DEPARTMENT OF PESTICIDE REGULATION Date: March 19, 2021

SURFACE WATER MONITORING REPORT

1. Study highlights

- DPR Study Number 299
- SURF Study Number 261
- Study Title Pesticide monitoring in urban areas of Northern California (FY2019/2020)
- Project Lead Michael Ensminger
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- Protocol Source Environmental Monitoring Protocol Page

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

- Study Area

  County: Alameda, Contra Costa, Placer, Sacramento, Santa Clara

  Waterbody/Watershed: Arcade Creek, Dry Creek, Guadalupe River, Pleasant Grove Creek, San Lorenzo Creek, Silver Creek, South San Ramon Creek, Upper American River, Walnut Creek

- 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) Identify the presence and concentrations of pesticide contamination in urban waterways;

2) Evaluate the magnitude of measured concentrations relative to water quality or aquatic toxicity thresholds;

3) At selected monitoring sites, determine the toxicity of water samples in laboratory toxicity tests conducted with *Hyalella azteca* or *Chironomus dilutus*;

4) Evaluate the effectiveness of surface water regulations or label changes through long-term (multi-year) monitoring at selected sampling locations;

5) Monitor the deposition of sediment-bound pyrethroids at long-term monitoring sites.

- Sampling period July 1, 2019 – June 30, 2020

- Pesticides monitored

2,4-D, abamectin, acetamiprid, atrazine, azoxystrobin, bensulide, bifenthrin, boscalid, bromacil, carbaryl, chlorantraniliprole, chlorpyrifos, clothianidin, cyfluthrin, cypermethrin, cyprodinil, deltamethrin, desulfinyl fipronil, desulfinyl fipronil amide, diazinon, dicamba, diflubenzuron, dimethoate, diuron,

esfenvalerate, ethoprop, etofenprox, fenamidone, fenhexamid, fipronil, fipronil amide, fipronil sulfide, fipronil sulfone, fludioxonil, hexazinone, imidacloprid, indoxacarb, isoxaben, kresoxim-methyl, lambda-cyhalothrin, malathion, MCPA, 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, triclopyr, trifloxystrobin, and trifluralin

- Major findings

INSECTICIDES. In the Northern California urban monitoring program, six insecticides were detected greater than 10% of the time. For the second straight year, imidacloprid was the most frequently detected insecticide, detected in 67% of the water samples. Bifenthrin was a close second, detected in 60% of the samples. Fipronil (33% detection frequency [DF]), permethrin (27 % DF), cyfluthrin (16 % DF), and deltamethrin (13% DF) rounded out the top six detected insecticides. All of the imidacloprid and deltamethrin detections, and most of the bifenthrin, fipronil, and permethrin detections, were above their respective lowest aquatic benchmark (BM).

Five of the other 24 insecticides in the study were occasionally detected (chlorantraniliprole, 9% DF; malathion, 7% DF; clothianidin, 3% DF, and cypermethrin, 2% DF, and indoxacarb, 2% DF). Clothianidin's one detection was above its BM.

Fipronil is the only pesticide which has its degradates monitored. Three of fipronil's five degrades were detected: sulfone (29% DF), amide (11% DF), and desulfinyl (7% DF). Except for one sulfone detection, there were no exceedances of their BMs (there are no BMs for the amide degradate).

HERBICIDES. Fourteen herbicides were detected during the year. The synthetic auxin herbicides 2,4-D and triclopyr were most frequently detected, both with a 73% DF (highest pesticide DF in the study). Other frequently detected herbicides included diuron (58% DF), isoxaben (40% DF), dicamba (38% DF), oryzalin (22% DF), pendimethalin (20% DF), MCPA (19% DF), and hexazinone (18% DF). Simazine, tebuthiuron, oxadiazon, bromacil, and oxyfluorfen were detected less than 10% of the time. None of the other 11 herbicides in the study were detected, and no herbicides were detected above their BM.

FUNGICIDES. Of the 14 fungicides monitored, only propiconazole (13% DF) and azoxystrobin (4% DF) were detected (Table 1). Neither was detected above its BM.

WATER TOXICITY. UC Davis Aquatic Health Program (AHP) conducted *Hyalella azteca* and *Chironomus dilutus* 96-hour water column toxicity tests from samples collected during two dry monitoring events at up to seven sites. Toxicity was only observed in the Sacramento area, at

storm drain outfall sites. One site in Folsom was toxic to both species in June but only to *H. azteca* in August. Of two sites in Roseville, one site was toxic to both species in June and August; a second site was only toxic to *H. azteca* in August. Samples collected during storm events have shown more toxicity than dry events, but during both storm events during this study, the new toxicity contract with AHP was not finalized.

