DEPARTMENT OF PESTICIDE REGULATION (DPR) Date: May 16, 2024

SURFACE WATER AMBIENT MONITORING REPORT

Study highlights

- DPR Study Number 329
- SURF (Surface Water Database) Study Number 261
- Study Title Pesticide monitoring in urban areas of Northern California (FY2022/2023)
- Project Lead Joshua Alvarado, Kari McClanahan
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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

- Study Area
  County: Alameda, Contra Costa, Placer, Sacramento, Santa Clara
  Waterbody/Watershed: Arcade Creek, Guadalupe River, Miner's Ravine, Pleasant Grove Creek, San Lorenzo Creek, Silver Creek, South San Ramon Creek, Upper American River, Walnut 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

- Objectives

1) Identify the presence and concentrations of pesticide contamination in urban runoff and waterways;
2) Evaluate the magnitude of measured concentrations relative to water quality or aquatic toxicity thresholds;
3) At selected monitoring sites, determine the toxicity of water samples in laboratory toxicity tests conducted with *Hyalella azteca* or *Chironomus dilutus*;
4) Evaluate the effectiveness of surface water regulations or label changes through long-term (multi-year) monitoring;
5) Monitor the concentration of sediment-bound pyrethroids at long-term monitoring sites.

- Sampling period July 1, 2022 – September 30, 2023

- Major Findings

  Note that the inclusion of an additional dry sampling period compared to previous years may influence the results.

INSECTICIDES: In the Northern California urban monitoring program, ten insecticides were detected at least 5% of the time. Imidacloprid and bifenthrin were the most frequently detected insecticides, with a detection frequency (DF) of 44% in water samples. Fipronil (16% DF), deltamethrin (14% DF), methoxyfenozide (11% DF), chlorantraniliprole (11% DF), permethrin (10% DF), dinotefuran (10% DF), cyfluthrin (5% DF), and clothianidin (5% DF) made up the rest of the top ten detected insecticides. All detections of imidacloprid, bifenthrin, and deltamethrin were above their lowest USEPA aquatic life benchmarks (BM); none of the chlorantraniliprole, methoxyfenozide, or dinotefuran samples exceeded their lowest BMs. Fipronil and permethrin had benchmark exceedance frequencies (EF) of 14% and 5%, respectively.

Five of the other 24 insecticides in the study were occasionally detected: carbaryl (2% DF) and lambda cyhalothrin, esfenvalerate, chlorpyrifos, and pyriproxyfen all had a DF of 1%.

Fipronil is the only pesticide which had its degradates monitored. Three of fipronil's five degradates were detected: sulfone (25% DF), desulfinyl (10% DF), and amide (6% DF). There were no exceedances of their respective BMs. Fipronil amide and desulfinyl fipronil amide do not have established benchmarks.

HERBICIDES. Twelve herbicides were detected during the year. 2,4-D was the most frequently detected pesticide in the study with a 53% DF. Other frequently detected herbicides included triclopyr (39% DF), diuron (30% DF), and dicamba (23% DF). MCPA, isobaxen, oxadiazon, pendimethalin, propanil, tebuthiuron, oxyfluorfen, and metribuzin were all detected in less than 10% of the samples. Diuron and oxadiazon were the only two herbicides to exceed their benchmark levels (8% EF and 2% EF, respectively). None of the other 13 herbicides monitored were detected.

FUNGICIDES. Of the 14 fungicides monitored, only propiconazole (5% DF), tebuconazole (2% DF), and thiabendazole (1% DF) were detected. None exceeded its lowest benchmark level.

TOXICITY. UC Davis Aquatic Health Program conducted *Hyalella azteca* and *Chironomus dilutus* 96-hour water column toxicity tests on 63 samples collected during three dry events and two storm events. *H. azteca* was tested in 27 dry event samples and 13 storm samples; *C. dilutus* was tested in 23 dry event samples. Fourteen whole water and one filtered water sample were significantly toxic to *H. azteca.* Of these samples, nine were collected during dry events in the Sacramento region (22-80% survival), five were collected during a storm event in Sacramento (0-14% survival), and one was collected during a storm event in the bay area (78% survival). Toxicity for *C. dilutus* was observed in six of the dry event samples: four collected from the Sacramento region (0-78% survival) and two collected from the bay area (69-79% survival).

