DEPARTMENT OF PESTICIDE REGULATION

SURFACE WATER AMBIENT MONITORING REPORT

Date: April 16, 2020

1. Study highlights

- DPR Study Number 299
- SURF Study Number 971
- Study Title Monitoring in Urban Areas in Northern California (FY 2018/2019)
- Project Lead Michael Ensminger
- Email Michael.Ensminger@cdpr.ca.gov
- Protocol url

  https://www.cdpr.ca.gov/docs/emon/pubs/protocol/study299_ensminger_urban_study_fy2018-19.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: 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

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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

- 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.

- Sampling period July 1, 2018 – June 30, 2019

- Pesticides monitored

  2,4-D, amabectin, atrazine, azoxystrobin, bensulide, bifenthrin, bromacil, carbaryl, chlorantraniliprole, chlorpyrifos, cyfluthrin, cypermethrin, cyprodinil, deltamethrin, desulfinyl fipronil, desulfinyl fipronil amide, diazinon, dicamba, diflubenzuron, dimethoate, diuron, esfenvalerate, etofenprox, fipronil, fipronil amide, fipronil sulfide, fipronil sulfone, imidacloprid, indoxacarb, isoxaben, kresoxim-methyl, lambda-cyhalothrin, malathion, MCPA, methidathion, methomyl, methoxyfenozide, metribuzin, norflurazon, oryzalin, oxadiazon, oxyfluorfen, pendimethalin, permethrin, prodiamine, prometon, propanil, propargite, propiconazole, pyraclostrobin, pyriproxyfen, quinoxyfen, simazine, S-metolachlor, tebufenozide, thiobencarb, triclopyr, trifloxystrobin, and trifluralin.

- Major findings

INSECTICIDES. Bifenthrin, fipronil, and imidacloprid were the most frequently detected insecticides in Northern California urban areas (Table 1). Among these three insecticides, there were higher detection frequencies (DFs) at storm drain outfalls than in waterways (i.e., creeks and rivers). DFs in storm drain outfalls ranged from 73-91% whereas DFs in waterways ranged from 23-37%. The lower DFs in waterways was attributed to dilution and lower DFs in the San Francisco Bay area. All imidacloprid detections, and most of the fipronil and bifenthrin detections, were above the lowest USEPA aquatic life benchmark (Tables 1, 3).

At storm drain outfalls, there was little difference in detections between dry and rain events with bifenthrin, fipronil, and imidacloprid. In waterways, however, large increases in detections occurred during rain events. Bifenthrin was never detected during dry events but frequently (70% DF) detected during rain events. Fipronil was infrequently detected during dry events (10% DF) but detections during rain events were more likely (50% DF). Imidacloprid detections were more common during dry events (25% DF) and increased to 60% DF during rain events. Waterways in the Sacramento area were four times more likely to contain fipronil and imidacloprid whereas bifenthrin was found equally in both areas.

Three of fipronil's five degradates were detected. Desulfinyl fipronil was detected with about equal frequency during dry and storm events (12-13% DF) whereas fipronil amide and fipronil sulfone were detected at higher concentrations during storm events (4/40% and 19/53% DF [dry/storm], respectively). No fipronil degradate was detected above its lowest USEPA benchmark (there are no benchmarks for fipronil amide).

Cyfluthrin was the only other insecticide to be detected in more than 10% of the samples, where it was only detected during storm events (31% DF in storm events; 0% DF in dry events). Deltamethrin, chlorantraniliprole, carbaryl, malathion, and permethrin were infrequently detected (2-7% DF). None of the other16 insecticides monitored were detected (some were only monitored in a June dry event).

HERBICIDES. 2,4-D was the most frequently detected herbicide (56% DF), although detections were reduced from previous years due to a high number of non-detects in waterways in the San Francisco Bay area during June and August dry event sampling. Three other herbicides with the same mode of action (triclopyr, dicamba, and MCPA) were also frequently detected (53%, 34%, and 19% DF, respectively). In addition, six other herbicides were detected with various frequencies: diuron (29% DF), isoxaben (20% DF), pendimethalin (16% DF), prodiamine (3% DF), oxadiazon (5% DF), and oryzalin (7% DF). DF's of these herbicides were similar to FY2017-18, and, as with insecticides, storms increased herbicide detections. No other herbicides were detected, and no herbicides were detected at concentrations above their respective BMs (Table 1).

FUNGICIDES. Of the seven fungicides monitored, only propiconazole was detected (Table 1). Propiconazole was exclusively detected in the Sacramento area (35% DF) both at storm drain outfalls and in waterways but never above its lowest USEPA benchmark.

