DEPARTMENT OF PESTICIDE REGULATION (DPR) Date: May 24, 2024

SURFACE WATER AMBIENT MONITORING REPORT

Study highlights

- DPR Study Number 320
- SURF (Surface Water Database) Study Number 464
- Study Title Ambient Surface Water and Mitigation Monitoring in Urban Areas in Southern California (WY2022/2023)
- Project Lead Harihar Nepal
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- Protocol Source (*protocol available online for five years, thereafter, request a copy from the SWPP list of archived files)* Environmental Monitoring Protocol Page

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- Study Area

  County: Los Angeles, Orange, San Diego

  Waterbody/Watershed: Ballona Creek, Bouquet Creek, Dominguez Channel, Los Angeles River, San Gabriel River, Bolsa Chica Channel, Salt Creek, San Diego Creek, Wood Canyon Creek, Chollas Creek, San Diego River

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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

- Objectives
  1. Determine presence and concentrations of selected priority pesticides in runoff and receiving waters of Southern California urban watersheds during 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 midges *Chironomus dilutus*.
  5. Monitor deposition of sediment-bound pyrethroids within selected watersheds;
  6. Evaluate land-use gradients to determine source contributions of pesticides to urban waterways;
  7. Evaluate effectiveness of carbon-filled socks to reduce pesticides in urban runoff under field conditions;
  8. Evaluate effect of filtering samples on pyrethroid concentrations and *Hyalella azteca* toxicity.

- Sampling period July 1, 2022 – September 30, 2023[a]

[a]This sampling period consists of more than one year's data as the project sampling period was changed from a fiscal year (July 1 to June 30) to a water year (WY; October 1 to September 30).

- Major findings

INSECTICIDES: In the Southern California urban monitoring program, 8 out of 36 insecticides detected in water samples exceeded their USEPA aquatic life benchmark (BM) at a level >10% during the study period. Imidacloprid was the most frequently detected insecticide, detected in 92% of the water samples. Bifenthrin was second with an 85% detection frequency (DF). Fipronil sulfone (71% DF), fipronil (64% DF), desulfinyl fipronil (50% DF), cyfluthrin (40% DF), deltamethrin/tralomethrin (40% DF), fipronil amide (40% DF), lambda cyhalothrin (37% DF), permethrin (37% DF), thiamethoxam (32% DF), desulfinyl fipronil amide (17% DF), malathion (13% DF), cypermethrin (12% DF) and chlorantraniliprole (11% DF) made up the remaining top 15 most-detected insecticides. However, only the detections of imidacloprid (92 % exceedance frequency (EF), bifenthrin (85% EF), fipronil (62% EF), cyfluthrin (40% EF), deltamethrin (40% EF), lambda cyhalothrin (37% EF), permethrin (25% EF), cypermethrin (12% EF), esfenvalerate (6% EF), and malathion (2% EF) were above their minimum USEPA BM. Fipronil sulfone, desulfinyl fipronil, fipronil amide, thiamethoxam, desulfinyl fipronil amide, or chlorantraniliprole concentrations did not exceed their associated BM (Table 1). Clothianidin (7% DF), esfenvalerate (6% DF), carbaryl (2% DF), acetamiprid (1% DF), and fipronil sulfide (1% DF) were occasionally detected in the study.

Fipronil is the only pesticide which has its degradates monitored. All fipronil's degradates were detected: fipronil sulfone (71% DF), desulfinyl fipronil (50% DF), fipronil amide (40% DF), desulfinyl fipronil amide (17% DF), and fipronil sulfide (1% DF). Out of all fipronil degradate detections, none exceeded aquatic life BMs. Fipronil amide desulfinyl and fipronil amide do not have established BM.

HERBICIDES. Eleven herbicides were detected during the sampling period. Diuron was the most frequently detected (68% DF) herbicides in the study. Other detected herbicides included 2,4-D (45% DF), triclopyr (40% DF), dicamba (15% DF), isoxaben (7% DF), bromacil (5% DF), simazine (4% DF), oxadiazon (2% DF), S-metolachlor (2% DF), oryzalin (1% DF) and prometon (1% DF). Diuron was the only herbicide to exceed its lowest BM (35% EF). None of the other 14 herbicides monitored in the study were detected (Table 2).

