DEPARTMENT OF PESTICIDE REGULATION (DPR) Date: March 7, 2023

SURFACE WATER AMBIENT MONITORING REPORT

1. Study highlights

- DPR Study Number 329
- SURF (Surface Water Database) Study Number 261
- Study Title Surface Water Monitoring for Pesticides in Urban Areas of Northern California (FY2020/2021)
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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: Alameda, Contra Costa, Placer, Sacramento, Santa Clara

  Waterbody/Watershed: Arcade Creek, Guadalupe River, Pleasant Grove Creek, San Lorenzo Creek, Silver Creek, South San Ramon Creek, Upper American River, Walnut 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) 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 concentration of sediment-bound pyrethroids at long-term monitoring sites.

- Sampling period July 1, 2020 – June 30, 2021

- Major findings

INSECTICIDES. In the Northern California urban monitoring program, six insecticides were detected in greater than 10% of the samples. Three pesticides were most frequently detected and had the highest percentage detection frequency [DF] in the samples collected: imidacloprid (68%), bifenthrin (59%), and fipronil (39%). For the third straight year, imidacloprid was the most frequently detected insecticide. Among the top three insecticides, there were higher DFs during storm events (ranging from 70-82%) than non-storm events (ranging from 17-30%). For imidacloprid, the DF was higher in waterways (67%) than in storm drains (33%). Similarly, bifenthrin DF was higher in waterways (54%) than in storm drains (46%). In contrary, for fipronil the DF was slightly-higher in storm drains (53%) than waterways (47%). Permethrin (23 % DF), chlorantraniliprole (14 % DF), and deltamethrin (14% DF) rounded out the top six most-detected insecticides. All the imidacloprid, bifenthrin, and deltamethrin detections, and some of the fipronil (36%), and permethrin (5%) detections, were above their respective lowest United States Environmental Protection Agency (US EPA) aquatic life benchmark (BM). No chlorantraniliprole detections exceeded the BM.

Five of the other 24 insecticides analyzed in the study were infrequently detected (lambda cyhalothrin, 7% DF; carbaryl, 5% DF; clothianidin, 5% DF; cyfluthrin, 5% DF; and diazinon, 2% DF). All the detections for lambda cyhalothrin, cyfluthrin, and diazinon were above their respective lowest US EPA BMs.

Fipronil is the only pesticide which has its degradates monitored. Three of fipronil's five degradates were detected: sulfone (39% DF), amide (14% DF), and desulfinyl (14% DF). Except for one desulfinyl detection, there were no exceedances of their BMs. Currently, there is no established BM for fipronil amide.

HERBICIDES. Twelve herbicides were detected during the sampling year. The synthetic auxin herbicides 2,4-D and triclopyr were most frequently detected, with a 60% and 56% DF, respectively. Other frequently detected herbicides included diuron (55% DF), pendimethalin (39% DF), isoxaben (34% DF), dicamba (23% DF), and MCPA (12% DF). Oxadiazon, prodiamine, oryzalin, oxyfluorfen, and tebuthiuron were detected less than 10% of the time. There were no detections of the herbicide, triflualin. The herbicides, diuron, pendimethalin, prodiamine, and oxyfluorfen were detected above their lowest US EPA BMs.

FUNGICIDES.

Of the two monitored fungicides, only propiconazole (32% DF) was detected (Table 1), but the detected concentrations did not exceed its lowest BM.

WATER TOXICITY. UC Davis Aquatic Health Program (AHP) conducted *Hyalella azteca* and *Chironomus dilutus* 96-hour water column acute toxicity tests from samples collected during two dry monitoring events and two wet monitoring events, at nine sites. Toxicity was only observed in the Sacramento area, at mainly storm drain outfall sites and one waterway site. During the dry events, a total of six samples were toxic at sites in Arcade Creek, Pleasant Grove Creek, and the Upper American River. The majority of samples that were toxic to at least one species were collected in August, with water collected in Folsom toxic to both species. For the two storm events there were a total of 10 samples that were toxic; seven samples were toxic to *H. azteca* and three samples were toxic to *C. dilutus.*

SEDIMENTS.
Eight sediments samples were collected during two dry events in Roseville and Folsom and one dry event in Pleasanton and San Jose. Sediments were analyzed for seven pyrethroids (bifenthrin, cyfluthrin, cypermethrin, deltamethrin, esfenvalerate, lambda-cyhalothrin, permethrin). All seven pyrethroids were detected with various DFs, with concentrations exceeding their BMs. All analytes detected exceeded their toxicity thresholds (OC normalized sediment LC_{50})(Table 2).

CONCLUSIONS.

1. Of the 74 pesticides monitored in the study, 27 pesticides (or their degradates) were detected either in water or sediment.
2. In water, imidacloprid, bifenthrin, and fipronil had the highest potential to consistently (across years) adversely impact aquatic invertebrates. Other pesticides occasionally had some potential toxicity (cyfluthrin, deltamethrin, diazinon, lambda cyhalothrin, and 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 in the Sacramento area all year round. There were more toxic samples observed during the wet monitoring events.

