DEPARTMENT OF PESTICIDE REGULATION

AMBIENT MONITORING REPORT

Date: March 1, 2019

1. Study highlights

- Study Number: 270
- Title: Urban monitoring in Southern California watersheds FY 2017-2018
- Author: Robert Budd

- Study area:
  - County: Los Angeles, Orange, San Diego
  - Waterbody/ Watershed: Ballona Creek, Bolsa Chica Channel, Bouquet Creek, Coyote Creek, Donminguez Channel, Garden Grove Creek, Los Angeles River, Salt Creek, San Diego River, San Gabriel River, Wood Canyon Creek

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

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

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, 2017 – June 30, 2018

- Pesticides monitored:

  2,4-D, azoxystrobin, bifenthrin, bromacil, carbaryl, chlorantraniliprole, chlorfenapyr, chlorpyrifos, cyfluthrin, cypermethrin, deltamethrin, desulfinyl fipronil, desulfinyl fipronil amide, dicamba, diflubenzuron, diuron, etofenprox, esfenvalerate, fipronil, fipronil amide, fipronil sulfide, fipronil sulfone, imidacloprid, indoxacarb, isoxaben, lambda cyhalothrin, malathion, MCPA, oryzalin, oxadiazon, oxyfluorfen, pendimethalin, permethrin, prodiamine, propiconazole, pyraclostrobin, pyriproxyfen, simazine, triclopyr, trifluralin.

- Major findings:

Bifenthrin was the most frequently detected (72%) pyrethroid insecticide in water samples collected at southern California monitoring locations between July 1, 2017 and June 30, 2018. Bifenthrin concentrations exceeded the lowest aquatic benchmark (BM) set by the US EPA in 70% of samples. Six other pyrethroids were detected at lower frequencies. All detections of permethrin (28%) and deltamethrin (21%) exceeded their respective aquatic benchmarks. Almost all lambda cyhalothrin detections (32%) were benchmark exceedances (30%). Detected cyfluthrin (49%) concentrations exceeded BM in 30% of samples, while cypermethrin was detected in 17% of samples with an associated 2% exceedance. Esfenvalerate and etofenprox were both detected in 1 sample (2%); only etofenprox concentrations exceeded BM.

Fipronil was also detected frequently (76%) at concentrations above its aquatic BM (73%). Several of fipronils degradate by-products were also detected in surface waters, including fipronil sulfone (67%), desulfinyl fipronil (63%), fipronil amide (35%), desulfinyl fipronil amide (20%), and fipronil sulfide (12%). Only fipronil sulfone exceeded BM values in 47% of samples. Fipronil amide and desulfinyl fipronil amide do not have established aquatic BM values.

The neonicotinoid imidacloprid was the most frequently detected pesticide (92%). All of the imidacloprid detection concentrations were above the US EPA aquatic benchmark of 0.01 µg /L. The only other insecticides detected above reporting limits were the organophosphate malathion (20%) and the carbamate carbaryl (18%), with 6% of malathion concentrations above BM.

Several herbicides and fungicides were present in surface water samples, including triclopyr (78%), 2,4-D (78%), diuron (69%), dicamba (22%), chlorfenapyr (15%), propiconazole (14%), isoxaben (14%), oryzalin (10%), oxadiazon (10%), simazine (8%), MCPA (6%), and chlorantraniliprole (4%). Pendimethalin (7%), pyraclostrobin (2%), and pyriproxyfen (2%) were each detected in one sample. None of the herbicides or fungicide concentrations were above their respective 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 organisms *Hyalella azteca* and *Chironomus dilutus*. For toxicity testing using *H. azteca*, three samples were collected at storm drain outlets; one during a storm event and two during the dry season. Fifteen samples were collected within receiving waters; thirteen during the dry season and two during storm events. Significant toxicity was observed in all samples collected at storm drains, with 96–100 percent mortality during all events. Samples collected within receiving waters experienced a wide range of toxicity, with 100% mortality observed during storm events and 0–100% mortality during the dry season. For *Chironomus* testing, two samples were collected at storm drains; one during the dry season and one during a storm event. Two samples were collected at receiving waters during the dry season. Both storm drain samples were significantly toxic (98–100% mortality), but both receiving water samples were not significantly toxic (0–6%).

Six sediment samples were analyzed for the pyrethroids bifenthrin, cyfluthrin, cypermethrin, deltamethrin, esfenvalerate, lambda cyhalothrin, and permethrin. Bifenthrin was detected in every sample. Cyfluthrin, deltamethrin, esfenvalerate, and permethrin were detected in five samples (83%). Lambda cyhalothrin was detected in 67% of samples, while cypermethrin was detected in 33% of samples. Neither resmethrin or fenpropathrin were detected in any of the three samples they were analyzed for. Bifenthrin accounted for the largest average percentage (56%) of toxicity units (TUs; an indicator of potential toxicity) per sampling event, followed by deltamethrin (25%), cyfluthrin (8%), lambda cyhalothrin (6%), cypermethrin (2%), esfenvalerate (2%), and permethrin (<1%).

