DEPARTMENT OF PESTICIDE REGULATION

AMBIENT MONITORING REPORT

Date: February 21, 2019

1. Study highlights

- Study Number: 299
- Title: Ambient and Mitigation Monitoring in Urban Areas in Northern California FY 2017/2018
- Author: Michael Ensminger

- Study area:
  - County: Alameda, Contra Costa, Placer, Sacramento, Santa Clara
  - Waterbody/ Watershed: Arcade Creek WS, Guadalupe River WS, Pleasant Grove Creek WS, South San Ramon Creek WS, Upper American River WS, Walnut Creek WS

- Land Use Type: ☐ Ag ☒ Urban ☐ Forested ☐ Mixed ☐ Other

- Water body type: ☒ Storm drain outfall ☒ Creek ☒ River ☐ Pond ☐ Lake ☐ Drainage ditch ☐ 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, 2017 – June 30, 2018

- Pesticides monitored:
  2,4-D, azoxystrobin, bensulide, bifenthrin, bromacil, carbaryl, chlorantraniliprole, chlorpyrifos, cyfluthrin, cypermethrin, deltamethrin, desulfinyl fipronil, desulfinyl fipronil amide, diazinon, dicamba, diuron, esfenvalerate, etofenprox, fenpropathrin (sediment only), fipronil, fipronil amide, fipronil sulfide, fipronil sulfone, imidacloprid, indoxacarb, isoxaben, lambda-cyhalothrin, malathion, MCPA, oryzalin, oxadiazon, oxyfluorfen, pendimethalin, permethrin, prodiamine, propiconazole, pyraclostrobin, pyriproxyfen, resmethrin (sediment only), triclopyr, and trifloxystrobin

---

- Major findings:

INSECTICIDES. Bifenthrin was the most frequently detected insecticide in the water samples (76% detection frequency [DF]; Table 1), similar to what has been reported in previous years. Bifenthrin has been consistently the most detected insecticide in northern California urban monitoring. Of other monitored pyrethroids, cyfluthrin (33% DF), permethrin (30% DF), and deltamethrin (27% DF) were detected occasionally, whereas lambda-cyhalothrin and cypermethrin were rarely detected (6% DF each) and esfenvalerate was not detected. The DFs of most pyrethroids have remained consistent over years, but deltamethrin detections have increased since 2014, shadowing deltamethrin's rise in use since 2013.

Most (bifenthrin, cyfluthrin) or all (deltamethrin, lambda-cyhalothrin, permethrin) detections were at concentrations higher than their minimum USEPA benchmark (BM) (Table 1), making them potentially toxic to sensitive aquatic organisms. None of the cypermethrin detections was above its benchmark.

Imidacloprid was the second most frequently detected insecticide; it was detected in 58% of the water samples. All detections of imidacloprid were above its BM. Fipronil was detected in almost half of the samples (48% DF), also always above its BM. Several fipronil degrades were also detected; fipronil sulfone, fipronil amide, and desulfinyl fipronil are the most common of these (70%, 24%, and 24% DF, respectively). In all, fipronil or at least one of its degradates was detected in 72% of the samples. Of other insecticides, chlorantraniliprole (15% DF) and carbaryl (6% DF) were also detected, none above their lowest BM. No other insecticide was detected (Table 1).

HERBICIDES. 2,4-D was the most frequently detected herbicide (84% DF). Three other herbicides with the same mode of action (triclopyr, dicamba, and MCPA) were also frequently detected (50%, 47%, and 31% DF, respectively). In addition, six other herbicides were detected with various frequencies: diuron (39% DF), isoxaben (27% DF), pendimethalin (25% DF), prodiamine (16% DF), oxadiazon (12% DF), and oryzalin (6% DF). No other herbicides were detected, and no herbicides were detected at concentrations above their respective BMs (Table 1).

FUNGICIDES. Of the three fungicides monitored, two were detected: azoxystrobin (18% DF) and propiconazole (15% DF). Pyraclostrobin was not detected, and no fungicide was detected above their respective BM.

OTHER. Rain events compared to non-storm (dry season) events: Overall, detections almost tripled during rain events when compared to dry event monitoring. Biggest differences were with fipronil, bifenthrin, cyfluthrin, pendimethalin, permethrin, deltamethrin, isoxaben, and diuron, having between 35–64% higher DFs during rain events.

Storm drain outfalls compared to receiving waters: Overall detections were higher at storm drain outfall sites (25% DF) when compared to receiving water sites (16% DF).