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

Dithiopyr, Sulfometuron-methyl, Dichlobenil, Mecoprop-P, Chlorsulfuron, Sulfometuron-methyl, Dithiopyr, PCNB, Spinosad

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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 (%)
2,4-D	43	26	60	0.05	299.2	VA	0	0
Acetamiprid	44	0	0	0.02	2.1	IC	0	0
Bifenthrin	44	26	59	0.001	0.00005	IC	26	59

Carbaryl	44	2	5	0.02	0.5	IC	0	0
Chlorantraniliprole	44	6	14	0.02	3.02	IC	0	0
Chlorfenapyr	33	0	0	0.1	2.915	IA	0	0
Chlorpyrifos	44	0	0	0.02	0.04	IC	0	0
Clothianidin[3]	44	2	5		0.05	IC		
Cyfluthrin	44	2	5	0.002	0.00012	IC	2	5
Cypermethrin	44	0	0	0.005	0.00005	IC	0	0
Deltamethrin/ Tralomethrin	44	6	14	0.004	0.000026	IC	6	14
Desulfinyl Fipronil	44	6	14	0.01	0.53	FC	1	2
Desulfinyl Fipronil Amide	44	0	0	0.01		(no BM)	0	0
Diazinon	44	1	2	0.02	0.105	IA	1	2
Dicamba	43	10	23	0.05	61	NVA	0	0
Diuron	44	24	55	0.02	0.13	VA	9	20
Esfenvalerate/ Fenvalerate	44	0	0	0.005	0.0000309	IC	0	0
Fipronil	44	17	39	0.01	0.011	IC	16	36
Fipronil Amide	44	6	14	0.01		(no BM)	0	0
Fipronil Sulfide	44	0	0	0.01		(no BM)	0	0
Fipronil Sulfone	44	17	39	0.01	0.22	IC	0	0
Imidacloprid	44	30	68	0.01	0.01	IC	30	68
Indoxacarb	44	0	0	0.02	75	IC	0	0
Isoxaben	44	15	34	0.02	10	VA	0	0
Lambda Cyhalothrin	44	3	7	0.002	0.00004	IA	3	7
Malathion	44	0	0	0.02	0.049	IA	0	0
MCPA	43	5	12	0.05	170	VA	0	0
Oryzalin	44	2	5	0.02	13	VA	0	0
Oxadiazon	44	3	7	0.02	0.88	FC	0	0
Oxyfluorfen	44	1	2	0.05	0.29	NVA	1	2
Pendimethalin	44	17	39	0.05	5.2	NVA	1	2
Permethrin Total	44	10	23	0.001	0.0033	IA	2	5
Prodiamine	44	3	7	0.05	1.5	IC	1	2
Propiconazole	44	14	32	0.02	15	FC	0	0
Pyraclostrobin	44	0	0	0.02	1.5	NVA	0	0
Pyriproxyfen	44	0	0	0.015	0.015	IC	0	0
Tebuthiuron	44	1	2	0.02	50	NVA	0	0
Thiamethoxam	44	0	0	0.02	0.74	IC	0	0
Triclopyr	43	24	56	0.05	5900	NVA	0	0
Trifluralin	44	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	8	6	75	520	62.5
Cyfluthrin	8	3	38	1080	0
Cypermethrin	8	3	38	380	0
Deltamethrin/Tralomethrin	8	6	75	790	25
Esfenvalerate/Fenvalerate	8	3	38	1540	0
Lambda Cyhalothrin	8	3	38	450	0
Permethrin Total	8	3	38	10830	0

*LC50 is derived from published values from the literature (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. <u>Tracking Exceedances of Aquatic Benchmarks or Sediment LC50 values</u>

<u>For further data analysis</u>: 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)

Pesticide	Matrix	Current year (2020)	2019	2018	Last written evaluation (reference)	Further data analysis (Y/N)
Bifenthrin	Water	59	60	41	Budd et al. (2020)	N
Fipronil	Water	36	27	34	Budd et al. (2015)	Y
Imidacloprid	Water	68	67	51	Ensminger et al. (2013)	Y
Bifenthrin	Sediment	63	50	100	Budd et al. (2020)	N

4. <u>Quality Control</u>

Table 4. Laboratory Quality Control (QC) summary

QC Type	Sample Matrix	Total Number	Number of QC Out of Control Limits
Blind Spike	Water	3	0
Lab Blank	Water	301	0
Matrix Spike	Water	307	0
Surrogate Spike	Water	96	10
Lab Blank	Sediment	18	0
Matrix Spike	Sediment	18	0

There were 10 surrogate spikes from storm samples that had low recoveries that were out of the lab control limits. Actual concentrations may have been higher than reported. All lab blanks, blind spikes, and matrix 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 for the data.