DEPARTMENT OF PESTICIDE REGULATION

SURFACE WATER AMBIENT MONITORING REPORT

Date: March 4, 2021

1. Study highlights

- DPR Study Number 320
- SURF Study Number 464
- Study Title Ambient Surface Water and Mitigation Monitoring in Urban Areas in Southern California during Fiscal Year 2019–2020
- Project Lead Aniela Burant
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- Protocol url
  https://www.cdpr.ca.gov/docs/emon/pubs/protocol/study320_sampling_plan_fy_19_20.pdf
  Protocol available online for five years, thereafter, please request a copy from the SWPP list of archived files

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- Study Area
  County: Los Angeles, Orange, San Diego
  Waterbody/Watershed: Anaheim-Barber City Channel, Ballona Creek, Bolsa Chica Channel, Bouquet Creek, Chollas Creek, Compton Creek, Dominguez Channel, Los Angeles River, Salt Creek, San Diego River, San Gabriel River, Wood Canyon Creek

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- Land use type ☐ Ag ☒ Urban ☐ Forested ☐ Mixed ☐ Other

- Water body type
  ☒ Creek ☒ River ☐ Pond ☐ Lake
  ☐ Drainage Ditch ☒ Storm drain outfall ☒ Other Wetland Outfall

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- Objectives
  1. Determine presence and concentrations of selected priority pesticides in runoff and receiving waters of Southern California urban watersheds under dry and storm conditions.
  2. Compare measured concentrations of pesticides to aquatic toxicity thresholds.
  3. Evaluate pesticide concentration trends through long-term monitoring.
  4. Determine the acute toxicity of water samples using laboratory tests conducted with the amphipod *Hyalella azteca* and the midge *Chironomus* species.
  5. Evaluate the effectiveness of a small constructed wetland to remove pesticides from runoff.
  6. Monitor deposition of sediment-bound pyrethroids within selected watersheds.
  7. Evaluate commercial land-use as potential source of pesticides to urban waterways.

- Sampling period July 1, 2019 – June 30, 2020

- Pesticides monitored
  2,4-D, abamectin, acetamiprid, atrazine, azoxystrobin, bensulide, bifenthrin, boscalid, bromacil, carbaryl, chlorantraniliprole, chlorfenapyr, chlorpyrifos, clothianidin, cyfluthrin, cypermethrin, cyprodinil,

deltamethrin/tralomethrin, desulfinyl fipronil, desulfinyl fipronil amide, diazinon, dicamba, diflubenzuron, dimethoate, diuron, esfenvalerate/fenvalerate, ethoprop, etofenprox, fenamidone, fenhexamid, fipronil, fipronil amide, fipronil sulfide, fipronil sulfone, fludioxonil, hexazinone, imidacloprid, indoxacarb, isoxaben, kresoxim-methyl, lambda cyhalothrin, malathion, MCPA, mefenoxam, methidathion, methomyl, methoxyfenozide, metribuzin, norflurazon, oryzalin, oxadiazon, oxyfluorfen, pendimethalin, permethrin total, prodiamine, prometon, prometryn, propanil, propargite, propiconazole, pyraclostrobin, pyriproxyfen, quinoxyfen, simazine, s-metolachlor, tebuconazole, tebufenozide, tebuthiuron, thiabendazole, thiacloprid, thiamethoxam, thiobencarb, triclopyr, trifloxystrobin, trifluralin

- Major findings

  Bifenthrin, imidacloprid, and fipronil were the most frequently detected insecticides in Southern California (Table 1). These three insecticides had the highest exceedances of the lowest aquatic life benchmarks set by the United States Environmental Protection Agency (US EPA). Among the three insecticides, there were higher detection frequencies (DF) during storm events (ranging from 93 – 100% DF) than non-storm events (ranging from 57 – 90% DF). The DF for bifenthrin was higher in storm drains (96% DF) than waterways (85% DF). Fipronil and imidacloprid DF was slightly higher in waterways (76% DF for fipronil and 94% DF for imidacloprid) than storm drains (75% DF for fipronil and 92% DF for imidacloprid). All imidacloprid and fipronil detections and most of the bifenthrin detections (85%) were above the lowest US EPA aquatic life benchmarks.

  Bifenthrin was the most frequently detected pyrethroid in water samples in Southern California. Six other pyrethroids were detected at lower frequencies. All detections of deltamethrin (40% DF) and lambda-cyhalothrin (32% DF) exceeded their respective lowest US EPA aquatic life benchmark. Almost all permethrin (63% DF) detections were benchmark exceedances (58%). Cyfluthrin was detected in 65% of samples, but had a 40% benchmark exceedance. Cypermethrin and esfenvalerate had lower DFs (<20%) and benchmark exceedances (<3%).