SEDIMENTS. Sixteen sediment samples were collected from the bay area (Alameda and Santa Clara counties) and the Sacramento region (Placer and Sacramento counties) during the 2022 and 2023 dry sampling events. Sediments were analyzed for seven pyrethroids: bifenthrin, cyfluthrin, cypermethrin, deltamethrin, esfenvalerate, lambda-cyhalothrin, and permethrin. Bifenthrin and deltamethrin were detected in all 12 samples taken from the Sacramento area and none collected from the bay area. Other pyrethroids were detected in the Sacramento area as follows (# of samples): lambda-cyaholthrin (9),

cyfluthrin (8), permethrin (6), and cypermethrin (5). In the bay area, one sample collected from Santa Clara County contained cypermethrin while esfenvalerate was only detected in the Sacramento area with five samples collected from Placer County (Table 2).

- Recommendations for pesticides that need a California Department of Food and Agriculture analytical method (from the Surface Water Monitoring Prioritization model):

  2,2-dibromo-3-nitrilopropionamide (DBNPA), dithiopyr, PCNB

Pesticide 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. Pesticide detection in water

Pesticide	Number of samples	Number of detections	Detection frequency (%)	Minimum Reporting Limit (µg/L)	Lowest USEPA benchmark (BM) (µg/L)[1]	BM Type[2]	Number of BM exceed-ances	BM exceedance frequency (%)
2,4-D	75	40	53	0.05	299.2	VA	0	0
Abamectin	88	0	0	0.02	0.17	IA	0	0
Acetamiprid	87	0	0	0.02	2.1	IC	0	0
Atrazine	88	0	0	0.02	1	NVA	0	0
Azoxystrobin	88	0	0	0.02	44	IC	0	0
Bensulide	88	0	0	0.02	11	IC	0	0
Bifenthrin	87	38	44	0.001	0.00005	IC	38	44
Boscalid	88	0	0	0.02	116	FC	0	0
Bromacil	88	0	0	0.02	6.8	NVA	0	0
Carbaryl	88	2	2.3	0.02	0.5	IC	0	0
Chlorantraniliprole	88	10	11	0.02	3.02	IC	0	0
Chlorfenapyr	76	0	0	0.1	2.915	IA	0	0
Chlorpyrifos	88	1	1.1	0.02	0.005	IC	1	1.1
Clothianidin[3]	87	4	4.6	0.02	0.05	IC	1	1.2
Cyfluthrin	87	4	4.6	0.002	0.00012	IC	4	4.6
Cypermethrin	87	0	0	0.005	0.00005	IC	0	0
Cyprodinil	88	0	0	0.02	8.2	IC	0	0
Deltamethrin/Tralomethrin	87	12	14	0.004	0.000026	IC	12	14
Desulfinyl Fipronil	88	9	10	0.01	0.53	FC	0	0
Desulfinyl Fipronil Amide	88	0	0	0.01		(no BM)	0	0
Diazinon	88	0	0	0.02	0.105	IA	0	0
Dicamba	75	17	23	0.05	61	NVA	0	0
Diflubenzuron	88	0	0	0.02	0.00025	IC	0	0
Dimethoate	88	0	0	0.02	0.5	IC	0	0
Dinotefuran	10	1	10	0.02	6360	FC	0	0
Diuron	88	26	30	0.02	0.13	VA	7	8
Esfenvalerate/Fenvalerate	87	1	1.2	0.005	0.0000309	IC	1	1.2
Ethoprop	88	0	0	0.02	0.8	IC	0	0
Etofenprox	88	0	0	0.02	0.17	IC	0	0
Fenamidone	88	0	0	0.02	4.7	FC	0	0
Fenhexamid	88	0	0	0.02	101	FC	0	0
Fenpropathrin	5	0	0	0.005	0.0015	IC	0	0
Fipronil	88	14	16	0.01	0.011	IC	12	14
Fipronil Amide	88	5	5.7	0.01		(no BM)	0	0

