DEPARTMENT OF PESTICIDE REGULATION

AMBIENT MONITORING REPORT

Date: November 16, 2017

1. Study highlights

- Study Number: 299
- Title: Ambient Monitoring in Urban Areas in Northern California for FY 2016-2017
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- Study area:
  - County: Alameda, Contra Costa, Placer, Sacramento, Santa Clara
  - Waterbody/ Watershed: Alameda Creek watershed (WS) Arcade Creek WS, Coyote Creek WS, Pleasant Grove Creek WS, South San Ramon Creek WS, Upper American River 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) Determine the toxicity of water samples at selected monitoring sites;
  3) Evaluate the magnitude of measured concentrations relative to water quality or aquatic toxicity thresholds;
  4) Evaluate the effectiveness of CDPR's surface water regulation Section 6970 through long term (multi-year) monitoring at selected sampling locations.

- Sampling period: July 1, 2016 – June 30, 2017

- Pesticides monitored:

2,4-D, azoxystrobin, bensulide, bifenthrin, bromacil, carbaryl, chlorantraniliprole, chlorpyrifos, cyfluthrin, cypermethrin, deltamethrin, desulfinyl fipronil, desulfinyl fipronil amide, diazinon, dicamba, diuron, fenpropathrin (sediments only), esfenvalerate, fipronil, fipronil amide, fipronil sulfide, fipronil sulfone, imidacloprid, indoxacarb, isoxaben, lambda cyhalothrin, malathion, MCPA, oryzalin, oxadiazon, oxyfluorfen, pendimethalin, permethrin, prodiamine, prometon, propiconazole, pyraclostrobin, pyriproxyfen, simazine, S-metolachlor, tebuthiuron, triclopyr, and trifloxystrobin

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- Major findings:

INSECTICIDES. In water samples, bifenthrin was the most frequently detected insecticide (74% detection frequency [DF]; Table 1). This DF is similar to what has been reported in previous years and bifenthrin has been consistently the most detected insecticide in Northern California urban monitoring. Other pyrethroids were detected less frequently: cyfluthrin (29% DF), deltamethrin, and permethrin (24% DF each). Deltamethrin detections have been increasing in past four years, whereas the four year DF average for cyfluthrin and permethrin are similar to what was observed in FY15/16 monitoring results. Of other pyrethroids monitored, lambda-cyhalothrin was rarely detected and esfenvalerate and cypermethrin were never detected in water samples Northern California urban monitoring. Generally, all pyrethroids, except for cyfluthrin, were detected at concentrations higher than their minimum US EPA benchmark (BM) (Table 1), making them potentially toxic to sensitive aquatic organisms. Bifenthrin is of highest concern for potential toxicity (Table 3).

Imidacloprid was the second highest detected insecticide; it was detected in 59% of the water samples. Imidacloprid detections have been increasing in Northern California urban monitoring, almost doubling since FY 13/14. The US EPA BM has recently been updated for this pesticide, and all imidacloprid detections were above its lowest BM for chronic invertebrate toxicity of 0.01 µg/L. The current analytical reporting limit is higher than this new BM; therefore, trace detections (an additional 21% DF) could also be above imidacloprid's lowest BM.

Fipronil was almost detected a frequency as imidacloprid, with 50% DF. In Northern California's FY15/16 report, it was noted that fipronil detections were decreasing; however, in FY16/17 this trend has reversed. CDFA has a lower RL for fipronil and degradates that accounts for some, but not all, of the increased DF. All fipronil's detections were above its lowest US EPA BM. Three degradates were detected; sulfone (56% DF), desulfinyl (21% DF), and amide (12% DF). Only one sulfone degradate was detected above its US EPA BM. There is no BM for the amide degradate, but all detections were at or above fipronil's BM.

Malathion and carbaryl were detected twice; malathion's detections were above its lowest US EPA BM. There were no detections of chlorantraniliprole, chlorpyrifos, diazinon, indoxacarb, or pyriproxyfen in this study.

HERBICIDES. 2,4-D was the most frequently detected herbicide (82% DF). Three other herbicides with the same mode of action (MOA; dicamba, MCPA, and triclopyr) were also frequently detected (50%, 38%, and 53% DF, respectively). In addition to herbicides with this MOA, two others were also frequently detected: diuron and pendimethalin (65% and 19% DF, respectively). DPR historically monitored herbicides bromacil, oryzalin, oxyfluorfen, prodiamine, prometon, simazine, and tebuthiuron were rarely, or never detected in FY 16/17. With CDFA's new LC multi-analyte screen, bensulide, isoxaben, oxadiazon, and S-metolachlor were added to our monitoring program. Of these, only isoxaben and oxadiazon were detected (17% and 23% DF, respectively), all below their US EPA BM.

