

Date: October 26, 2023

DEPARTMENT OF PESTICIDE REGULATION (DPR)

SURFACE WATER AMBIENT MONITORING REPORT

Stu

<u>udy</u>	<u>highlights</u>									
•	DPR Study Number	320								
•	SURF (Surface Water Database) Study Number 464									
•	Study Title California	Ambient S	Surface Water a	nd Mitigation Mo	onitoring in Urba	an Areas in Southern				
•	Project Lead	Robert Bu	ıdd							
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•	Protocol Source (prot	ocol available	e online for five yea	ars, thereafter, reque	st a copy from the S	SWPP list of archived files)				
	Environmental Moni	toring Proto	ocol Page							
•	•	hed: Ballo Bolsa Chic	ona Creek, Bou	•	•	Los Angeles River, Canyon Creek, Chollas				
•	Land use type	□ Ag	⊠ Urban	⊠ Forested	☐ Mixed	☐ Other				
•	Water body type									
	⊠ Creek	⊠ River	\square Pond	☐ Lake						
	☐ Drainage Ditch	⊠ Storm	drain outfall	\square Other						
•	Objectives									
1)	Determine presence waters of Southern C					· ·				
2)	Compare measured	concentrati	ons of pesticide	s to aquatic toxici	ty thresholds;					
3)	Evaluate pesticide co	oncentration	n trends through	long-term monit	oring;					
4)	Determine the acute amphipod <i>Hyalella</i> d	-	-	•	ests conducted v	vith the				
5)	Monitor concentration	on of sedim	ent-bound pyret	hroids within sele	ected watershed	s;				
6)	Determine relative lo	oads of pest	icides to urban	waterways by cor	ntributing land u	se type;				
7)	Evaluate effectivene conditions	ss of carbor	n-filled socks to	reduce pesticides	in urban runof	f under field -				

8) Evaluate effect of filtering samples on pyrethroid concentrations and *Hyalella azteca* toxicity.

• Sampling period July 1, 2021 – June 30, 2022

Major findings

INSECTICIDES: In the Southern California urban monitoring program, 12 insecticides were detected greater than 10% of the time. Imidacloprid was the most frequently detected insecticide, detected in 87% of the water samples. Bifenthrin was a close second, with an 83% detection frequency [DF]. Fipronil (72% DF), deltamethrin (47% DF), permethrin (47% DF), cyfluthrin (43% DF), lambda cyhalothrin (43% DF), thiamethoxam (39% DF), methoxyfenozide (25% DF), chlorantraniloprole (15% DF), cypermethrin (14% DF), and malathion (11% DF) made up the rest of the top twelve detected insecticides. All detections of imidacloprid, bifenthrin, deltamethrin, cyfluthrin, lambda cyhalothrin, and cypermethrin were above their minimum US EPA aquatic life benchmarks (BM). Additionally, the exceedance frequency (EF) for BMs was surpassed for fipronil (70% EF), permethrin (40% EF), and malathion (9% EF). None of the chlorantraniliprole, methoxyfenozide, or thiamethoxam samples exceeded its BM.

Four of the other 20 insecticides in the study were occasionally detected (esfenvalerate, 7% DF; acetamiprid, 4% DF; clothianidin 2% DF; carbaryl, 2% DF). The only concentrations above BM values were found in every sample of esfenvalerate.

Fipronil is the only pesticide which has its degradates monitored. All five degradates were detected: desulfinyl (96% DF), amide (85% DF), sulfone (76% DF), desulfinyl fipronil amide (69% DF), and sulfide (6% DF). Out of all fipronil degradate detections, only desulfinyl concentrations exceeded BM in 2% of samples. Fipronil amide and desulfinyl fipronil amide do not have established BM.

HERBICIDES. Ten herbicides were detected during the year. Diuron was the highest detected pesticide in the study with an 83% DF. Other frequently detected herbicides included 2,4-D (80% DF), triclopyr (80% DF), dicamba (50% DF), isoxaben (17% DF), oxadiazon (9% DF), simazine (6% DF), bromacil (6% DF), metribuzin (4% DF), and S-metolachlor (2% DF). Diuron was the only herbicide to exceed its BM (35% exceedance). None of the other 15 herbicides in the study were detected.

FUNGICIDES. Seven fungicides were detected sporadically throughout the sampling period. Tebuconazole was the most-frequently detected fungicide (33% DF), followed by propiconazole (19% DF), thiabendazole (8% DF), mefenoxam (6% DF), boscalid (2% DF), azoxystobin (2% DF), and pyraclostrobin (2% DF). No fungicide was detected over its lowest BM level.

TOXICITY. UC Davis Aquatic Health Program (AHP) conducted *Hyalella azteca* and *Chironomus dilutus* 96-hour water column toxicity tests on 16 samples collected during one dry event, one storm event, and one winter non-storm event. Six whole water and four filtered water samples were significantly toxic to *H. azteca*. Two storm event samples and one winter non-storm sample was also significantly toxic to *C. dilutus*. Both dry season and one winter non-storm event sample were not toxic to *C. dilutus*.