Pesticide	Number of samples	Number of detections	Detection frequency (%)	Minimum Reporting Limit (µg/L)	Lowest USEPA benchmark (BM) (µg/L)[1]	BM Type[2]	Number of BM exceed-ances	BM exceedance frequency (%)
Fipronil Sulfide	88	0	0	0.01	0.83	FC	0	0
Fipronil Sulfone	88	22	25	0.01	0.22	IC	0	0
Fludioxonil	88	0	0	0.02	14	IC	0	0
Hexazinone	88	0	0	0.02	7	NVA	0	0
Imidacloprid	87	38	44	0.01	0.01	IC	38	44
Indoxacarb	88	0	0	0.02	75	IC	0	0
Isoxaben	88	6	6.8	0.02	10	VA	0	0
Kresoxim-methyl	88	0	0	0.02	30.3	NVA	0	0
Lambda Cyhalothrin	87	1	1.2	0.002	0.00004	IA	1	1.2
Malathion	88	0	0	0.02	0.049	IA	0	0
MCPA	75	7	9.3	0.05	170	VA	0	0
Mefenoxam	88	0	0	0.02	1200	IC	0	0
Methidathion	88	0	0	0.02	0.66	IC	0	0
Methomyl	88	0	0	0.02	0.6	IC	0	0
Methoxyfenozide	88	10	11	0.02	3.1	IC	0	0
Metribuzin	88	1	1.1	0.02	8.1	NVA	0	0
Norflurazon	88	0	0	0.02	6.03	NVA	0	0
Oryzalin	88	0	0	0.02	13	VA	0	0
Oxadiazon	88	5	5.7	0.02	0.88	FC	2	2.3
Oxyfluorfen	76	2	2.6	0.05	0.33	VA	0	0
Pendimethalin	76	4	5.3	0.05	5.2	NVA	0	0
Permethrin	87	9	10	0.001	0.0033	IA	4	4.6
Prodiamine	76	0	0	0.05	1.5	IC	0	0
Prometon	88	0	0	0.02	98	NVA	0	0
Prometryn	88	0	0	0.02	1.04	NVA	0	0
Propanil	88	4	4.6	0.02	2.4	FC	0	0
Propargite	88	0	0	0.02	7	IA	0	0
Propiconazole	88	4	4.6	0.02	15	FC	0	0
Pyraclostrobin	88	0	0	0.02	1.5	NVA	0	0
Pyriproxyfen	88	1	1.1	0.015	0.015	IC	1	1.1
Quinoxyfen	88	0	0	0.02	13	FC	0	0
Simazine	88	0	0	0.02	6	NVA	0	0
S-Metolachlor	88	0	0	0.02	8	NVA	0	0
Sulfoxaflor	10	0	0	0.02	660	FC	0	0
Tebuconazole	88	2	2.3	0.02	11	FC	0	0
Tebufenozide	88	0	0	0.02	29	IC	0	0
Tebuthiuron	88	3	3.4	0.02	50	NVA	0	0
Thiabendazole	88	1	1.1	0.02	42	IC	0	0
Thiacloprid	87	0	0	0.02	0.97	IC	0	0
Thiamethoxam	87	0	0	0.02	0.74	IC	0	0
Thiobencarb	88	0	0	0.02	1	IC	0	0
Triclopyr	75	29	39	0.05	4200	NVA	0	0

Pesticide	Number of samples	Number of detections	Detection frequency (%)	Minimum Reporting Limit (µg/L)	Lowest USEPA benchmark (BM) (µg/L)[1]	BM Type[2]	Number of BM exceed-ances	BM exceedance frequency (%)
Trifloxystrobin	88	0	0	0.02	2.76	IC	0	0
Trifluralin	76	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

[3] Clothianidin detections are qualitative only

Table 2. Pesticide detection in sediment

Pesticide	Number of samples	Number of detections	Detection frequency (%)	LC_{50} (µg/kg OC)*	Detection Frequency > LC_{50} (%)
Bifenthrin	16	12	75	520	69
Cyfluthrin	16	8	50	1080	0
Cypermethrin	16	6	38	380	6.3
Deltamethrin/Tralomethrin	16	12	75	790	38
Esfenvalerate/Fenvalerate	16	5	31	1540	0
Lambda Cyhalothrin	16	9	56	450	6.3
Permethrin	16	6	38	10830	0

*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)

Tracking Exceedances of Aquatic Benchmarks or Sediment LC50 values

For further data analysis: pesticides that have ≥ 10% aquatic benchmark exceedance frequency or exceed their OC normalized sediment LC_{50} for three consecutive years are recommended for further detailed data analysis if no analysis has been completed 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 benchmarks 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	44	58	61	Budd et al. (2020)	N
Deltamethrin/Tralomethrin	Water	14	11	15	Budd et al. (2020)	N
Fipronil	Water	14	22	37	Budd et al. (2015)	Y
Imidacloprid	Water	44	60	70	Ensminger et al. (2013)	Y
Bifenthrin	Sediment	69	50	50	Budd et al. (2020)	N

Quality Control

Table 4. Laboratory Quality Control (QC) summary

QC Type	Sample Matrix	Total Number	Number of QC Out of Control
Field Matrix Spike	Water	9	0
Field Matrix Spike Duplicate	Water	9	0
Lab Blank	Water	963	0
Matrix Spike	Water	963	9
Surrogate Spike	Water	216	0
Lab Blank	Sediment	36	0
Matrix Spike	Sediment	36	0

Nine matrix spikes had recoveries outside of their QC limits. The rest of the QA samples were within the QC limits.

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.