	0	16	0
Matrix Spikes/Duplicates	267	0	16	0
Blind Spikes	19	0	0	0
Surrogate Spikes	24	0	0	0

All lab blanks, matrix spikes, blind spikes, and surrogate spikes 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 (https://www.cdpr.ca.gov/docs/emon/surfwtr/surfdata.htm) for the data.