DEPARTMENT OF PESTICIDE REGULATION

AMBIENT MONITORING REPORT

Date: May 31, 2018

1. Study highlights

- Study Number: 270
- Title: Urban monitoring in Southern California watersheds FY 2016-2017
- Author Robert Budd

- Study area:
  - County: Los Angeles, Orange, San Diego
  - Waterbody/ Watershed: Ballona Creek, Bouquet Creek, Dominguez Channel, Los Angeles River, Salt Creek, San Diego River, San Gabriel River, Tecolote Canyon Creek, Wood Canyon Creek

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

- Water body type: ☒ Storm drain outfall ☒ Creek ☒ River ☐ Pond ☐ Lake ☐ Drainage ditch ☐ Other: type

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- Objectives: 1. Determine pesticide presence and concentrations in runoff from urban neighborhoods in southern California watersheds; 2. Compare pesticide concentrations to aquatic benchmarks; 3. Determine the toxicity of a subset of samples to Hyalella azteca in 96-hr water column testing; 4. Determine potential pyrethroid toxicity of sediments.

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

- Pesticides monitored:

2,4-D, atrazine, azoxystrobin, bifenthrin, bromacil, carbaryl, chlorantraniliprole, chlorfenapyr, chlorpyrifos, cyfluthrin, cypermethrin, deltamethrin/tralomethrin, desulfinyl fipronil, desulfinyl fipronil amide, dicamba, dichlorvos, diflubenzuron, diuron, etofenprox, fenvalerate/esfenvalerate, fipronil, fipronil amide, fipronil sulfide, fipronil sulfone, imidacloprid, lambda cyhalothrin, malathion, MCPA, oryzalin, oxadiazon, pendimethalin, permethrin, prodiamine, prometon, propiconazole, pyraclostrobin, simazine, triclopyr, trifloxystrobin, trifluralin.

- Major findings:

Bifenthrin was the most frequently detected (79%) pyrethroid insecticide in water samples collected at southern California monitoring locations between July 1, 2016 and June 30, 2017. Bifenthrin concentrations exceeded the lowest aquatic benchmark (BM) set by the US EPA in 77% of samples. Six other pyrethroids were detected at lower frequencies. All detections of permethrin (43%), deltamethrin/tralomethrin (34%), and lambda-cyhalothrin (30%) exceeded their respective aquatic benchmarks. Detected cyfluthrin (53%) concentrations exceeded BM in 34% of samples, while fenvalerate/esfenvalerate was detected in 19% of samples with an associated 4% exceedance. Cypermethrin was detected in 21% of samples; however none of the concentrations were above toxicity thresholds.

Fipronil was also detected frequently (79%) at concentrations above its aquatic BM. Several of fipronils degradate by-products. Several of fipronils degradate by-products were also detected in surface waters, including fipronil sulfone (72%), desulfinyl fipronil (70%), fipronil amide (45%), desulfinyl fipronil amide (32%), and fipronil sulfide (4%). Only fipronil sulfone exceeded BM values in 55% of samples. Fipronil amide and desulfinyl fipronil amide do not have established aquatic BM values.

The neonicotinoid imidacloprid was the most frequently detected pesticide (81%). The US EPA aquatic benchmark for imidacloprid was lowered in November 2017 from 1.05 µg/L to 0.01 µg /L. Using the new benchmark value, the imidacloprid exceedance rate was 81%. The only other insecticides detected above reporting limits were the organophosphate malathion (24%) and the carbamate carbaryl (42%). Their concentrations exceeded BM thresholds in 18% and 8% of samples, respectively.

Several herbicides and fungicides were present in surface water samples, including triclopyr (71%), 2,4-D (68%), diuron (76%), dicamba (26%), propiconazole (21%), isoxaben (18%), oxadiazon (18%), azoxystrobin (6%), MCPA (5%), simazine (5%) and chlorantraniliprole (3%). None of the concentrations were above aquatic BM.

No other pesticide was detected in water samples within the sampling period.

96-hr water column toxicity tests were conducted using the test organism *Hyalella azteca*. Three samples were collected at storm drain outlets; one during a storm event and two during the dry season. Twelve samples were collected within receiving waters; eight during the dry season and four during storm events. Significant toxicity was observed in all samples collected at storm drains, with 86-100 percent mortality during all events. Samples collected within receiving waters experienced a wide range of toxicity, with 100% mortality observed during storm events and 6-100% mortality during the dry season.

Six sediment samples were analyzed for the pyrethroids bifenthrin, cyfluthrin, cypermethrin, deltamethrin, esfenvalerate, lambda cyhalothrin, and permethrin. Bifenthrin, cyfluthrin, deltamethrin and permethrin were detected in every sample. Esfenvalerate and lambda cyhalothrin were detected in 83% of samples, while cypermethrin was detected in 67% of the samples. Bifenthrin accounted for the largest average percentage (51%) of toxicity units (TUs; an indicator of potential toxicity), followed by deltamethrin (14%), cyfluthrin (11%), cypermethrin (10%), lambda cyhalothrin (9%), esfenvalerate (4%), and permethrin (1%).

