California Department of Pesticide Regulation
Environmental Monitoring Branch

DEPARTMENT OF PESTICIDE REGULATION

AMBIENT MONITORING REPORT

Date: November 28, 2016

1. Study highlights:

- Study Number: 299
- Title: Ambient Monitoring in Urban Areas in Northern California
- Author Michael Ensminger

- Study area:
  - County: Alameda, Contra Costa, Placer, Sacramento, Santa Clara
  - Waterbody/ Watershed: Arcade Creek watershed (WS), Coyote Creek WS, Guadalupe River 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: Click here to enter describe other

- Objectives: 1. Determine the presence and concentrations of selected pesticides in urban runoff at stormdrain outfalls (both during the dry season and during storm runoff) in Roseville and Folsom; 2 Determine the presence and concentrations of selected pesticides from creeks or rivers in the Sacramento area (Folsom, Roseville, and Sacramento) and in the San Francisco Bay area (Dublin, Martinez, and in Santa Clara County); 3. Determine the toxicity of water samples at long term monitoring locations, using toxicity tests conducted with Hyalella azteca; 4. Assess if detected pesticides are at concentrations that could be potentially toxic to aquatic organisms by comparing the data to aquatic toxicity criteria.

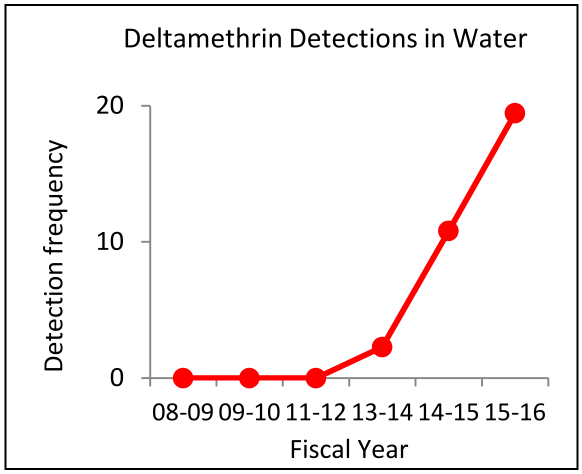
- Sampling period: July 1, 2015- June 30, 2016

- Pesticides monitored:

  2,4-D, bifenthrin, bromacil, carbaryl, chlorfenapyr, chlorpyrifos, cyfluthrin, cypermethrin, deltamethrin, diazinon, dicamba, diuron, fenpropathrin (sediments only), esfenvalerate (sediments only), fipronil, fipronil amide, fipronil desulfinyl, fipronil desulfinyl amide, fipronil sulfide, fipronil sulfone, imidacloprid, lambda-cyhalothrin, malathion, MCPA, oryzalin, oxyfluorfen, pendimethalin, permethrin, prometon, prodiamine, simazine, tebuthiuron, and triclopyr

- Major findings:

  INSECTICIDES. In water samples, bifenthrin was the most frequently detected insecticide (83% detection frequency [DF]). This DF is slightly higher than what was observed during the past two years, likely due to more detections in the San Francisco Bay (SFB) area. In FY15-16, one storm sample was added to the four SFB area sites; bifenthrin was detected at all four sites in this rain event. In the pyrethroid analysis, there are five additional pyrethroids; all were detected. Deltamethrin, cyfluthrin, and permethrin were detected more frequently (19, 17, and 11% DF, respectively); cypermethrin and lambda-cyhalothrin less (6 and 3% DF, respectively). Permethrin and lambda-cyhalothrin were only detected in the Sacramento area, whereas cypermethrin was mostly detected in the SFB area. Deltamethrin and cyfluthrin were detected at similar DF in both areas. Deltamethrin detections have been increasing in the past few years, as seen in the figure to the right.