  In addition to fipronil, several fipronil degradates by-products were detected in surface waters, including fipronil sulfone (77% DF), desulfinyl fipronil (64% DF), fipronil amide (39% DF), desulfinyl fipronil amide (15% DF), and fipronil sulfide (10% DF). Only fipronil sulfone exceeded benchmark values in 41% of samples. Fipronil amide and desulfinyl fipronil amide do not have established benchmarks.

  Other neonicotinoids, in addition to imidacloprid, were sampled this year. Thiamethoxam was detected in 23% of samples, exceeding its aquatic life benchmark in one sample (2% exceedance). Acetamiprid had a DF of 7%, with no aquatic life benchmark exceedances. Clothianidin was not detected.

  The other insecticides concentrations above reporting limits were malathion (30% DF), methoxyfenozide (25% DF), carbaryl (15% DF), chlorfenapyr (13% DF), chlorantraniliprole (5% DF), and pyriproxyfen (2% DF). Only malathion (15% benchmark exceedance) and pyriproxyfen (2% benchmark exceedance) exceeded their respective US EPA aquatic life benchmarks.

  Several herbicides and fungicides were present in surface water samples, including diuron (87% DF), triclopyr (81% DF), 2,4-D (63% DF), tebucanazole (43% DF), dicamba (38% DF), isoxaben (18% DF), propiconazole (16% DF), oryzalin (15% DF), oxadiazon (10% DF), MCPA (6% DF), oxyfluorfen (6% DF), pendimethalin (6% DF), azoxystrobin (3% DF), bromacil (3% DF), and pyraclostrobin (3% DF). Only one fungicide concentration, pyraclostrobin, exceeded its US EPA aquatic life benchmark (2%

exceedance). No herbicide exceeded its respective US EPA aquatic life benchmark. No other pesticide was detected within the sampling period.

96-hour water column toxicity tests were conducted using the tests organisms *Hyalella azteca* and *Chironomus* species. For toxicity testing using *H. azteca*, four samples were collected at storm drain outlets; two during a storm event and two during the dry season. Significant toxicity was observed in all samples collected at storm drains with 78 – 100% mortality during all events. Ten samples were collected in receiving waters; eight during the dry season and two during storm events. Samples were collected within receiving waters experienced a wide range of toxicity, with 100% mortality observed during storm events and 0 – 100% mortality observed during the dry season. Two of the samples during dry events had statistically significant toxicity.

For *Chironomus* testing, four samples were collected at storm drain outlets; two during storm events and two during the dry season. Significant toxicity was observed in all samples collected at storm drains, with 55 – 100% mortality during all events. Eleven samples were collected in receiving waters, three during storm events and eight during the dry season. All of the storm event samples were significantly toxic (100% mortality). One sample collected during the dry season was significantly toxic, with 48% mortality. The other samples were not significantly toxic (7 – 25% mortality).

Three sediment samples were analyzed for pyrethroids (Table 2). Bifenthrin was detected in every single sample above the lowest organic carbon-normalized sediment LC_{50}. Deltamethrin was detected in every sample and exceeded the lowest organic carbon-normalized sediment LC_{50} in one sample. There were no other LC_{50} exceedances. Cyfluthrin, esfenvalerate, and permethrin were detected in every sample. Cypermethrin and lambda-cyhalothrin were detected in 67% of the samples.

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

DDVP, sulfometuron-methyl, PCNB, dichlobenil

2. Pesticide detection frequency

Data available in SURF (https://www.cdpr.ca.gov/docs/emon/surfwtr/surfdata.htm) upon yearly update. Contact Project Lead for data not yet uploaded. In SURF, use "SURF Study Number" (Section 1) for obtaining the data.

Table 1. Pesticides detected in water

Pesticide	Sample Number	Detection Number[1]	Detection frequency (%)[1]	Minimum Reporting Limit (µg/L)	Lowest USEPA benchmark (BM) (µg/L)[2]	BM Type[3]	Number of BM exceed-ances	BM exceedance frequency (%)
2,4-D	16	10	63	0.05	299.2	VA	0	0
Abamectin	4	0	0	0.02	0.17	IA	0	0
Acetamiprid	61	4	7	0.02	2.1	IC	0	0
Atrazine	4	0	0	0.02	1	NA	0	0
Azoxystrobin	61	2	3	0.02	44	IC	0	0
Bensulide	4	0	0	0.02	11	IC	0	0
Bifenthrin	65	59	91	0.001	0.0013	IC	55	85