- Recommendations for pesticides that need a CDFA analytical method (from SWMP): Sulfometuron-methyl, PCNB

2. Pesticide detection frequency

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

Pesticide	Number of samples	Number of detections	Detection frequency (%)	Reporting limit (µg/L)	Lowest USEPA benchmark (BM) (µg/L)		Number of BM exceedances	BM exceedance frequency (%)
2,4-D	38	26	68	0.05	13.1	VA	-	0
Atrazine	4		0	0.05	0.001	VA	-	0
Azoxystrobin	34	2	6	0.02	44	IC	-	0
Bifenthrin	47	37	79	0.001	0.0013	IC	36	77
Bromacil	38		0	0.02	6.8	NVA	-	0
Carbaryl	12	5	42	0.05	0.5	IC	1	8
Chlorantraniliprole	34	1	3	0.02	4.5	IC	-	0
Chlorfenapyr	12		0	0.1	2.915	IA	-	0
Chlorpyrifos	38		0	0.01	0.04	IC	-	0
Cyfluthrin	47	25	53	0.002	0.0074	IC	16	34
Cypermethrin	47	10	21	0.005	0.069	IC	-	0
Deltamethrin/ Tralomethrin	47	16	34	0.005	0.0041	IC	16	34
Desulfinyl fipronil	47	33	70	0.01	0.59	FC	-	0
Desulfinyl fipronil amide	47	15	32	0.01	na	-	-	0
Dicamba	38	10	26	0.05	61	NVA	-	0
Dichlorvos	4		0	0.05	0.0058	IC	-	0
Diflubenzuron	34		0	0.02	0.00025	IC	-	0
Diuron	38	29	76	0.02	2.4	NVA	-	0
Etofenprox	34		0	0.02	0.17	IC	-	0
Fenvalerate/ Esfenvalerate	47	9	19	0.005	0.017	IC	2	4
Fipronil	47	37	79	0.01	0.011	IC	37	79
Fipronil amide	47	21	45	0.01	na	-	-	0
Fipronil sulfide	47	2	4	0.01	0.11	IC	-	0
Fipronil sulfone	47	34	72	0.01	0.037	IC	26	55
Imidacloprid	47	38	81	0.02	0.01	IC	38	81
Indoxacarb	34		0	0.02	75	IC	-	0
Isoxaben	34	6	18	0.02	10	VA	-	0
Lambda Cyhalothrin	47	14	30	0.002	0.002	IC	14	30
Malathion	38	9	24	0.02	0.035	IC	7	18

Pesticide	Number of samples	Number of detections	Detection frequency (%)	Reporting limit (µg/L)	Lowest USEPA benchmark (BM) (µg/L)		Number of BM exceedances	BM exceedance frequency (%)
MCPA	38	2	5	0.05	170	VA	-	0
Oryzalin	42		0	0.02	15.4	VA	-	0
Oxadiazon	34	6	18	0.02	5.2	NVA	-	0
Pendimethalin	12		0	0.05	5.2	NVA	-	0
Permethrin	47	20	43	0.002	0.0014	IC	20	43
Prodiamine	12		0	0.05	1.5	IC	-	0
Prometon	4		0	0.05	98	NVA	-	0
Propiconazole	34	7	21	0.02	21	NVA	-	0
Pyraclostrobin	34		0	0.02	1.5	NVA	-	0
Pyriproxyfen	34		0	0.015	0.015	IC	-	0
Simazine	38	2	5	0.02	2.24	NVA	-	0
Triclopyr	38	27	71	0.05	5900	NVA	-	0
Trifloxystrobin	34		0	0.02	2.76	IC	-	0
Trifluralin	12		0	0.05	1.14	FC	-	0

* Only most recent RL listed, FA, fish acute; FC, fish chronic; IA, invertebrate acute; IC, invertebrate chronic; NVA, non-vascular acute; VA, vascular acute; na, value not available; dash, not applicable

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 $\geq$ 1 TU*	Median TUs*
Bifenthrin	6	6	100	0.52	67	1.86
Cyfluthrin	6	6	100	1.08	17	0.55
Cypermethrin	6	4	67	0.38	17	0.24
Deltamethrin	6	6	100	0.79	33	0.47
Esfenvalerate	6	5	83	1.54	0	0.20
Lambda Cyhalothrin	6	5	83	0.45	0	0.45
Permethrin	6	6	100	10.83	0	0.04

*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 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 5 years							Last written evaluation (reference)	Further data analysis (Y/N)
Area	Pesticide	Water	Sediment	Current year (i)	i - 1	i - 2		
	Bifenthrin	X		77	68	73	2013	Y
	Cyfluthrin	X		34	39	35	2013	Y
	Deltamethrin	X		34	23	25	2013	Y
	Fipronil	X		79	59	75	2015	N
	Fipronil sulfone	X		55	39	55	2015	N
	Imidacloprid*	X		81	68	73	na	Y
	Lambda-cyhalothrin	X		30	25	15	2013	Y
	Permethrin	X		43	41	43	2013	Y
	Bifenthin		X	1.86	2.28	6.68	2013	Y

*Imidacloprid benchmark lowered by USEPA November 2017. Past exceedance rate based on new value.

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	217	0	9	0
Matrix Spikes/Duplicates	224	0	9	0
Laboratory Control Spikes/Duplicates	0	-	Enter No.	Enter No.
Blind Spikes	43	0	Enter No.	Enter No.
Surrogate Spikes	64	8	Enter No.	Enter No.
Other QC: Describe	Enter No.	Enter No.	Enter No.	Enter No.
Explain out of control QC and interpretation of data:	Two labeled surrogates are used in the multi-analyte LC screen; atrazine-d5 and imidacloprid-d4. All atrazine-d5 surrogates were within QC controls (58-95%). Nine imidacloprid-d4 samples were below acceptable recovery levels. All surrogates below acceptable levels were samples collected during the first rain event, which had a high level of matrix effects.			

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