Bifenthrin was generally detected at concentrations higher than its minimum US EPA benchmark (BM), and all deltamethrin, lambda-cyhalothrin, and permethrin detections were above their respective BMs. Cypermethrin was never, and cyfluthrin rarely, detected at concentrations above their BM.

Imidacloprid detections were fairly high, with a 44% DF. This is higher than FY15-16 (17% DF), and slightly higher than the five year average in Northern California urban monitoring (35% DF). Imidacloprid was not monitored in the SFB area, but is currently being monitored in FY16-17. Results from FY16-17 will help define the detection trends of this pesticide. No detections of imidacloprid were above its US EPA BM (1.05 ppb).

Fipronil was also commonly detected (DF, 29%). However, fipronil detections in Northern California urban monitoring have decreased in the past few years as more receiving waters in the SFB area are monitored. Two of the degradates are more commonly detected (sulfone, 20% DF; desulfinyl, 11% DF). All of the fipronil detections and some of the sulfone detections (14%) were above their respective BMs. The CDFA laboratory reporting limit is higher than the lowest fipronil BM; therefore fipronil detections (23% DF) may be at concentrations above fipronil's lowest BM.

Carbaryl was the only other insecticide detected. It was detected once in Pleasant Grove Creek during a February rain event. No organophosphates were detected this year, unlike previous years when chlorpyrifos and malathion have been detected. Chlorfenapyr, a pyrrole insecticide, was not detected in 17 samples (reporting limit, 0.1 μL^{-1} [Table 1]).

HERBICIDES. 2,4-D was the most frequently detected herbicide (93% DF). Three other herbicides with the same mode of action (dicamba, triclopyr, and MCPA) were also frequently detected (59%, 52%, and 22% DF, respectively). In addition to this class of herbicides, two others were also frequently detected: diuron and pendimethalin (53% and 24% DF, respectively). Pendimethalin and diuron were detected during their peak use (fall, winter, or spring) but not in August sampling. None of the herbicides were detected above their respective BMs. Bromacil, oryzalin, prometon, prodiamine, simazine, and tebuthiuron were not detected.

OTHER. Rain events compared to non-storm (dry season) events: Detections doubled during rain events. Biggest differences were with dicamba, bifenthrin, MCPA, triclopyr, and fipronil. Interestingly, the two pesticides that had the largest difference between storm
and nonstorm sampling were the very hydrophilic herbicide dicamba and the very lipophilic insecticide bifenthrin.

Storm drain outfalls compared to receiving waters: Detections also doubled between stormdrain outfalls (32% DF) and receiving waters (16% DF).

SF Bay area compared to Sacramento area (receiving waters only): In the SFB area, only pyrethroids and fipronil were monitored. In the four SFB area sites, fipronil was never detected, but bifenthrin, cyfluthrin, cypermethrin, and deltamethrin were detected (DF of these pyrethroids, 25%). In the Sacramento area, fipronil was occasionally detected (25% DF), as were the sulfone and desulfinyl degradates (13% DF each). Of pyrethroids, bifenthrin, cyfluthrin, and deltamethrin were detected in receiving waters, with DF similar to those found in the SFB area. Except for one bifenthrin detection in August (Sacramento area), all receiving water detections occurred only during storm sampling.

TOXICITY. UC Davis Aquatic Health Program conducted 96-hour water column toxicity tests with *Hyalella azteca* from samples collected at the Roseville monitoring sites (three storm drain outfalls; one receiving water) during one dry and two rain sampling events. At all but one stormdrain outfall during dry and rain sampling events, *H. azteca* survival ranged from 0 - 6% (one stormdrain outfall in August 2015 had no toxicity). *H. azteca* survival at the receiving water site was also significantly reduced during rainstorm monitoring (28 and 75% survival for the November 2015 and February 2016 rain, respectively), but there was no toxicity at the receiving water site during the dry sampling event. Based on BM exceedances, bifenthrin likely contributed most to toxicity, but fipronil, permethrin, deltamethrin, and cyfluthrin also likely contributed.