2,4-D, dicamba, diuron, MCPA, pendimethalin, and triclopyr are routinely detected in the Northern California urban monitoring program, some with fairly high DFs. However, these detections never exceed minimum US EPA BMs (except for one 2,4-D detection in FY13/14). These herbicides are included to the monitoring program for trend analysis; upcoming data analysis of these herbicides will determine future monitoring needs.

FUNGICIDES. With the new LC multi-analyte screen, four fungicides were added to our monitoring program: azoxystrobin, propiconazole, pyraclostrobin, and trifloxystrobin. Two were detected: azoxystrobin and propiconazole (7% DF each). These were not detected above their respective US EPA BMs.

OTHER. Rain events compared to non-storm (dry season) events: Detections more than doubled during rain events. Biggest differences were with fipronil, diuron, MCPA, triclopyr, and bifenthrin, having between 50% - 76% higher DFs during rain events.

Storm drain outfalls compared to receiving waters: Overall detections almost doubled at stormdrain outfall sites (40% DF) when compared to receiving water sites (23% DF).

San Francisco Bay area (SFB) compared to Sacramento area (SAC; receiving waters only): SFB was only sampled twice, a fall rain event and a June dry event. During the fall rain event, the overall DF between the two areas was about the same. However, during dry monitoring in June, SAC had an overall higher DF than SFB (20% and 3% DF, respectively).

TOXICITY. UC Davis Aquatic Health Program conducted 96-hour water column toxicity tests with *Hyalella azteca* from samples collected from selected sites in SAC. In the first flush rain event in October, water from three stormdrain outfalls and one receiving water site (all in Roseville) was tested for toxicity. In the lab tests, *H. azteca* survival ranged from 0 - 8% at these sites. At these same sites during the June dry sampling, only one stormdrain outfall had toxicity (0% survival); water from the other sites in Roseville did not show toxicity. In Folsom, toxicity tests were conducted from water collected during the first flush rain event and in a storm in April 2017. There was no apparent toxicity during these tests as *H. azteca* survivability was equal to the controls.

SEDIMENTS (see Table 2). Sediments were collected at five monitoring sites in SAC and analyzed for eight pyrethroids (bifenthrin, cyfluthrin, cypermethrin, deltamethrin, fenpropathrin, esfenvalerate, lambda-cyhalothrin, permethrin). All four stormdrain outfall sites had sediment that contained > 1 toxicity unit (TU); ranging from 1.8 – 16 TUs. A receiving water site in Roseville had 2.4 and 0.7 TUs in June 2016 and June 2017, respectively (June 2016 data is reported here as this data was not available for FY15/16 report). As observed in previous years, bifenthrin accounted for the largest percentage (79%) of TUs, distantly followed lambda cyhalothrin, cypermethrin, deltamethrin, and cyfluthrin (4 - 6% of the TU total). All other pyrethroids contributed < 1% of the total TUs.

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

  Dithiopyr, PCNB, sulfometuron-methyl

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2. Pesticide detection frequency

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

Pesticide	Number of samples	Number of detections	Reporting Limit (μg/L)	Detection frequency (DF) (%)	Lowest USEPA benchmark (BM) (μg/L)*		Number of BM exceed-ances	BM exceedance frequency (%)
2,4-D	34	28	0.05	82	13.1	VA	0	0
Azoxystrobin	30	2	0.02	7	44	IC	0	0
Bensulide	30	0	0.02	0	290	IA	0	0
Bifenthrin	34	25	0.001	74	0.0013	IC	24	71
Bromacil	34	1	0.02	3	6.8	NA	0	0
Carbaryl	20	2	0.05	10	0.5	IC	0	0
Chlorantraniliprole	30	0	0.02	0	4.5	IC	0	0
Chlorpyrifos	34	0	0.02	0	0.04	IC	0	0
Cyfluthrin	34	10	0.002	29	0.0074	IC	0	0
Cypermethrin	34	0	0.005	0	0.069	IC	0	0
Deltamethrin	34	8	0.005	24	0.004	IC	8	24
Desulfinyl fipronil	34	7	0.01	21	0.59	FC	0	0
Desulfinyl fipronil amide	34	0	0.01	0	NA	--	--	--
Diazinon	4	0	0.01	0	0.105	IA	0	0
Dicamba	34	17	0.05	50	61	NA	0	0
Diuron	34	22	0.02	65	2.4	NA	0	0
Esfenvalerate	16	0	0.005	0	0.017	IC	0	0
Fipronil	34	17	0.01	50	0.011	IC	17	50
Fipronil amide	34	4	0.01	12	NA	--	--	--
Fipronil sulfide	34	0	0.01	0	0.11	IC	0	0
Fipronil sulfone	34	19	0.01	56	0.037	IC	1	3
Imidacloprid	34	20	0.02	59	0.01	IC	20	59
Indoxacarb	30	0	0.02	0	75	IC	0	0
Isoxaben	30	5	0.02	17	10	VA	0	0
Lambda Cyhalothrin	34	2	0.005	6	0.002	IC	2	6
Malathion	34	2	0.02	6	0.035	IC	2	6
MCPA	34	13	0.05	38	170	VA	0	0
Oryzalin	34	1	0.035	3	30.8	VA	0	0
Oxadiazon	30	7	0.02	23	5.2	NA	0	0
Oxyfluorfen	31	0	0.05	0	0.33	VA	0	0
Pendimethalin	31	6	0.05	19	5.2	NA	0	0
Permethrin	34	8	0.005	24	0.0014	IC	8	24