Pesticide	Sample Number	Detection Number[1]	Detection frequency (%)[1]	Minimum Reporting Limit (µg/L)	Lowest USEPA benchmark (BM) (µg/L)[2]	BM Type[3]	Number of BM exceed-ances	BM exceedance frequency (%)
Boscalid	4	0	0	0.02	116	FC	0	0
Bromacil	61	2	3	0.02	6.8	NA	0	0
Carbaryl	61	9	15	0.02	0.5	IC	0	0
Chlorantraniliprole	61	3	5	0.02	4.47	IC	0	0
Chlorfenapyr	16	2	13	0.1	2.915	IA	0	0
Chlorpyrifos	61	0	0	0.02	0.04	IC	0	0
Clothianidin	4	0	0	0.02	0.05	IC	0	0
Cyfluthrin	65	42	65	0.002	0.0074	IC	26	40
Cypermethrin	65	13	20	0.005	0.069	IC	1	2
Cyprodinil	4	0	0	0.02	8.2	IC	0	0
Deltamethrin/Tralomethrin	65	26	40	0.004	0.0041	IC	26	40
Desulfinyl Fipronil	61	39	64	0.01	0.54	FC	0	0
Desulfinyl Fipronil Amide	61	9	15	0.01		(no BM)	0	0
Diazinon	4	0	0	0.02	0.105	IA	0	0
Dicamba	16	6	38	0.05	61	NA	0	0
Diflubenzuron	4	0	0	0.02	0.00025	IC	0	0
Dimethoate	4	0	0	0.02	0.5	IC	0	0
Diuron	61	53	87	0.02	2.4	NA	0	0
Esfenvalerate/Fenvalerate	65	8	12	0.005	0.017	IC	2	3
Ethoprop	4	0	0	0.02	0.8	IC	0	0
Etofenprox	4	0	0	0.02	0.17	IC	0	0
Fenamidone	4	0	0	0.02	4.7	FC	0	0
Fenhexamid	4	0	0	0.02	101	FC	0	0
Fipronil	61	46	75	0.01	0.011	IC	46	75
Fipronil Amide	61	24	39	0.01		(no BM)	0	0
Fipronil Sulfide	61	6	10	0.01	0.11	IC	0	0
Fipronil Sulfone	61	47	77	0.01	0.037	IC	25	41
Fludioxonil	4	0	0	0.02	14	IC	0	0
Hexazinone	4	0	0	0.02	7	NA	0	0
Imidacloprid	61	57	93	0.01	0.01	IC	57	93
Indoxacarb	61	0	0	0.02	75	IC	0	0
Isoxaben	61	11	18	0.02	10	VA	0	0
Kresoxim-methyl	4	0	0	0.02	30.3	NA	0	0
Lambda Cyhalothrin	65	21	32	0.002	0.002	IC	21	32
Malathion	61	18	30	0.02	0.049	IA	9	15
MCPA	16	1	6	0.05	170	VA	0	0
Mefenoxam	4	0	0	0.02	1200	IC	0	0
Methidathion	4	0	0	0.02	0.66	IC	0	0
Methomyl	4	0	0	0.02	0.6	IC	0	0

Pesticide	Sample Number	Detection Number[1]	Detection frequency (%)[1]	Minimum Reporting Limit (µg/L)	Lowest USEPA benchmark (BM) (µg/L)[2]	BM Type[3]	Number of BM exceed-ances	BM exceedance frequency (%)
Methoxyfenozide	4	1	25	0.02	3.1	IC	0	0
Metribuzin	4	0	0	0.02	8.1	NA	0	0
Norflurazon	4	0	0	0.02	9.7	NA	0	0
Oryzalin	61	9	15	0.02	13	VA	0	0
Oxadiazon	61	6	10	0.02	5.2	NA	0	0
Oxyfluorfen	16	1	6	0.05	0.29	NA	0	0
Pendimethalin	16	1	6	0.05	5.2	NA	0	0
Permethrin Total	65	41	63	0.001	0.0014	IC	38	58
Prodiamine	16	0	0	0.05	1.5	IC	0	0
Prometon	4	0	0	0.02	98	NA	0	0
Prometryn	4	0	0	0.02	1.04	NA	0	0
Propanil	4	0	0	0.02	9.1	FC	0	0
Propargite	4	0	0	0.02	7	IA	0	0
Propiconazole	61	10	16	0.02	21	NA	0	0
Pyraclostrobin	61	2	3	0.02	1.5	NA	1	2
Pyriproxyfen	61	1	2	0.015	0.015	IC	1	2
Quinoxyfen	4	0	0	0.02	13	FC	0	0
Simazine	4	0	0	0.02	6	NA	0	0
S-Metolachlor	4	0	0	0.02	8	NA	0	0
Tebuconazole	61	26	43	0.02	11	FC	0	0
Tebufenozide	4	0	0	0.02	29	IC	0	0
Tebuthiuron	4	0	0	0.02	50	NA	0	0
Thiabendazole	4	0	0	0.02	42	IC	0	0
Thiacloprid	4	0	0	0.02	0.97	IC	0	0
Thiamethoxam	61	14	23	0.02	0.74	IC	1	2
Thiobencarb	4	0	0	0.02	1	IC	0	0
Triclopyr	16	13	81	0.05	5900	NA	0	0
Trifloxystrobin	4	0	0	0.02	2.76	IC	0	0
Trifluralin	16	0	0	0.05	1.9	FC	0	0