TOXICITY. The UC Davis Aquatic Health Program conducted 96-hour water column toxicity tests with *Hyalella azteca* and *Chironomus dilutus* from samples collected from selected sites in Roseville and

Folsom during one rain and one dry event. During the rain event, water from three Roseville sites was significantly more toxic than the controls; survival ranged from 0–14% for *H. azteca* or *C. dilutus*. However, water from two Folsom sites was not toxic to *H. azteca*. In the dry event, only water from one Roseville site was toxic to *C. dilutus* whereas at another Roseville site, water was toxic to *H. azteca*. Water from one site in Folsom was tested, which was not toxic to either tested species.

SEDIMENTS. Ten sediments samples were collected from four storm drain and one receiving water sites during two dry events in Roseville and Folsom. Sediments were analyzed for nine pyrethroids (bifenthrin, cyfluthrin, cypermethrin, deltamethrin, esfenvalerate, fenpropathrin, lambda-cyhalothrin, permethrin, resmethrin). Seven pyrethroids were detected (Table 2): bifenthrin (100% DF), cyfluthrin (80% DF), deltamethrin (80% DF), permethrin (70% DF), cypermethrin (60% DF), lambda-cyhalothrin (50% DF), and resmethrin (20% DF).

To estimate potential toxicity, pyrethroid concentrations were converted to toxicity units (TUs) with literature-established LC50 values normalized to organic carbon content of the sediments. Sediments from storm drain sites had > 1 TU, whereas the receiving water site had 0.3 and 0.7 TU depending on the sampling date. Bifenthrin accounted for the largest percentage (78%) of TUs, followed distantly by deltamethrin (12%), cyfluthrin (4%), cypermethrin, (4%), lambda-cyhalothrin, (2%), and permethrin (1%). TUs cannot be calculated for resmethrin due to lack of a sediment LC50 value. TUs were higher in September than in June, possibly due to higher warm-season use.

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

  Dithiopyr, PCNB, sulfometuron-methyl

2. Pesticide detection frequency

Table 1. Pesticides detected in water. Complete data set in Appendix.

Pesticide	Type *	Number of samples	Number of detections	Reporting Limit (µg/L)	Detection frequency (%)	Lowest USEPA benchmark (BM) (µg/L)**		Number of BM exceed-ances	BM exceedance frequency (%)
2,4-D	H	32	27	0.05	84	299.2	VA	0	0
Azoxystrobin	F	33	6	0.02	18	44	IC	0	0
Bensulide	H	33	0	0.02	0	11	IC	0	0
Bifenthrin	I	33	25	0.001	76	0.0013	IC	23	70
Bromacil	H	33	0	0.02	0	6.8	NA	0	0
Carbaryl	I	33	2	0.02	6	0.5	IC	0	0
Chlorantraniliprole	I	33	5	0.02	15	4.4	IC	0	0
Chlorpyrifos	I	33	0	0.02	0	0.04	IC	0	0
Cyfluthrin	I	33	11	0.002	33	0.0074	IC	9	27
Cypermethrin	I	33	2	0.005	6	0.069	IC	0	0
Deltamethrin	I	33	9	0.005	27	0.004	IC	9	27

Pesticide	Type *	Number of samples	Number of detections	Reporting Limit (µg/L)	Detection frequency (%)	Lowest USEPA benchmark (BM) (µg/L)**		Number of BM exceed-ances	BM exceedance frequency (%)
Desulfinyl fipronil	D	33	8	0.01	24	0.59	FC	0	0
Desulfinyl fipronil amide	D	33	2	0.01	6	(none)		--	--
Diazinon	I	33	0	0.02	0	0.105	IA	0	0
Dicamba	H	32	15	0.05	47	61	NA	0	0
Diuron	H	33	13	0.02	39	2.4	NA	0	0
Esfenvalerate	I	33	0	0.005	0	0.0017	IC	0	0
Etofenprox	I	33	0	0.02	0	0.17	IC	0	0
Fipronil	I	33	16	0.01	48	0.011	IC	16	48
Fipronil amide	D	33	8	0.01	24	(none)		--	--
Fipronil sulfide	D	33	0	0.01	0	0.11	IC	0	0
Fipronil sulfone	D	33	23	0.01	70	0.037	IC	4	12
Imidacloprid	I	33	19	0.02/ 0.01§	58	0.01	IC	19	58
Indoxacarb	I	33	0	0.02	0	75	IC	0	0
Isoxaben	H	33	9	0.02	27	10	VA	0	0
Lambda-cyhalothrin	I	33	2	0.002	6	0.002	IC	2	6
Malathion	I	33	0	0.02	0	0.049	IA	0	0
MCPA	H	32	10	0.05	31	170	VA	0	0
Oryzalin	H	33	2	0.02	6	13	VP	0	0
Oxadiazon	H	33	4	0.02	12	5.2	NA	0	0
Oxyfluorfen	H	32	0	0.05	0	0.29	NA	0	0
Pendimethalin	H	32	8	0.05	25	5.2	NA	0	0
Permethrin	I	33	10	0.002	30	0.001 4	IC	10	30
Prodiamine	H	32	5	0.05	16	1.5	IC	0	0
Propiconazole	F	33	5	0.02	15	21	NA	0	0
Pyraclostrobin	F	33	0	0.02	0	1.5	NA	0	0
Pyriproxyfen	I	33	0	0.02	0	0.015	IC	0	0
Triclopyr	H	32	16	0.05	50	5900	NA	0	0
Trifluralin	H	27	0	0.05	0	1.9	FC	0	0