SEDIMENTS. Six sediments samples were collected from three storm drain outfalls during two dry events in Roseville and Folsom. Sediments were analyzed for seven pyrethroids (bifenthrin, cyfluthrin, cypermethrin, deltamethrin, esfenvalerate, lambda-cyhalothrin, permethrin) and all were detected with various DFs. Only bifenthrin was detected above toxicity thresholds (Table 2).

CONCLUSIONS.

1. Of the 74 pesticides monitored in the study, 32 pesticides (or their degradates) were detected either in water or sediment.
2. In water, bifenthrin, fipronil, and imidacloprid had the highest potential to consistently (across years) adversely impact aquatic invertebrate organisms. Other pesticides occasionally had some potential toxicity (cyfluthrin, clothianidin, deltamethrin, permethrin) but most of the pesticides monitored did not.
3. In sediments, bifenthrin continues to be the major pyrethroid contaminant.
4. Water toxicity was observed at storm drain outfall sites in the Sacramento area during dry events (storm samples were not tested).

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

Dithiopyr, sulfometuron-methyl

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[1]	Detection frequency (%)[1]	Minimum Reporting Limit (µg/L)	Lowest USEPA benchmark (BM) (µg/L)[2]	BM Type[3]	Number of BM exceed-ances	BM exceedance frequency (%)
2,4-D	37	27	73	0.05	299.2	VA	0	0
Abamectin	11	0	0	0.02	0.17	IA	0	0
Acetamiprid	34	0	0	0.02	2.1	IC	0	0
Atrazine	11	0	0	0.02	1	NA	0	0
Azoxystrobin	27	1	4	0.02	44	IC	0	0
Bensulide	27	0	0	0.02	11	IC	0	0
Bifenthrin	45	27	60	0.001	0.0013	IC	24	53
Boscalid	11	0	0	0.02	116	FC	0	0
Bromacil	27	1	4	0.02	6.8	NA	0	0

Pesticide	Sample Number	Detection Number[1]	Detection frequency (%)[1]	Minimum Reporting Limit (µg/L)	Lowest USEPA benchmark (BM) (µg/L)[2]	BM Type[3]	Number of BM exceed-ances	BM exceedance frequency (%)
Carbaryl	45	0	0	0.02	0.5	IC	0	0
Chlorantraniliprole	45	4	9	0.02	4.47	IC	0	0
Chlorpyrifos	45	0	0	0.02	0.04	IC	0	0
Clothianidin	34	1	3	0.02	0.05	IC	1	3
Cyfluthrin	45	7	16	0.002	0.0074	IC	1	2
Cypermethrin	45	1	2	0.005	0.069	IC	0	0
Cyprodinil	11	0	0	0.02	8.2	IC	0	0
Deltamethrin	45	6	13	0.004	0.0041	IC	6	13
Desulfinyl Fipronil	45	3	7	0.01	0.54	FC	0	0
Desulfinyl Fipronil Amide	45	0	0	0.01	(no BM)		0	0
Diazinon	45	0	0	0.02	0.105	IA	0	0
Dicamba	37	14	38	0.05	61	NA	0	0
Diflubenzuron	11	0	0	0.02	0.00025	IC	0	0
Dimethoate	11	0	0	0.02	0.5	IC	0	0
Diuron	45	26	58	0.02	2.4	NA	0	0
Esfenvalerate	45	0	0	0.005	0.017	IC	0	0
Ethoprop	11	0	0	0.02	0.8	IC	0	0
Etofenprox	27	0	0	0.02	0.17	IC	0	0
Fenamidone	11	0	0	0.02	4.7	FC	0	0
Fenhexamid	11	0	0	0.02	101	FC	0	0
Fipronil	45	15	33	0.01	0.011	IC	12	27
Fipronil Amide	45	5	11	0.01	(no BM)		0	0
Fipronil Sulfide	45	0	0	0.01	0.11	IC	0	0
Fipronil Sulfone	45	13	29	0.01	0.037	IC	1	2
Fludioxonil	11	0	0	0.02	14	IC	0	0
Hexazinone	11	2	18	0.02	7	NA	0	0
Imidacloprid	45	30	67	0.01	0.01	IC	30	67
Indoxacarb	45	1	2	0.02	75	IC	0	0
Isoxaben	45	18	40	0.02	10	VA	0	0
Kresoxim-methyl	11	0	0	0.02	30.3	NA	0	0
Lambda Cyhalothrin	45	0	0	0.002	0.002	IC	0	0
Malathion	45	3	7	0.02	0.049	IA	0	0
MCPA	37	7	19	0.05	170	VA	0	0
Mefenoxam	11	0	0	0.02	1200	IC	0	0
Methidathion	11	0	0	0.02	0.66	IC	0	0
Methomyl	11	0	0	0.02	0.6	IC	0	0
Methoxyfenozide	11	0	0	0.02	3.1	IC	0	0
Metribuzin	11	0	0	0.02	8.1	NA	0	0
Norflurazon	11	0	0	0.02	9.7	NA	0	0