[1] Clothianidin detections are qualitative only

[2] Benchmarks are used as a screening tool for risk analysis

[3] 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

Pesticide	Sample Number	Detection Number	Detection frequency (%)	LC_{50} (µg/kg OC)*	Detection Frequency > LC_{50} (%)
Bifenthrin	3	3	100	520	100
Cyfluthrin	3	3	100	1080	0
Cypermethrin	3	2	67	380	0

Pesticide	Sample Number	Detection Number	Detection frequency (%)	LC_{50} (µg/kg OC)*	Detection Frequency > LC_{50} (%)
Deltamethrin/Tralomethrin	3	3	100	790	33
Esfenvalerate/Fenvalerate	3	3	100	1540	0
Lambda Cyhalothrin	3	2	67	450	0
Permethrin Total	3	3	100	10830	0

*LC50 is derived from 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)

3. Tracking Exceedances of Aquatic Benchmarks or Sediment LC50 values

For further data analysis: pesticides that have ≥ 10% aquatic benchmark exceedance rate or exceed their OC normalized sediment LC_{50} for three consecutive years are recommended for further detailed data analysis if no analysis has been complete in the past five years (Ambient Urban Monitoring Methodology SOP METH014).

Table 3. Pesticides with three consecutive years of either 1) ≥ 10% of their detections exceeding their lowest USEPA aquatic life water benchmark or 2) percentage of sediment detections exceeding their sediment LC_{50} (normalized to OC)

Pesticide In Water	Water BM exceedance frequency (%)	Pesticide in Sediment	Sediment DF > LC50 (%)	Year	Last written evaluation (reference)	Further data analysis (Y/N)
Bifenthrin	85	Bifenthrin	100	320 FY19_20	Budd et al. (2020)	N
Bifenthrin	68	Bifenthrin	80	270 FY18_19	Budd et al. (2020)	N
Bifenthrin	75	Bifenthrin	62.5	270 FY17_18	Budd et al. (2020)	N
Cyfluthrin	40			320 FY19_20	Budd et al. (2020)	N
Cyfluthrin	26			270 FY18_19	Budd et al. (2020)	N
Cyfluthrin	35			270 FY17_18	Budd et al. (2020)	N
Deltamethrin/ Tralomethrin	40			320 FY19_20	Budd et al. (2020)	N
Deltamethrin/ Tralomethrin	25			270 FY18_19	Budd et al. (2020)	N
Deltamethrin/ Tralomethrin	28			270 FY17_18	Budd et al. (2020)	N
Fipronil	75			320 FY19_20	Budd et al. (2015)	Y
Fipronil	64			270 FY18_19	Budd et al. (2015)	Y
Fipronil	77			270 FY17_18	Budd et al. (2015)	Y
Fipronil Sulfone	41			320 FY19_20	Budd et al. (2015)	Y
Fipronil Sulfone	42			270 FY18_19	Budd et al. (2015)	Y
Fipronil Sulfone	46			270 FY17_18	Budd et al. (2015)	Y

Pesticide In Water	Water BM exceedance frequency (%)	Pesticide in Sediment	Sediment DF > LC50 (%)	Year	Last written evaluation (reference)	Further data analysis (Y/N)
Imidacloprid	93			320 FY19_20	Ensminger et al. (2013)	Y
Imidacloprid	88			270 FY18_19	Ensminger et al. (2013)	Y
Imidacloprid	90			270 FY17_18	Ensminger et al. (2013)	Y
Lambda Cyhalothrin	32			320 FY19_20	Budd et al. (2020)	N
Lambda Cyhalothrin	19			270 FY18_19	Budd et al. (2020)	N
Lambda Cyhalothrin	35			270 FY17_18	Budd et al. (2020)	N
Permethrin Total	58			320 FY19_20	Budd et al. (2020)	N
Permethrin Total	25			270 FY18_19	Budd et al. (2020)	N
Permethrin Total	33			270 FY17_18	Budd et al. (2020)	N

4. QC

Table 4. Laboratory Quality Control (QC) summary

QC Type	Sample Matrix	Total Number	Number of QC Out of Control
Blind Spike	Water	11	2
Lab Blank	Water	438	0
Matrix Spike	Water	447	4
Lab Blank	Sediment	9	0
Matrix Spike	Sediment	9	0

5. Data: water quality, aquatic toxicity, and analytical chemistry results

Water quality data, aquatic toxicity data, and monitoring results are available upon request. Please contact the Project Lead or SURF database administrator (https://www.cdpr.ca.gov/docs/emon/surfwtr/surfdata.htm) for the data.