FUNGICIDES. Four fungicides were detected throughout the sampling period. Propiconazole was the most-frequently detected fungicide (26% DF), followed by tebuconazole (24% DF), thiabendazole (5% DF), and azoxystrobin (1% DF). No fungicides was detected over its lowest BM level (Table 3).

TOXICITY. UC Davis Aquatic Health Program conducted *Hyalella azteca, Ceriodaphnia dubia* and *Chironomus dilutus* 96-hour water column toxicity tests on 38 samples collected during at least one dry event, one storm event, and one winter non-storm event. Three samples were tested on *C. dubia,* six samples were tested on *C. dilutus* and 29 samples were tested on *H. azteca*. Seventeen whole water and four filtered water samples were significantly toxic to *H. Azteca.* Two non-storm samples were also significantly toxic to *C. dilutus*. Both dry season and one winter non-storm event sample were not toxic to *C. dilutus.* All three storm event samples were not toxic to *C. dubia.*

SEDIMENTS. Two sediment samples were collected during this study period. Sediments were analyzed for seven pyrethroids: bifenthrin, cyfluthrin, cypermethrin, deltamethrin, esfenvalerate, lambda cyhalothrin, and permethrin. Bifenthrin, cyfluthrin, cypermethrin, deltamethrin, lambda cyhalothrin, and permethrin were detected in both samples (Table 4). Detection frequencies (LC_{50}) for WY 22-23 were not calculated, as sediment TOC values were not available for these samples.

- Recommendations for pesticides that need a CDFA analytical method:

  The following pesticides were recommended by the Surface Water Monitoring Prioritization (SWMP) model for monitoring: DDVP, dithiopyr, glufosinate-ammonium, imazapyr isopropylamine salt, PCNB, and sulfometuron methyl. These analytes are in need of analytical methods and were therefore not monitored during WY 22-23.

Pesticide (insecticide, herbicide, and fungicide) detection frequency

Data available in SURF 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. Insecticide detection in water

Insecticide	Number of samples	Number of detections	Detection frequency (%)[1]	Minimum Reporting Limit (µg/L)	Lowest USEPA BM (µg/L)[2]	BM Type[3]	Number of BM exceedances	BM exceedance frequency (%)
Abamectin	84	0	0	0.02	0.17	IA	0	0
Acetamiprid	84	1	1	0.02	2.1	IC	0	0
Bifenthrin	84	71	85	0.001	0.00005	IC	71	85
Carbaryl	84	2	2	0.02	0.5	IC	0	0
Chlorantraniliprole	84	9	11	0.02	3.02	IC	0	0
Chlorfenapyr	14	0	0	0.1	2.915	IA	0	0
Chlorpyrifos	84	0	0	0.02	0.005	IC	0	0
Clothianidin	84	6	7	0.02	0.05	IC	-	-
Cyfluthrin	84	34	40	0.002	0.00012	IC	34	40
Cypermethrin	84	10	12	0.005	0.00005	IC	10	12
Deltamethrin/Tralomethrin	84	34	40	0.004	0.000026	IC	34	40
Desulfinyl Fipronil	84	42	50	0.01	0.53	FC	0	0