SEDIMENTS. Four sediments samples were collected from Orange County in August 2021. Sediments were analyzed for seven pyrethroids: bifenthrin, cyfluthrin cypermethrin, deltamethrin, esfenvalerate, lambdacyhalothrin, and permethrin. Bifenthrin, deltamethrin, and permethrin were detected in all four samples, esfenvalerate was detected in two samples, and the remaining three pesticides were detected in three samples

(75%) (Table 2). Bifenthrin was above the LC_{50} value in 75% of samples; deltamethrin in 50% of samples; and cypermethrin and lambda cyhalothrin in 25% of samples.

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

The following pesticides were recommended by the 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 FY 21-22.

Pesticide detection frequency

Data available in <u>SURF</u> 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 detection in water

Pesticide	Number of samples	Number of detections ¹	Detection frequency (%)	Minimum Reporting Limit (µg/L)	Lowest USEPA benchmark (BM) (µg/L) ¹	BM Type²	Number of BM exceed ances	BM exceed ance frequen cy (%)
2,4-D	10	8	80	0.05	299.2	VA	0	0
Abamectin	51	0	0	0.02	0.17	IA	0	0
Acetamiprid	54	2	4	0.02	2.1	IC	0	0
Atrazine	51	0	0	0.02	1	NVA	0	0
Azoxystrobin	54	1	2	0.02	44	IC	0	0
Bensulide	51	0	0	0.02	11	IC	0	0
Bifenthrin	58	48	83	0.001	0.00005	IC	48	83
Boscalid	51	1	2	0.02	116	FC	0	0
Bromacil	54	3	6	0.02	6.8	NVA	0	0
Carbaryl	54	1	2	0.02	0.5	IC	0	0
Chlorantraniliprole	54	8	15	0.02	3.02	IC	0	0
Chlorfenapyr	10	0	0	0.1	2.915	IA	0	0
Chlorpyrifos	54	0	0	0.02	0.04	IC	0	0
Clothianidin ³	51	1	2	0.02	0.05	IC	0	0
Cyfluthrin	58	25	43	0.002	0.00012	IC	25	43
Cypermethrin	58	8	14	0.005	0.00005	IC	8	14
Cyprodinil	51	0	0	0.02	8.2	IC	0	0
Deltamethrin/Tralo methrin	58	27	47	0.004	0.000026	IC	27	47
Desulfinyl Fipronil	54	52	96	0.01	0.53	FC	1	2
Desulfinyl Fipronil Amide	54	37	69	0.01		(no BM)	0	0
Diazinon	51	0	0	0.02	0.105	IA	0	0
Dicamba	10	5	50	0.05	61	NVA	0	0

Pesticide	Number of samples	Number of detections ¹	Detection frequency (%)	Minimum Reporting Limit (µg/L)	Lowest USEPA benchmark (BM) (µg/L) ¹	BM Type²	Number of BM exceed ances	BM exceed ance frequen cy (%)
Diflubenzuron	51	0	0	0.02	0.00025	IC	0	0
Dimethoate	51	0	0	0.02	0.5	IC	0	0
Diuron	54	45	83	0.02	0.13	VA	19	35
Esfenvalerate/Fen valerate	58	4	7	0.005	0.0000309	IC	4	7
Ethoprop	51	0	0	0.02	0.8	IC	0	0
Etofenprox	51	0	0	0.02	0.17	IC	0	0
Fenamidone	51	0	0	0.02	4.7	FC	0	0
Fenhexamid	51	0	0	0.02	101	FC	0	0
Fenpropathrin	1	0	0	0.005	0.0015	IC	0	0
Fipronil	54	39	72	0.01	0.011	IC	38	70
Fipronil Amide	54	46	85	0.01		(no BM)	0	0
Fipronil Sulfide	54	3	6	0.01	0.83	FC	0	0
Fipronil Sulfone	54	41	76	0.01	0.22	IC	0	0
Fludioxonil	51	0	0	0.02	14	IC	0	0
Hexazinone	51	0	0	0.02	7	NVA	0	0
Imidacloprid	54	47	87	0.01	0.01	IC	47	87
Indoxacarb	54	0	0	0.02	75	IC	0	0
Isoxaben	54	9	17	0.02	10	VA	0	0
Kresoxim-methyl	51	0	0	0.02	30.3	NVA	0	0
Lambda Cyhalothrin	58	25	43	0.002	0.00004	IA	25	43
Malathion	54	6	11	0.02	0.049	IA	5	9
MCPA	10	0	0	0.05	170	VA	0	0
Mefenoxam	51	3	6	0.02	1200	IC	0	0
Methidathion	51	0	0	0.02	0.66	IC	0	0
Methomyl	51	0	0	0.02	0.6	IC	0	0
Methoxyfenozide	51	13	25	0.02	3.1	IC	0	0
Metribuzin	51	2	4	0.02	8.1	NVA	0	0
Norflurazon	51	0	0	0.02	9.7	NVA	0	0
Oryzalin	54	0	0	0.02	13	VA	0	0
Oxadiazon	54	5	9	0.02	0.88	FC	0	0
Oxyfluorfen	10	0	0	0.05	0.29	NVA	0	0
Pendimethalin	10	0	0	0.05	5.2	NVA	0	0
Permethrin Total	58	27	47	0.001	0.0033	IA	23	40
Prodiamine	10	0	0	0.05	1.5	IC	0	0