Pesticide	Number of samples	Number of detections	Reporting Limit (µg/L)	Detection frequency (DF) (%)	Lowest USEPA benchmark (BM) (µg/L)*		Number of BM exceed-ances	BM exceedance frequency (%)
Prodiamine	31	0	0.05	0	1.5	IC	0	0
Prometon	9	0	0.02	0	98	NA	0	0
Propiconazole	30	2	0.02	7	21	NA	0	0
Pyraclostrobin	30	0	0.02	0	1.5	NA	0	0
Pyriproxyfen	30	0	0.02	0	0.015	IC	0	0
Simazine	34	0	0.02	0	2.24	NA	0	0
S-Metolachlor	30	0	0.02	0	8	NA	0	0
Tebuthiuron	4	0	0.05	0	50	NA	0	0
Triclopyr	34	18	0.05	53	5900	NA	0	0
Trifloxystrobin	30	0	0.02	0	2.76	IC	0	0
*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. Complete data set in Appendix.

Pesticide	Number of samplesɫ	Number of detections	Detection frequency (%)	LC_{50} (µg/g OC)*	Detection frequency of sediments $\geq$ 1 TU*	Median TUs*
Bifenthrin	10	10	100	0.52	90	3.9
Cyfluthrin	10	9	90	1.08	0	0.17
Cypermethrin	10	8	80	0.38	10	0.26
Deltamethrin	10	10	100	0.79	0	0.3
Fenpropathrin	10	0	0	--	--	--
Esfenvalerate	10	3	30	1.54	0	0
Lambda Cyhalothrin	10	7	70	0.45	10	0.26
Permethrin	10	7	70	0.38	0	0.02
Resmethrin	5	0	0	--	--	--

ɫ Includes one sample from receiving water site PGC040 that was not analyzed until FY16_17

* 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: AT ALL SITES, 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 Strategy SOP [http://cdpr.ca.gov/docs/emon/pubs/protocol.htm?filter=surfwater])

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	Further data analysis (Y/N)
Area	**Pesticide**	**Water**	**Sediment**	**Current year (i)**	**i - 1**	**i - 2**		
Northern CA	Bifenthrin	X		71%	75%	67%	2013	Y
	Deltamethrin	X		24%	19%	11%	2013	Y
	Permethrin	X		24%	11%	46%	2013	Y
	Fipronil	X		50%	29%	43%	2015	N
	Imidacloprid [A]	X		≥ 59%	≥ 44%	≥ 17%	(none)	Y
	Bifenthrin		X	3.9 TU	7.4 TU	6.7 TU	2013	Y

[A] "≥" is indicated because the reporting limit is above the lowest imidacloprid BM. Trace detections may be above the BM.

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	28	0	3	0
Matrix Spikes/Duplicates	28	0	5	0
Laboratory Control Spikes/Duplicates	0	0	2	0
Blind Spikes	4	0	0	0
Surrogate Spikes	79	12	19	0
Explain out of control QC and interpretation of data:	The first time CDFA's new LC multi-analyte screen was use for storm samples, nine imidacloprid-d4 and three atrazine-d5 surrogates had low recoveries. Higher than normal levels of sediment and CDFA's first time to use these two surrogates may have contributed to the low recoveries. Low recoveries do not affect the DF of the detected analytes, although reported concentrations may have been higher. However, other analytes may have been in these samples; most likely trace detections could have been in concentrations > RL. This likely affected azoxystrobin, chlorantraniliprole, propiconazole, and fipronil amide; all were detected at trace levels in most of the 9 samples. Of these, only chlorantraniliprole was not detected at other sampling dates.			

5. Supporting Information

Submit the following Supporting Information combined into one PDF file with your report:

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