DEPARTMENT OF PESTICIDE REGULATION

AMBIENT MONITORING REPORT

Date: January 26, 2016

1. Study highlights:

- Study Number: 269 FY14-15
- Title: Ambient and Mitigation Monitoring in Urban Areas in Northern California
- Author Michael Ensminger
- Study area:
  - County: Alameda, Contra Costa, Placer, Sacramento, Santa Clara
  - Waterbody/ Watershed: South San Ramon Creek Watershed (WS), Walnut Creek WS, Pleasant Grove Creek WS, Arcade Creek WS, Upper American River WS, Guadalupe River WS, Metcalfe Canyon-Coyote 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. 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, 2014 – June 30, 2015
- Pesticides monitored:

  2,4-D, benfluralin, bifenthrin, bromacil, carbaryl, chlorfenapyr, chlorpyrifos, cyfluthrin, cypermethrin, deltamethrin/tralomethrin, diazinon, dicamba, diuron, ethalfluralin, fenpropathrin (sediments only), fenvalerate/esfenvalerate (sediments only), fipronil, fipronil amide, fipronil desulfinyl, fipronil desulfinyl amide, fipronil sulfide, fipronil sulfone, imidacloprid, lambda-cyhalothrin, malathion, MCPA, norflurazon, oryzalin, oxyfluorfen, pendimethalin, permethrin, prometon, prodiamine, simazine, triclopyr, trifluralin
- Major findings:

  INSECTICIDES. In water samples, bifenthrin was the most frequently detected insecticide (67% detection frequency [DF]). This was slightly lower than in previous years because bifenthrin was not detected in four creeks/rivers in the San Francisco (SF) Bay area during summer sampling in July and August (2014). With the drought and water restrictions, runoff was reduced. In addition, these sites were not sampled during rainstorm events when detections are higher. Two of these sites

(Coyote Creek, Guadalupe River) are reservoir fed; lack of detections could be the result of the diluting effect of the respective reservoir.

Four other pyrethroids were detected more than 10% of the time: permethrin (46% DF), cyfluthrin (32% DF), lambda-cyhalothrin (14% DF), and deltamethrin/tralomethrin (11% DF). Bifenthrin, permethrin, lambda-cyhalothrin, and deltamethrin/tralomethrin were always detected at concentrations above their respective minimum US EPA benchmark (BM) concentrations, whereas cyfluthrin was infrequently detected above its BM. Cypermethrin was also detected a few times (5% DF; never above its BM).

Fipronil and some of its degradates were also detected. Fipronil was detected in slightly less than half of the samples (43% DF), with two degradates commonly detected (sulfone, 41% DF; desulfinyl, 24% DF). All of the fipronil detections and some of the sulfone detections (24%) were above their respective BM. In CDFA analysis, fipronil's reporting limit is higher than the BM, such that trace detections (22% DF) may have also been detected at concentrations above its BM. Detections of fipronil were slightly decreased in FY14-15. This was due to the lack of detections in the four San Francisco Bay area sites in July and August (as previously described for bifenthrin).

Diazinon and chlorfenapyr were not detected, but chlorpyrifos (19% DF), carbaryl (19% DF), imidacloprid (16% DF), and malathion (13% DF) were. Of these, only malathion was detected at concentrations above its minimum BM (all malathion detections). Chlorpyrifos and carbaryl were only detected during rain events, whereas malathion was only detected during dry events. The detections of chlorpyrifos (all in stormdrain outfalls in Placer County) are curious; it was detected in the February 2015 rain event but not in the preceding November 2014 rain event. There were no reported urban uses of chlorpyrifos between the November and February storms, but there was one agricultural application (to apples) about 20 miles northeast from the detections, three days before the February rain event. Perhaps this accounts for the chlorpyrifos detections in February.

HERBICIDES. 2,4-D was the most frequently detected herbicide (67% DF). Three other herbicides with the same mode of action (dicamba, triclopyr, and MCPA) were also frequently detected (32%, 27%, and 22% DF, respectively). Five other herbicides were also detected at various times: pendimethalin and diuron (both, 44% DF), oryzalin and prodiamine (both, 19% DF), and oxyfluorfen (6% DF). None of the herbicides, except for the one oxyfluorfen detection, were detected above their respective BM.

OTHER.

Rain events compared to storm events: Detections doubled with rain events, from an overall 16% DF during dry (nonstorm) events, compared to 32% DF during storm events.

Storm drain outfalls compared to receiving waters: Detections more than doubled in stormdrain outfalls, from an overall 12% DF for receiving waters to 29% DF in stormdrain outfalls. Between stormdrain outfalls and receiving water sites, pesticides are diluted, degraded, or sequestered.