Pesticide	Number of samples	Number of detections ¹	Detection frequency (%)	Minimum Reporting Limit (µg/L)	Lowest USEPA benchmark (BM) (μg/L) ¹	BM Type ²	Number of BM exceed ances	BM exceed ance frequen cy (%)
Prometon	51	0	0	0.02	98	NVA	0	0
Prometryn	51	0	0	0.02	1.04	NVA	0	0
Propanil	51	0	0	0.02	9.1	FC	0	0
Propargite	51	0	0	0.02	7	IA	0	0
Propiconazole	54	10	19	0.02	15	FC	0	0
Pyraclostrobin	54	1	2	0.02	1.5	NVA	0	0
Pyriproxyfen	54	0	0	0.015	0.015	IC	0	0
Quinoxyfen	51	0	0	0.02	13	FC	0	0
Simazine	51	3	6	0.02	6	NVA	0	0
S-Metolachlor	51	1	2	0.02	8	NVA	0	0
Tebuconazole	51	17	33	0.02	11	FC	0	0
Tebufenozide	51	0	0	0.02	29	IC	0	0
Tebuthiuron	54	0	0	0.02	50	NVA	0	0
Thiabendazole	51	4	8	0.02	42	IC	0	0
Thiacloprid	51	0	0	0.02	0.97	IC	0	0
Thiamethoxam	54	21	39	0.02	0.74	IC	0	0
Thiobencarb	51	0	0	0.02	1	IC	0	0
Triclopyr	10	8	80	0.05	5900	NVA	0	0
Trifloxystrobin	51	0	0	0.02	2.76	IC	0	0
Trifluralin	10	0	0	0.05	1.9	FC	0	0

¹ Benchmarks are used as a screening tool for risk analysis

Table 2. Pesticide detection in sediment

Pesticide	Number of samples	Number of detection s	Detection frequency (%)	LC₅₀ (µg/kg OC)*	Detection Frequency > LC₅₀ (%)
Bifenthrin	4	4	100	520	75
Cyfluthrin	4	3	75	1080	0
Cypermethrin	4	3	75	380	25
Deltamethrin/Tralomethrin	4	4	100	790	50
Esfenvalerate/Fenvalerate	4	2	50	1540	0
Lambda Cyhalothrin	4	3	75	450	25
Permethrin	4	4	100	10830	0

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

*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)

Tracking Exceedances of Aquatic Benchmarks or Sediment LC50 values

For further data analysis: pesticides that have $\geq 10\%$ aquatic benchmark exceedance rate or exceed their OC normalized sediment LC₅₀ 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) \geq 10% of their detections exceeding their lowest USEPA aquatic life water benchmark or 2) percentage of sediment detections exceeding their sediment LC₅₀ (normalized to OC)

Pesticide	Matrix	Current year (2020)	2019	2018	Last written evaluation (reference)	Further data analysis (Y/N)
Imidacloprid	Water	87	81	93	Ensminger et al. (2013)	Υ
Bifenthrin	Water	83	83	91	Budd et al. (2020)	N
Fipronil	Water	70	78	75	Budd et al. (2015)	N
Deltamethrin/Tralomethrin	Water	46	54	40	Budd et al. (2020)	N
Cyfluthrin	Water	43	40	65	Budd et al. (2020)	N
Lambda Cyhalothrin	Water	43	39	32	Budd et al. (2020)	N
Permethrin	Water	40	43	42	Budd et al. (2020)	N
Diuron	Water	35	46	48	Ensminger et al. (2013)	Υ
Cypermethrin	Water	14	25	20	Budd et al. (2020)	N
Bifenthrin	Sediment	75	50	100	Budd et al. (2020)	N
Deltamethrin/Tralomethrin	Sediment	50	50	33	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	
Blind Spike	Water	0	0	
Lab Blank	Water	447	1	
Matrix Spike	Water	449	67	
Surrogate Spike	Water	108	2	
Lab Blank	Sediment	18	0	
Matrix Spike	Sediment	18	0	

Sixty-seven matrix spikes, one lab blank and two surrogate spikes had recoveries below/above 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 <u>SURF database administrator</u> for the data.