SEDIMENTS. Sediments were collected at five monitoring sites and analyzed for eight pyrethroids (bifenthrin, cyfluthrin, cypermethrin, deltamethrin, fenpropathrin, esfenvalerate, lambda-cyhalothrin, permethrin). As observed in previous years, bifenthrin accounted for the largest percentage (74%) of toxicity units (TUs; an indicator of potential toxicity), distantly followed cypermethrin and deltamethrin (8 and 7% of the TUs, respectively). All other pyrethroids contributed little to potential toxicity (1-5% of the TUs).

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 (%)	Lowest USEPA benchmark (BM) (µg/L)*		Number of BM exceed-ances	BM exceedance frequency (%)
2,4-D	27	25	0.05	93	13.1	VA	0	0
bifenthrin	36	30	0.001	83	0.0013	IC	27	75
bromacil	17	0	0.05	0	6.8	NA	0	0
carbaryl	17	1	0.05	6	0.5	IC	0	0
chlorfenapyr	17	0	0.1	0	2.9	IA	0	0
chlorpyrifos	17	0	0.04	0	0.04	IC	0	0
cyfluthrin	36	6	0.002	17	0.0074	IC	2	6
cypermethrin	36	2	0.005	6	0.069	IC	0	0
deltamethrin	36	7	0.005	19	0.0041	IC	7	19
diazinon	17	0	0.01	0	0.105	IA	0	0
dicamba	27	16	0.05	59	61	NA	0	0
diuron	17	9	0.05	53	2.4	NA	0	0
fipronil	35	10	0.02	29	0.011	IC	10	29
fipronil amide	35	1	0.03	3	--	--	--	--
fipronil desulfinyl	35	4	0.02	11	0.59	FC	0	0
fipronil desulfinyl amide	35	0	0.03	0	--	--	--	--
fipronil sulfide	35	0	0.02	0	0.11	IC	0	0
fipronil sulfone	35	7	0.03	20	0.037	IC	5	14
imidacloprid	27	12	0.05	44	1.05	IC	0	0
lambda-cyhalothrin	36	1	0.002	3	0.002	IC	1	3
malathion	17	0	0.05	0	0.035	IC	0	0
MCPA	27	6	0.05	22	170	VA	0	0
oryzalin	17	0	.05	0	15	VA	0	0
oxyfluorfen	17	0	0.05	0	0.33	VA	0	0
pendimethalin	17	4	0.05	24	5.2	NA	0	0
permethrin	36	4	0.002	11	0.0014	IC	4	11
prometon	17	0	0.05	0	98	NA	0	0
prodiamine	17	0	0.05	0	1.5	IC	0	0
simazine	17	0	0.05	0	2.24	NA	0	0
tebuthiuron	17	0	0.05	0	50	NA	0	0
triclopyr	27	14	0.05	52	5900	NA	0	0

*FA, fish acute; FC, fish chronic; IA, invertebrate acute; IC, invertebrate chronic; NA, non-vascular acute; VA, vascular acute; “—“ indicates no benchmark available.

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	11	11	100	0.52	100%	7.4
cyfluthrin	11	11	100	1.08	27%	0.5
cypermethrin	11	11	100	0.38	27%	0.8
deltamethrin	11	11	100	0.79	18%	0.7
fenpropathrin	11	0	0	--	--	--
esfenvalerate	11	11	100	1.54	0%	0.1
lambda-cyhalothrin	11	11	100	0.45	27%	0.4
permethrin	11	11	100	0.38	0%	0.1

*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. Laboratory 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	154	0	18	0
Matrix Spikes/Duplicates	154	0	0	0
Laboratory Control Spikes/Duplicates	0	0	18	0
Blind Spikes	12	0	0	0
Surrogate Spikes	20	0	17	0
Explain out of control QC and interpretation of data:	All QC was within control limits			

4. Supporting Information

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