Insecticide	Number of samples	Number of detections	Detection frequency (%)[1]	Minimum Reporting Limit (µg/L)	Lowest USEPA (BM) (µg/L)[2]	BM Type[3]	Number of BM exceedances	BM exceedance frequency (%)
Desulfinyl Fipronil Amide	84	14	17	0.01		(no BM)	0	0
Diazinon	84	0	0	0.02	0.105	IA	0	0
Diflubenzuron	84	0	0	0.02	0.00025	IC	0	0
Dimethoate	84	0	0	0.02	0.5	IC	0	0
Esfenvalerate/Fenvalerate	84	5	6	0.005	0.0000309	IC	5	6
Ethoprop	84	0	0	0.02	0.8	IC	0	0
Etofenprox	84	0	0	0.02	0.17	IC	0	0
Fipronil	84	54	64	0.01	0.011	IC	52	62
Fipronil Amide	84	34	40	0.01		(no BM)	0	0
Fipronil Sulfide	84	1	1	0.01	0.83	FC	0	0
Fipronil Sulfone	84	60	71	0.01	0.22	IC	0	0
Imidacloprid	84	77	92	0.01	0.01	IC	77	92
Indoxacarb	84	0	0	0.02	75	IC	0	0
Lambda Cyhalothrin	84	31	37	0.002	0.00004	IA	31	37
Malathion	84	11	13	0.02	0.049	IA	2	2
Methidathion	84	0	0	0.02	0.66	IC	0	0
Methomyl	84	0	0	0.02	0.6	IC	0	0
Methoxyfenozide	84	0	0	0.02	3.1	IC	0	0
Permethrin Total	84	31	37	0.001	0.0033	IA	21	25
Propargite	84	0	0	0.02	7	IA	0	0
Pyriproxyfen	84	0	0	0.015	0.015	IC	0	0
Tebufenozide	84	0	0	0.02	29	IC	0	0
Thiacloprid	84	0	0	0.02	0.97	IC	0	0
Thiamethoxam	84	27	32	0.02	0.74	IC	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. Herbicide detection in water

Herbicide	Number of samples	Number of detections	Detection frequency (%)	Minimum Reporting Limit (µg/L)	Lowest USEPA BM (µg/L)[1]	BM Type[2]	Number of BM exceedances	BM exceedance frequency (%)
2,4-D	20	9	45	0.05	299.2	VA	0	0
Atrazine	84	0	0	0.02	1	NVA	0	0
Bensulide	84	0	0	0.02	11	IC	0	0

Herbicide	Number of samples	Number of detections	Detection frequency (%)	Minimum Reporting Limit (µg/L)	Lowest USEPA BM (µg/L)[1]	BM Type[2]	Number of BM exceedances	BM exceedance frequency (%)
Bromacil	84	4	5	0.02	6.8	NVA	0	0
Dicamba	20	3	15	0.05	61	NVA	0	0
Diuron	84	57	68	0.02	0.13	VA	29	35
Hexazinone	84	0	0	0.02	7	NVA	0	0
Isoxaben	84	6	7	0.02	10	VA	0	0
MCPA	20	0	0	0.05	170	VA	0	0
Metribuzin	84	0	0	0.02	8.1	NVA	0	0
Norflurazon	84	0	0	0.02	6.03	NVA	0	0
Oryzalin	84	1	1	0.02	13	VA	0	0
Oxadiazon	84	2	2	0.02	0.88	FC	0	0
Oxyfluorfen	14	0	0	0.05	0.33	VA	0	0
Pendimethalin	14	0	0	0.05	5.2	NVA	0	0
Prodiamine	14	0	0	0.05	1.5	IC	0	0
Prometon	84	1	1	0.02	98	NVA	0	0
Prometryn	84	0	0	0.02	1.04	NVA	0	0
Propanil	84	0	0	0.02	2.4	FC	0	0
Simazine	84	3	4	0.02	6	NVA	0	0
S-Metolachlor	84	2	2	0.02	8	NVA	0	0
Tebuthiuron	84	0	0	0.02	50	NVA	0	0
Thiobencarb	84	0	0	0.02	1	IC	0	0
Triclopyr	20	8	40	0.05	4200	NVA	0	0
Trifluralin	14	0	0	0.05	1.9	FC	0	0

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

[2]FA, fish acute; FC, fish chronic; IA, invertebrate acute; IC, invertebrate chronic; NA, non-vascular acute; VA, vascular acute