Pesticide	Sample Number	Detection Number[1]	Detection frequency (%)[1]	Minimum Reporting Limit (µg/L)	Lowest USEPA benchmark (BM) (µg/L)[2]	BM Type[3]	Number of BM exceed-ances	BM exceedance frequency (%)
Oryzalin	45	10	22	0.02	13	VA	0	0
Oxadiazon	45	3	7	0.02	5.2	NA	0	0
Oxyfluorfen	35	1	3	0.05	0.29	NA	0	0
Pendimethalin	35	7	20	0.05	5.2	NA	0	0
Permethrin	45	12	27	0.001	0.0014	IC	8	18
Prodiamine	35	0	0	0.05	1.5	IC	0	0
Prometon	11	0	0	0.02	98	NA	0	0
Prometryn	11	0	0	0.02	1.04	NA	0	0
Propanil	11	0	0	0.02	9.1	FC	0	0
Propargite	11	0	0	0.02	7	IA	0	0
Propiconazole	45	6	13	0.02	21	NA	0	0
Pyraclostrobin	45	0	0	0.02	1.5	NA	0	0
Pyriproxyfen	45	0	0	0.015	0.015	IC	0	0
Quinoxyfen	11	0	0	0.02	13	FC	0	0
Simazine	11	1	9	0.02	6	NA	0	0
S-Metolachlor	11	0	0	0.02	8	NA	0	0
Tebuconazole	11	0	0	0.02	11	FC	0	0
Tebufenozide	11	0	0	0.02	29	IC	0	0
Tebuthiuron	34	3	9	0.02	50	NA	0	0
Thiabendazole	11	0	0	0.02	42	IC	0	0
Thiacloprid	11	0	0	0.02	0.97	IC	0	0
Thiamethoxam	34	0	0	0.02	0.74	IC	0	0
Thiobencarb	11	0	0	0.02	1	IC	0	0
Triclopyr	37	27	73	0.05	5900	NA	0	0
Trifloxystrobin	11	0	0	0.02	2.76	IC	0	0
Trifluralin	35	0	0	0.05	1.9	FC	0	0

[1] Clothianidin detections are qualitative only

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

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

Table 2. Pesticides detected in sediment

Pesticide	Sample Number	Detection Number	Detection frequency (%)	LC_{50} (µg/kg OC)*	Detection Frequency > LC_{50} (%)
Bifenthrin	6	6	100	520	50
Cyfluthrin	6	3	50	1080	0
Cypermethrin	6	2	33	380	0
Deltamethrin	6	6	100	790	0
Esfenvalerate	6	2	33	1540	0
Lambda-Cyhalothrin	6	2	33	450	0

Pesticide	Sample Number	Detection Number	Detection frequency (%)	LC_{50} (µg/kg OC)*	Detection Frequency > LC_{50} (%)
Permethrin	6	3	50	10830	0

*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)

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) ≥ 50% of sediment detections exceeding their sediment LC_{50} (normalized to OC)

Pesticide	Matrix	Current year (i) (% frequency)	i – 1 (% frequency)	i – 2 (% frequency)	Last written evaluation (reference)	Further data analysis (Y/N)
Bifenthrin	Water	53	34	68	Budd et al. 2020	N
Fipronil	Water	27	34	47	Budd et al. 2015	N
Imidacloprid	Water	67	51	59	none	Y
Bifenthrin	Sediment	100	50	50	Budd et al. 2020	N

4. QC

Table 4. Laboratory Quality Control (QC) summary

Lab QC	Sample Matrix	Total Number	QC Out of Control
Blind Spike	Water	13	0
Lab Blank	Water	350	1
Matrix Spike	Water	350	0
Lab Blank	Sediment	9	0
Matrix Spike	Sediment	9	0

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.