SF Bay area compared to Sacramento area (receiving waters only): Detections in SF Bay area receiving waters sites were minimal; only permethrin and triclopyr were detected. Comparing the same pesticides, SF Bay area had a 5% DF, whereas receiving waters in the Sacramento area had a 22% DF. SF Bay sites were not sampled during storm events.

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 downstream receiving water) during two dry and one rain monitoring event. At all stormdrain outfalls at all sampling times, *H. azteca* survival ranged from 0% (nine samples) to 16% (one sample); all were significantly reduced when compared to the control. Samples collected at the receiving water during dry events had no effect on the organisms, but during the rain event, none of the organisms survived.

SEDIMENTS. Sediments were collected at seven monitoring sites and analyzed for eight pyrethroids (bifenthrin, cyfluthrin, cypermethrin, deltamethrin, fenpropathrin, fenvalerate/esfenvalerate, lambda-cyhalothrin, permethrin). As observed in previous years, bifenthrin accounted for the largest percentage (81%) of toxicity units (TUs; an indicator of potential toxicity), distantly followed by cypermethrin (7% of the TUs), lambda-cyhalothrin and cyfluthrin (both 4% of the TUs). All other pyrethroids contributed little to potential toxicity.

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	37	25	0.05	67%	13.1	VA	0	0%
Benfluralin	16	0	0.05	0%	1.9	FC	0	0%
Bifenthrin	37	25	0.001	67%	0.0013	IC	25	67%
Bromacil	16	0	0.05	0%	6.8	NA	0	0%
Carbaryl	16	3	0.05	19%	0.5	IC	0	0%
Chlorfenapyr	16	0	0.1	0%	2.915	IA	0	0%
Chlorpyrifos	16	3	0.01	19%	0.04	IC	0	0%
Cyfluthrin	37	12	0.002	32%	0.007	IC	3	8%
Cypermethrin	37	2	0.005	5%	0.069	IC	0	0%
Deltamethrin/ Tralomethrin	37	4	0.005	11%	0.0041	IC	4	11%
Desulfinyl fipronil	37	9	0.02	24%	0.59	FC	0	0%
Desulfinyl fipronil amide	37	0	0.03	0%	--	--	--	--
Diazinon	16	0	0.01	0%	0.11	IA	0	0%
Dicamba	37	12	0.05	32%	61	NA	0	0%
Diuron	16	7	0.05	44%	2.4	NA	0	0%
Ethalfluralin	16	0	0.05	0%	0.4	FC	0	0%
Fipronil	37	16	0.02	43%	0.011	IC	16	43%
Fipronil amide	37	2	0.03	5%	--	--	--	--
Fipronil sulfide	37	0	0.02	0%	0.11	IC	0	0%
Fipronil sulfone	37	15	0.03	41%	0.037	IC	9	24%
Imidacloprid	36	6	0.05	17%	1.05	IC	0	0%
Lambda-cyhalothrin	37	5	0.002	14%	0.002	IC	5	14%
Malathion	16	2	0.05	13%	0.035	IC	2	13%
MCPA	37	8	0.05	22%	170	VA	0	0%
Norflurazon	16	0	0.05	0%	9.7	NA	0	0%
Oryzalin	16	3	0.05	19%	15.4	VA	0	0%
Oxyfluorfen	16	1	0.05	6%	0.29	NA	1	6%
Pendimethalin	16	7	0.05	44%	5.2	NA	0	0%
Permethrin	37	17	0.002	46%	0.0014	IC	17	46%
Prodiamine	16	3	0.05	19%	1.5	IC	0	0%
Prometon	16	0	0.05	0%	98	NA	0	0%
Simazine	16	0	0.05	0%	36	NA	0	0%
Triclopyr	37	10	0.05	27%	100	NA	0	0%
Trifluralin	16	0	0.05	0%	1.14	FC	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 samples	Number of detections	Detection frequency (%)	LC_{50} (µg/g OC)*	Detection frequency of sediments ≥ 1 TU*	Median TUs*
Bifenthrin	16	16	100	0.52	16	6.7
Cyfluthrin	16	14	87.5	1.1	1	0.3
Cypermethrin	16	14	87.5	0.79	5	0.4
Deltamethrin/Tralomethrin	16	13	81.3	0.79	0	0.1
Fenpropathrin	16	0	0	not available	0	0
Fenvalerate/Esfenvalerate	16	11	68.8	1.54	0	0
Lambda-cyhalothrin	16	14	87.5	0.45	1	0.3
Permethrin Total	16	14	87.5	10.8	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	39	0	3	0
	Matrix Spikes/Duplicates	39	0	0	0
	Laboratory Control Spikes/Duplicates	0	0	3	0
	Blind Spikes	6	0	0	0
	Surrogate Spikes	19	0	45	0
Other QC:	None				
Other QC:	None				
Explain out of control QC and interpretation of data:	All water and sediment QC was within control limits; all data is acceptable.				

4. Supporting Information (attached as a PDF file)