

1. Study highlights

- Study Number: 304
- Title: Surface Water Monitoring for Pesticides in Agricultural Areas in the Central Coast and Southern California, 2018
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- Study area: County: Imperial, Monterey, Santa Barbara, San Luis Obispo
 Waterbody/Watershed: Alamo River, New River, Salinas River, Tembladero Slough, Santa Maria River

- Land Use Type: Ag Urban Forested Mixed Other

- Water body type: Storm drain outfall Creek River Pond Lake
 Drainage ditch Other:

- Objectives: 1. Determine pesticide presence and their concentrations in surface water runoff from agricultural areas of high pesticide uses; 2. Compare pesticide concentrations to the lowest US EPA aquatic life benchmarks; 3. Determine the toxicity of a subset samples to surrogate aquatic species in 96-hour or 10-day water column testing.

- Sampling period: March, 2018–November, 2018

- Pesticides monitored:
 Abamectin, Atrazine, Azoxystrobin, Benfluralin, Bensulide, Bifenthrin, Bromacil, Carbaryl, Chlorantraniliprole, Chlorpyrifos, Cyfluthrin, Cypermethrin, Cyprodinil, Desulfinyl Fipronil, Desulfinyl Fipronil Amide, Diazinon, Diflubenzuron, Dimethoate, Diuron, Esfenvalerate, Ethalfluralin, Ethoprop, Etofenprox, Fenpropathrin, Fipronil, Fipronil Amide, Fipronil Sulfide, Fipronil Sulfone, Hexazinone, Imidacloprid, Indoxacarb, Isoxaben, Kresoxim-methyl, Lambda Cyhalothrin, Malathion, Methidathion, Methomyl, Methoxyfenozide, Metribuzin, Norflurazon, Oryzalin, Oxadiazon, Oxyfluorfen, Pendimethalin, Permethrin, Prodiamine, Prometon, Prometryn, Propanil, Propargite, Propiconazole, Pyraclostrobin, Pyriproxyfen, Quinoxifen, S-Metolachlor, Simazine, Tebufenozide, Thiobencarb, Trifloxystrobin, Trifluralin

- Major findings:

INSECTICIDES IN WATER. The most frequently detected A.I.s were imidacloprid (94%), methoxyfenozide (88%), chlorantraniliprole (86%), and methomyl (60%). Bifenthrin was the most frequently detected pyrethroid (30%) followed by λ -cyhalothrin (28%), permethrin (20%), cypermethrin (12%), esfenvalerate (6%), cyfluthrin (4%), and fenpropathrin (0%). Insecticides with moderate detection frequencies were malathion (32%), dimethoate (24%), indoxacarb (16%), and chlorpyrifos (12%). Carbaryl and diazinon were detected at low frequencies at 2%. Other insecticides were not detected in any of the samples. Insecticides with concentrations exceeding their lowest U.S. EPA aquatic life benchmarks (BM) at high frequencies were imidacloprid (94%), bifenthrin (28%), λ -cyhalothrin (28%), permethrin (20%), malathion (18%), and methomyl (16%). BM exceedances for chlorpyrifos, dimethoate, and esfenvalerate were at low frequencies (2–4%). There were no BM exceedances for any other insecticides.

HERBICIDES AND FUNGICIDES IN WATER. A.I.s with high detection frequencies were bensulide (72%), prometryn (58%), and azoxystrobin (50%). A.I.s with moderate detection frequencies include pyraclostrobin (32%), oxyfluorfen (30%), diuron (30%), pendimethalin (24%), and cyprodinil (16%). A.I.s that had low detection frequencies were trifluralin (10%), atrazine (8%), oryzalin (6%), S-metolachlor (2%), simazine (2%), and trifloxystrobin (2%). No detections were reported for the rest of the herbicides and fungicides. BM exceedances for oxyfluorfen, prometryn, and diuron were at low frequencies (2–6%).

PYRETHROIDS IN SEDIMENT. Sediment samples from 16 monitoring sites were analyzed for 7 pyrethroids. Detection frequencies from the highest to the lowest were bifenthrin (44%), permethrin (38%), λ -cyhalothrin (25%), esfenvalerate (19%), cypermethrin (13%), and cyfluthrin (6%). Fenpropathrin was not detected in any of the samples. Both bifenthrin and λ -cyhalothrin had been reported in 12.5% of sediment samples (2 samples) with concentrations > 1 toxicity unit (TU). Cypermethrin and esfenvalerate were both reported in 6.3% of samples (1 sample) with concentrations > 1 TU. Cyfluthrin was detected at concentrations < 1 TU. TUs in all samples with reported concentrations ranged from 0.01 to 11.6.