Table 3. Fungicide detection in water

Fungicide	Number of samples	Number of detections	Detection frequency (%)	Minimum Reporting Limit (µg/L)	Lowest USEPA BM (µg/L)[1]	BM Type[2]	Number of BM exceedances	BM exceedance frequency (%)
Azoxystrobin	84	1	1	0.02	44	IC	0	0
Boscalid	84	0	0	0.02	116	FC	0	0
Cyprodinil	84	0	0	0.02	8.2	IC	0	0
Fenamidone	84	0	0	0.02	4.7	FC	0	0
Fenhexamid	84	0	0	0.02	101	FC	0	0
Fludioxonil	84	0	0	0.02	14	IC	0	0
Kresoxim-methyl	84	0	0	0.02	30.3	NVA	0	0
Mefenoxam	84	0	0	0.02	1200	IC	0	0
Propiconazole	84	22	26	0.02	15	FC	0	0
Pyraclostrobin	84	0	0	0.02	1.5	NVA	0	0

Fungicide	Number of samples	Number of detections	Detection frequency (%)	Minimum Reporting Limit (µg/L)	Lowest USEPA BM (µg/L)[1]	BM Type[2]	Number of BM exceedances	BM exceedance frequency (%)
Quinoxyfen	84	0	0	0.02	13	FC	0	0
Tebuconazole	84	20	24	0.02	11	FC	0	0
Thiabendazole	84	4	5	0.02	42	IC	0	0
Trifloxystrobin	84	0	0	0.02	2.76	IC	0	0

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

[2]FA, fish acute; FC, fish chronic; IA, invertebrate acute; IC, invertebrate chronic; NA, non-vascular acute; VA, vascular acute

Table 4. Pesticide detection in sediment

Pesticide	Number of samples	Number of detections	Detection frequency (%)	LC_{50} (µg/kg OC)*	Detection frequency > LC_{50} (%)**
Bifenthrin	2	2	100	520	NA
Cyfluthrin	2	2	100	1080	NA
Cypermethrin	2	2	100	380	NA
Deltamethrin/Tralomethrin	2	2	100	790	NA
Esfenvalerate/Fenvalerate	2	0	0	1540	NA
Lambda Cyhalothrin	2	2	100	45	NA
Permethrin Total	2	2	100	10830	NA

*LC_{50} 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)

** Detection frequency >LC50 for WY 22-23 was not calculated as sediment TOC values were not available for these samples.

Tracking Exceedances of Aquatic Benchmarks or Sediment LC50 values

For further data analysis: pesticides that have ≥ 10% aquatic benchmark exceedance rate or exceed their organic carbon content (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 5. 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	Matrix	Current year (2023)	2022	2021	Last written evaluation (reference)	Further data analysis (Y/N)
Bifenthrin	Water	85	81	83	Budd et al. (2020)	N
Cyfluthrin	Water	40	46	40	Budd et al. (2020)	N
Cypermethrin	Water	12	15	25	Budd et al. (2020)	N
Deltamethrin/ Tralomethrin	Water	40	49	54	Budd et al. (2020)	N
Diuron	Water	35	35	46	Ensminger et al. (2013)	Y
Fipronil	Water	62	69	78	Budd et al. (2015)	N
Imidacloprid	Water	92	85	81	Ensminger et al. (2013)	Y
Lambda Cyhalothrin	Water	37	44	39	Budd et al. (2015)	N
Bifenthrin	Sediment	NA*	75	50	Budd et al. (2020)	N
Deltamethrin/ Tralomethrin	Sediment	NA*	50	50	Budd et al. (2020)	N

* Detection frequency >LC_{50} for WY 22-23 was not calculated as sediment TOC values were not available for these samples.

Quality Control

Seventy-six matrix spikes, 71 lab blanks, 63 field matrix spikes, 63 field matrix spike duplicates, and 34 surrogate spikes had recoveries outside their QC limits (either below or above) (Table 6). The rest of the quality assurance samples were within the QC limits.

Table 6. Laboratory Quality Control (QC) summary

QC Type	Sample Matrix	Total Number	Number of QC Out of Control
Field Matrix Spike	Water	183	63
Field Matrix Spike Duplicate	Water	183	63
Lab Blank	Water	959	71
Matrix Spike	Water	959	76
Surrogate Spike	Water	138	34
Lab Blank	Sediment	9	0
Matrix Spike	Sediment	9	0

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 for the data.