DEPARTMENT OF PESTICIDE REGULATION

AMBIENT MONITORING REPORT

Date: May 8, 2015

1. Study highlights:

- Study Number: 270
- Title: Urban monitoring in southern California watersheds FY 2011 - 2014
- Author Robert Budd

- Study area:
  - County: Orange, Los Angeles, San Diego
  - Waterbody/ Watershed: Ballona Creek, Bouquet Creek, Chollas Creek, Salt Creek, Wood Canyon Creek

- 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 pesticide presence and concentrations in runoff from urban neighborhoods in southern California watersheds; 2. Compare pesticide concentrations to US EPA 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, 2011 – June 30, 2014

- Pesticides monitored:

  2,4-D, benfluralin, bifenthrin, bromacil, carbaryl, chlorothalonil, chlorpyrifos, cyfluthrin, cyhalothrin, cypermethrin, DACT, deltamethrin/tralomethrin, desulfinyl fipronil, desulfinyl fipronil amide, diazinon, dicamba, diuron, ethalfluralin, fenpropathrin, fenvalerate/esfenvalerate, fipronil, fipronil amide, fipronil sulfide, fipronil sulfone, hexazinone, imidacloprid, lambda-cyhalothrin, malathion, MCPA, norflurazon, oryzalin, oxyfluorfen, pendimethalin, permethrin, prodiamine, prometon, resmethrin, simazine, triclopyr, trifluralin

- Major findings:

  Fipronil was the most frequently detected (93%) pesticide in water samples collected in southern California between July 1, 2011 and June 30, 2014. The degradate by-products of fipronil were also detected at fairly high frequencies (DF), including sulfone (91% DF), desulfinyl (83% DF), amide (30% DF), desulfinyl amide (11% DF), and sulfide (11% DF). Fipronil concentrations exceeded the lowest aquatic benchmark (BM) set by the US EPA in 89% of the samples, while sulfone exceedances were 83% over the same period. There were no exceedances for either desulfinyl or sulfide concentrations. There is no BM for either the amide or desulfinyl amide degradates. The reporting limit (RL) for fipronil was lowered during the monitoring period in this analysis. The previous RL was higher than the minimum BM, therefore it is possible the seven trace detections during this period were higher than the BM.

  The presence of pyrethroid insecticides were varied within surface waters. Bifenthrin was the most frequently detected pyrethroid (88% DF), with an associated 82% exceedance frequency (EF). All concentrations of permethrin (58% DF), deltamethrin (18% DF), and lambda-cyhalothrin (14% DF) were above their respective BMs. Thirty-six percent of cyfluthrin samples (52% DF) exceeded BM values. There were no exceedances of either cypermethrin (7% DF) or esfenvalerate (1% DF). Fenpropathrin and resmethrin were not detected in any sample.

  The neonicotinoid imidacloprid was also detected at a fairly high frequency (76% DF). However, only two percent of samples were at concentrations exceeding the minimum BM. Other insecticides detected less frequently included the carbamate carbaryl (22% DF), and the organophosphates malathion (18% DF), diazinon (4% DF), and chlorpyrifos (0% DF). All malathion detections exceeded its BM.

  Several herbicides in the phenoxy analytical screen were detected at high frequency, including 2,4-D (86% DF), triclopyr (82% DF), dicamba (45% DF) and MCPA (10% DF). Only one pesticide in the triazine screen, diuron, had any detections (45% DF). Three dinitroanilines were detected at low rates, including oryzalin (13% DF), prodiamine (8% DF), and pedimethalin (3% DF). None of the herbicide concentrations were above their respective BM.

  The fungicide chlorothalonil was detected in two percent of samples, with no exceedances.

  96-hr water column toxicity tests were conducted using the test organism *Hyalella azteca*. Thirty-four samples collected at storm drain and receiving water monitoring locations for toxicity analysis. Twenty-seven samples had significant observed toxicity, with percent survival ranging between 0 – 63%. All of the samples that experienced minimal toxicity (84 – 100% survivability) were collected within the receiving waters.

  Twenty-five sediment samples were analyzed for the pyrethroids bifenthrin, cyfluthrin, cypermethrin, deltamethrin, fenpropathrin, fenvalerate, lambda-cyhalothrin, and permethrin. Bifenthrin was detected in every sample, ranging in concentrations 2.5 – 752 ug/kg dry weight. Other pyrethroids were detected at various rates, including permethrin (96% DF), deltamethrin (88% DF), cyfluthrin (84% DF), lambda-cyhalothrin (72% DF), cypermethrin (48% DF), and fenvalerate (40% DF). Fenpropathrin was not detected in any sediment sample. Bifenthrin accounted for the largest average percentage (61%) of toxicity units

(TUs; an indicator of potential toxicity), followed by deltamethrin (14%), cyfluthrin (11%), lambda-cyhalothrin (6%), permethrin (4%), and cypermethrin (3%).