*Type: D, degradate; F, fungicide; H; herbicide; I, insecticide

**FA, fish acute; FC, fish chronic; IA, invertebrate acute; IC, invertebrate chronic; NA, non-vascular acute; VA, vascular acute

§Imidacloprid RL was lowered to 0.01 µg/L

Table 2. Pesticides detected in sediment. Complete data set in Appendix.

Pesticide	Number of samples	Number of detections	Detection frequency (%)	LC_{50} (µg/g OC)*	Detection frequency of sediments ≥ 1 TU*	Median TUs*
Bifenthrin	10	10	100	0.52	60	2.4
Cyfluthrin	10	8	80	1.08	0	0.1
Cypermethrin	10	6	60	0.38	0	0.1
Deltamethrin	10	8	80	0.79	20	0.4
Esfenvalerate	10	0	0	1.54	0	0
Fenpropathrin	10	0	0	--	--	--
Lambda-cyhalothrin	10	5	0	0.45	0	0.1
Permethrin	10	7	70	0.38	0	0.03
Resmethrin	10	2	20	--	--	--

*Sediment Toxicity Units (TUs) are calculated using the formula, use TU = C/LC_{50} * % TOC * 10, where C = concentration (µg/kg dry weight), LC_{50} 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, and 10 is a conversion factor. One TU is equal to the LC_{50}. If using other LC_{50} values, list value and reference.

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

Table 3. For further data analysis: pesticides that have ≥ 10% aquatic benchmark exceedances [BME] [Table 1] or ≥ 1 sediment toxicity units [TU] [Table 2]) for 3 consecutive years are recommended for further detailed data analysis (Ambient Urban Monitoring Methodology SOP METH014)

BME (for pesticides with ≥ 10% BME) or Sediment TUs (for pesticides with ≥ 1 Sediment TU) (all sites) for the past 3 years							Last written evaluation (reference)	Further data analysis (Y/N)
Area	Pesticide	Water	Sediment	Current year (i)	i - 1	i - 2		
	Bifenthrin	X		70%	71%	75%	2018 (in review)	N
	Deltamethrin	X		27%	24%	19%	2018 (in review)	N
	Fipronil	X		46%	50%	29%	2013/2016	N
	Imidacloprid	X		58%	59%	44%	2018 (in review)	N
	Permethrin	X		30%	24%	11%	2018 (in review)	N
	Bifenthrin		X	2.4 TU	3.9	7.4	2018 (in review)	N

4. QC

Table 4. Laboratory Quality Control (QC) Summary

QC Type	Water Samples		Sediment Samples	
	Total Number	**Number of QC out of contro1**	**Total Number**	**Number of QC out of control**
Lab Blanks	284	0	22	0
Matrix Spikes/Duplicates	284	0	22	0
Blind Spikes	14	0	0	--
Surrogate Spikes	78	14	0	--
Explain out of control QC and interpretation of data:	14 surrogate spikes in the LC multi-analysis screen had low recoveries with samples collected in the October and November 2017 storm runoff due to dirty samples. Detections of certain analytes may have been higher than reported. All data were used in the report.			

5. Supporting Information

Supporting Information for this report (pdf file):

Index of Supporting Information
Appendix I. Study protocol
Appendix II. Sampling site information and pictures
Appendix III. Water quality data
Appendix IV. Water or sediment monitoring data
Appendix V. Aquatic toxicity data
Appendix VI. Analytical methods
Appendix VII. Aquatic toxicity methods