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

  Sulfometuron-methyl, prallethrin, DDVP

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 (ug/L)	Lowest USEPA benchmark (BM)(ug/L)*		Number of BM exceedances	BM exceedance frequency (%)
2,4-D	18	14	78	0.05	299.2	VA	0	0
Azoxystrobin	49	0	0	0.02	44	IC	0	0
Bifenthrin	53	38	72	0.001	0.0013	IC	37	70
Bromacil	49	0	0	0.02	6.8	NVA	0	0
Carbaryl	49	9	18	0.02	0.5	IC	0	0
Chlorantraniliprole	49	2	4	0.02	4.47	IC	0	0
Chlorfenapyr	13	2	15	0.1	2.915	IA	0	0
Chlorpyrifos	49	0	0	0.02	0.04	IC	0	0
Cyfluthrin	53	26	49	0.002	0.0074	IC	16	30
Cypermethrin	53	9	17	0.005	0.069	IC	1	2
Deltamethrin	53	11	21	0.005	0.0041	IC	11	21
Desulfinyl fipronil	49	31	63	0.01	0.59	FC	0	0
Desulfinyl fipronil amide	49	10	20	0.01	-	-	0	0
Dicamba	18	4	22	0.05	61	NVA	0	0
Diflubenzuron	49		0	0.02	0.00025	IC	0	0
Diuron	49	34	69	0.02	2.4	NVA	0	0
Esfenvalerate	53	1	2	0.005	0.017	IC	0	0
Etofenprox	49	1	2	0.02	0.17	IC	1	2
Fipronil	49	37	76	0.01	0.011	IC	36	73
Fipronil amide	49	17	35	0.01	-	-	0	0
Fipronil sulfide	49	6	12	0.01	0.11	IC	0	0
Fipronil sulfone	49	33	67	0.01	0.037	IC	23	47
Imidacloprid	49	45	92	0.01	0.01	IC	45	92
Indoxacarb	49	0	0	0.02	75	IC	0	0
Isoxaben	49	7	14	0.02	10	VA	0	0
Lambda Cyhalothrin	53	17	32	0.002	0.002	IC	16	30
Malathion	49	10	20	0.02	0.049	IA	3	6
MCPA	18	1	6	0.05	170	VA	0	0
Oryzalin	49	5	10	0.02	13	VA	0	0
Oxadiazon	49	5	10	0.02	5.2	NVA	0	0
Oxyfluorfen	14	0	0	0.05	0.29	NVA	0	0
Pendimethalin	14	1	7	0.05	5.2	NVA	0	0
Permethrin	53	15	28	0.002	0.0014	IC	15	28
Prodiamine	14	0	0	0.05	1.5	IC	0	0
Propiconazole	49	7	14	0.02	21	NVA	0	0
Pyraclostrobin	49	1	2	0.02	1.5	NVA	0	0
Pyriproxyfen	49	1	2	0.015	0.015	IC	1	2
Simazine	49	4	8	0.02	2.24	NVA	0	0

Pesticide	Number of samples	Number of detections	Detection frequency (%)	Reporting limit (ug/L)	Lowest USEPA benchmark (BM)(ug/L)*		Number of BM exceedances	BM exceedance frequency (%)
Triclopyr	18	14	78	0.05	5900	NVA	0	0
Trifluralin	14	0	0	0.05	1.9	FC	0	0

* Only current 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 IV.

Pesticide	Number of samples	Number of detection	Detection frequency (%)	LC_{50} (µg/g OC)*	Detection frequency of sediments ≥ 1	Median TUs*
Bifenthrin	6	6	100	0.52	50	1.27
Cyfluthrin	5	6	83	1.08	0	0.26
Cypermethrin	2	6	33	0.38	0	0.00
Deltamethrin	5	6	83	0.79	33	0.27
Esfenvalerate	5	6	83	1.54	0	0.02
Fenpropathrin		3	0		0	0.00
Lambda Cyhalothrin	4	6	67	0.45	0	0.10
Permethrin	5	6	83	10.83	0	0.00
Resmethrin		3	0		0	0.00

*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	77	68	2013	Y
	Cyfluthrin	X		30	34	39	2013	Y
	Deltamethrin	X		21	34	23	2013	Y
	Fipronil	X		73	79	59	2015	N
	Fipronil sulfone	X		47	55	39	2015	N
	Imidacloprid	X		92	81	68	na	Y
	Lambda Cyhalothrin	X		30	30	25	2013	Y

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**		
	Permethrin	X		28	43	41	2013	Y
	Bifenthin		X	1.27	1.86	2.28	2013	Y

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	208	0	9	0
Matrix Spikes/Duplicates	208	0	9	0
Laboratory Control Spikes/Duplicates	0	-	0	-
Blind Spikes	13	0	0	-
Surrogate Spikes	78	6	0	-
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. Six imidacloprid-d4 samples were below acceptable recovery levels. All surrogates below acceptable levels were samples collected during a rain event which had a high level of matrix effects.			

5. Supporting Information

<u>Submit the following Supporting Information combined into one PDF file with your report:</u>

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