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 US EPA OPP benchmark (BM) (ug/L)***		**Number of BM exceedances**	**BM exceedance frequency (%)**
2,4-D	106	91	86	0.05	13.1	VA	0	0
Benfluralin	15	0	0	0.05	1.9	FC	0	0
Bifenthrin	115	101	88	0.001	0.0013	IC	94	82
Bromacil	24	0	0	0.05	6.8	NA	0	0
Carbaryl	9	2	22	0.005	0.5	IC	0	0
Chlorothalonil	55	1	2	0.05	0.6	IC	0	0
Chlorpyrifos	76	0	0	0.01	0.04	IC	0	0
Cyfluthrin	115	60	52	0.002	0.007	IC	41	36
Cypermethrin	105	7	7	0.005	0.069	IC	0	0
DACT	15	0	0	0.05	50000	FA,IA	0	0
Deltamethrin/ tralomethrin	51	9	18	0.005	0.0041	IC	9	18
Desulfinyl fipronil	107	89	83	0.002	0.59	FC	0	0
Desulfinyl fipronil amide	107	12	11	0.004	na	-	-	na
Diazinon	76	3	4	0.01	0.11	IA	0	0
Dicamba	97	44	45	0.05	61	NA	0	0
Diuron	33	15	45	0.02	2.4	NA	0	0
Ethalfluralin	15	0	0	0.05	0.4	FC	0	0
Fenpropathrin	17	0	0	0.002	0.064	IC	0	0
Fenvalerate/ esfenvalerate	99	1	1	0.002	0.017	IC	0	0
Fipronil	107	100	93	0.002	0.011	IC	95	89
Fipronil amide	107	32	30	0.008	na	-	-	na
Fipronil sulfide	107	12	11	0.002	0.11	IC	0	0
Fipronil sulfone	107	97	91	0.002	0.037	IC	89	83
Hexazinone	15	0	0	0.05	7	NA	0	0
Imidacloprid	106	81	76	0.02	1.05	IC	2	2
Lambda-cyhalothrin	115	16	14	0.002	0.002	IC	16	14
Malathion	76	14	18	0.02	0.035	IC	14	18
MCPA	97	10	10	0.05	170	VA	0	0
Norflurazon	9	0	0	0.05	9.7	NA	0	0
Oryzalin	15	2	13	0.05	15.4	VA	0	0
Oxyfluorfen	15	0	0	0.05	0.29	NA	0	0
Pendimethalin	67	2	3	0.005	5.2	NA	0	0
Permethrin	115	67	58	0.002	0.0014	IC	67	58

Pesticide	Number of samples	Number of detections	Detection frequency (%)	Reporting Limit (ug/L)*	Lowest US EPA OPP benchmark (BM) (ug/L)*		Number of BM exceedances	BM exceedance frequency (%)
Prodiamine	12	1	8	0.05	1.5	IC	0	0
Prometon	9	0	0	0.05	98	NA	0	0
Resmethrin	8	0	0	0.01	0.14	FA	0	0
Simazine	24	0	0	0.05	36	NA	0	0
Triclopyr	106	87	82	0.05	100	NA	0	0
Trifluralin	12	0	0	0.05	1.14	FC	0	0

* Only most recent RL listed, multiple RLs possible during sampling period; FA, fish acute; FC, fish chronic; IA, invertebrate acute; IC, invertebrate chronic; NA, 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 (%)	LC50(ug/g OC)	Detection frequency (%) of sediments ≥1 TU*,**	Median TU*
Bifenthrin	25	25	100	0.52	95	3.74
Cyfluthrin	25	21	84	1.08	48	0.87
Cypermethrin	25	12	48	0.38	19	0.00
Deltamethrin/Tralomethrin	25	22	88	0.79	52	1.07
Fenpropathrin	25	0	0	NA	-	-
Fenvalerate/Esfenvalerate	25	10	40	1.54	0	0.00
Lambda-cyhalothrin	25	18	72	0.45	19	0.20
Permethrin	25	24	96	10.83	5	0.21

*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.

** Some data excluded from TU calculations due to missing sediment TOC values

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	374	0	80	0
	Matrix Spikes/Duplicates	374	0	98	26
	Laboratory Control Spikes/Duplicates	Enter No.	Enter No.	94	5
	Blind Spikes	50	0	0	-
	Surrogate Spikes	60	1	94	0
Other QC:	Laboratory Duplicates	Enter No.	Enter No.	18	17
Other QC:	Describe	Enter No.	Enter No.	Enter No.	Enter No.
Explain out of control QC and interpretation of data:	All water except for one surrogate spike was within control limits. For sediment QC, the matrix spike and laboratory duplicates were conducted using sediments containing high concentrations of the respective pyrethroid relative to the spike concentration. This led to an abnormal number of recovery percentages. By calculating recoveries based on total concentrations (spike + nominal), all recoveries were within range.				

4. 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 (recommended)

Appendix III. Water quality data

Appendix IV. Water or sediment monitoring data

Appendix V. Aquatic toxicity data

Appendix VI. Analytical methods