WATER TOXICITY. UC Davis Aquatic Health Program (UCDAHP) conducted 96-hour water column toxicity tests from samples collected from selected sites in Sacramento or San Francisco Bay areas. In one rain event (February), UCDAHP tested *Hyalella azteca* in water samples collected from four sites in the Sacramento area. Two storm drain outfall sites in Roseville were significantly more toxic than the controls; survival ranged around 37%. However, water from two waterways were not significantly different from the controls. In one dry event (June), UCDAHP tested *Hyalella azteca* and *Chironomus dilutus* in water samples collected from five sites in the Sacramento area and three sites from the San Francisco Bay. Only one site showed toxicity, a storm drain outfall in Folsom.

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 (Table 2). Bifenthrin accounted for most (76%) of estimated toxicity (toxicity unit, TU) based on literature established LC50 values normalized to sediment organic carbon. Deltamethrin (10%) and cyfluthrin, cypermethrin, lambda-cyhalothrin (4% each) accounted for a minor fraction of the estimated toxicity. Sites in Roseville had higher TUs than Folsom, and TUs were higher in June than in September.

CONCLUSIONS.

1. Bifenthrin, fipronil, and imidacloprid have the highest potential for adverse impact to aquatic invertebrate organisms in Northern California urban waterways. Other pesticides occured at concentrations likely not toxic to aquatic organisms (this study did not investigate interactive effects).
2. Storms drive pesticide runoff; waterways and storm drain outfalls had higher detection frequencies during storm events.
3. Time-weighted storm samples give evidence that pesticide runoff occurs during entire storm runoff (previous FYs collected grab storm samples at the beginning of storms);
4. In sediments, bifenthrin continues to be the major pyrethroid contaminant (based on estimated TUs) at source (storm drain outfall) sites.

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

  Dithiopyr, sulfometuron-methyl, PCNB, spinosad

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

	Type*	Sample Number	Detection Number	Detection frequency (%)	Reporting Limit (µg/L)	Lowest UESPA benchmark (BM) (µg/L)**	BM Type ***	Number of BM exceed -ances	BM exceedance frequency (%)
2,4-D	H	32	18	56	0.05	299.2	VA	0	0
Abamectin	I	4	0	0	0.02	0.17	IA	0	0
Atrazine	H	4	0	0	0.02	1	VA	0	0
Azoxystrobin	F	41	0	0	0.02-0.1	44	IC	0	0
Bensulide	H	41	0	0	0.02-0.1	11	IC	0	0
Bifenthrin	I	41	17	41	0.001	0.0013	IC	14	34
Bromacil	H	41	0	0	0.02-0.1	6.8	NA	0	0
Carbaryl	I	41	1	2	0.02-0.1	0.5	IC	0	0
Chlorantraniliprole	I	41	2	5	0.02-0.1	4.47	IC	0	0
Chlorpyrifos	I	41	0	0	0.02-0.1	0.04	IC	0	0
Cyfluthrin	I	41	5	12	0.002	0.0074	IC	2	5
Cypermethrin	I	41	0	0	0.005	0.069	IC	0	0
Cyprodinil	F	4	0	0	0.02	8.27	IC	0	0
Deltamethrin	I	41	3	7	0.005	0.0041	IC	3	7
Desulfinyl fipronil	I	41	5	12	0.01-0.05	0.54	FC	0	0
Desulfinyl fipronil amide	I	41	0	0	0.01-0.05	N/A	N/A	N/A	N/A
Diazinon	I	41	0	0	0.02-0.1	0.105	IA	0	0
Dicamba	H	32	11	34	0.05	61	NA	0	0
Diflubenzuron	I	4	0	0	0.02	0.00025	IC	0	0
Dimethoate	I	4	0	0	0.02	0.5	IC	0	0
Diuron	H	41	12	29	0.02-0.1	2.4	NA	0	0
Esfenvalerate	I	41	0	0	0.005	0.017	IC	0	0
Ethoprop	I	4	0	0	0.02	0.8	IC	0	0
Etofenprox	I	41	0	0	0.02-0.1	0.17	IC	0	0
Fipronil	I	41	15	37	0.01-0.05	0.011	IC	14	34
Fipronil amide	I	41	7	17	0.01-0.05	N/A	N/A	N/A	N/A
Fipronil sulfide	I	41	0	0	0.01-0.05	0.11	IC	0	0
Fipronil sulfone	I	41	13	32	0.01-0.05	0.037	IC	0	0
Hexazinone	H	4	0	0	0.02	7	NA	0	0
Imidacloprid	I	41	21	51	0.01-0.05	0.01	IC	21	51
Indoxacarb	I	41	0	0	0.02-0.1	75	IC	0	0
Isoxaben	H	41	8	20	0.02-0.1	10	VA	0	0
Kresoxim-methyl	F	4	0	0	0.02	30.37	NA	0	0
Lambda Cyhalothrin	I	41	0	0	0.002	0.002	IC	0	0
Malathion	I	41	1	2	0.02-0.1	0.049	IA	0	0
MCPA	H	32	6	19	0.05	170	VA	0	0
Methidathion	I	4	0	0	0.02	0.66	IC	0	0
Methomyl	I	4	0	0	0.02	0.7	IC	0	0
Methoxyfenozide	I	4	0	0	0.02	3.17	IC	0	0

	Type*	Sample Number	Detection Number	Detection frequency (%)	Reporting Limit (µg/L)	Lowest USEPA benchmark (BM) (µg/L)**	BM Type ***	Number of BM exceed-ances	BM exceedance frequency (%)
Metribuzin	H	4	0	0	0.02	8.1	NA	0	0
Norflurazon	H	4	0	0	0.02	9.7	NA	0	0
Oryzalin	H	41	3	7	0.02-0.1	13	VA	0	0
Oxadiazon	H	41	2	5	0.02-0.1	5.2	NA	0	0
Oxyfluorfen	H	32	0	0	0.05	0.29	NA	0	0
Pendimethalin	H	32	5	16	0.05	5.2	NA	0	0
Permethrin	I	41	1	2	0.002	0.0014	IC	1	2
Prodiamine	H	32	1	3	0.05	1.5	IC	0	0
Prometon	H	4	0	0	0.02	98	NA	0	0
Prometryn	H	4	0	0	0.02	1.04	NA	0	0
Propanil	H	4	0	0	0.02	9.1	FC	0	0
Propargite	I	4	0	0	0.02	7	IA	0	0
Propiconazole	F	41	8	20	0.02-0.1	21	NA	0	0
Pyraclostrobin	F	41	0	0	0.02-0.1	1.5	NA	0	0
Pyriproxyfen	I	41	0	0	0.015-0.075	0.015	IC	0	0
Quinoxyfen	F	4	0	0	0.02		IC	0	0
Simazine	H	4	0	0	0.02	6	NA	0	0
S-Metolachlor	H	4	0	0	0.02	8	NA	0	0
Tebufenozide	I	4	0	0	0.02	29	IC	0	0
Thiobencarb	H	4	0	0	0.02	1	IC	0	0
Triclopyr	H	32	17	53	0.05	5900	NA	0	0
Trifloxystrobin	F	4	0	0	0.02	2.76	IC	0	0
Trifluralin	H	32	0	0	0.05	1.9	FC	0	0

*Type: F = Fungicide, H = Herbicide, I = Insecticide
**Benchmarks are used as a screening tool for risk analysis
*** FA, fish acute; FC, fish chronic; IA, invertebrate acute; IC, Invertebrate chronic; NA, non-vascular; VA, vascular

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	6	6	100	0.52	50	1.35
Cyfluthrin	6	3	50	1.08	0	0.06
Cypermethrin	6	3	50	0.38	0	0.13
Deltamethrin	6	4	67	0.79	17	0.27
Esfenvalerate	6	1	17	1.54	0	0
Lambda-cyhalothrin	6	3	50	0.45	0	0.15
Permethrin	6	3	50	0.38	0	0.02

*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	Sediment	Current year (i)	i - 1	i - 2	Last written evaluation	Further data analysis (Y/N)
Bifenthrin	X		34%	70%	71%	2020	N
Fipronil	X		34%	46%	50%	2016	N
Imidacloprid	X		51%	58%	59%	None	Y
Bifenthrin		X	1.4 TU	2.4 TU	3.9 TU	2020	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	299	3	18	0
Matrix Spikes/Duplicates	299	0	18	0
Blind Spikes	12	0	0	0
Surrogate Spikes	84	6	0	0

In the LC screen, three carbaryl lab blanks had trace detections. In these screens, carbaryl was reported twice at concentrations slightly higher than the RL. Carbaryl was considered not detected in these two instances due to the background carbaryl trace detections. Six imidacloprid surrogate spikes from February and April storm samples had low recoveries. Imidacloprid was detected in five of the six samples; the 6th sample had a trace detection. Data from these samples were accepted, but actual concentrations may have been higher than reported. The imidacloprid data from these sampling events were evaluated as received from the analytical lab.

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

Water quality data, aquatic toxicity data, aquatic toxicity methods, 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.