TOXICITY. UC Davis Granite Canyon Marine Pollution Laboratory conducted 96-hour *Hyalella azteca* and 10-day *Chironomus dilutus* toxicity tests concurrently with 22 water samples collected from 8 monitoring sites during the monitoring period. *Hyalella* survival and *Chironomus* survival and growth (measured by the final dry weight of individual organism) were evaluated for toxicological effects. Compared to lab controls, 73% of samples (16 of 22 samples) caused statistically significant toxicological effects. Exposures to 59% of samples resulted in acute toxicity (i.e., mortality) to either *Hyalella* or *Chironomus* or both. Exposures to 36% of samples resulted in inhibition of *Chironomus* growth.

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

Fenhexamid, Fenamidone, Fludioxonil, Spinetoram, Linuron, PCNB

2. Pesticide detection frequency

Table 1. Pesticides detected in water. Complete data set in Appendix.

Pesticide	Number of samples	Number of detections	Reporting Limit ($\mu\text{g/L}$)	Detection frequency (%)	Lowest USEPA benchmark (BM) ($\mu\text{g/L}$)*		Number of BM exceedances	BM exceedance frequency (%)
Abamectin	2	0	0.02	0	0.17	IA	0	0
Atrazine	50	4	0.02	8	1	NVA	0	0
Azoxystrobin	50	25	0.02	50	44	IC	0	0
Benfluralin	50	0	0.05	0	1.9	FC	0	0
Bensulide	50	36	0.02	72	11	IA	0	0
Bifenthrin	50	15	0.001	30	0.0013	IC	14	28
Bromacil	2	0	0.02	0	6.8	NA	0	0
Carbaryl	50	1	0.02	2	0.5	IC	0	0
Chlorantraniliprole	50	43	0.02	86	4.47	IC	0	0
Chlorpyrifos	50	6	0.02	12	0.04	IC	2	4
Cyfluthrin	50	2	0.002	4	0.0074	IC	1	2
Cypermethrin	50	6	0.005	12	0.069	IC	0	0
Cyprodinil	50	8	0.02	16	8	IC	0	0
Desulfinyl Fipronil	2	0	0.01	0	0.59	FC	0	0
Desulfinyl Fipronil Amide	2	0	0.01	0	NA			
Diazinon	50	1	0.02	2	0.105	IA	0	0
Diflubenzuron	50	0	0.02	0	0.00025	IC	0	0
Dimethoate	50	12	0.02	24	0.5	IC	2	4
Diuron	50	15	0.02	30	2.4	NVA	1	2
Esfenvalerate	50	3	0.005	6	0.017	IC	1	2
Ethalfuralin	50	0	0.05	0	0.4	FC	0	0
Ethoprop	2	0	0.02	0	0.8	IC	0	0
Etofenprox	2	0	0.02	0	0.17	IC	0	0
Fenpropathrin	50	0	0.005	0	0.064	IC	0	0
Fipronil	2	0	0.01	0	0.011	IC	0	0
Fipronil Amide	2	0	0.01	0	NA			
Fipronil Sulfide	2	0	0.01	0	0.11	IC	0	0
Fipronil Sulfone	2	0	0.01	0	0.037	IC	0	0
Hexazinone	50	0	0.02	0	7	NVA	0	0
Imidacloprid	50	47	0.01	94	0.01	IC	47	94
Indoxacarb	50	8	0.02	16	75	IC	0	0
Isoxaben	2	0	0.02	0	10	VA	0	0
Kresoxim-methyl	2	0	0.02	0	29.2	NVA	0	0
Lambda-cyhalothrin	50	14	0.002	28	0.002	IC	14	28
Malathion	50	16	0.02	32	0.049	IC	9	18
Methidathion	2	0	0.02	0	0.66	IC	0	0
Methomyl	50	30	0.02	60	0.7	IC	8	16
Methoxyfenozide	50	44	0.02	88	6.3	IC	0	0
Metribuzin	2	0	0.02	0	8.1	NVA	0	0

Norflurazon	2	0	0.02	0	9.7	NVA	0	0
Oryzalin	50	3	0.02	6	13	VA	0	0
Oxadiazon	2	0	0.02	0	5.2	NA	0	0
Oxyfluorfen	50	15	0.05	30	0.29	NVA	3	6
Pendimethalin	50	12	0.05	24	5.2	NVA	0	0
Permethrin	50	10	0.002	20	0.0014	IC	10	20
Prodiamine	50	0	0.05	0	1.5	IC	0	0
Prometon	2	0	0.02	0	98	NVA	0	0
Prometryn	50	29	0.02	58	1.04	NVA	3	6
Propanil	2	0	0.02	0	9.1	FC	0	0
Propargite	2	0	0.02	0	7	AI	0	0
Propiconazole	2	0	0.02	0	21	NVA	0	0
Pyraclostrobin	50	16	0.02	32	1.5	NVA	0	0
Pyriproxyfen	2	0	0.02	0	0.015	IC	0	0
Quinoxifen	50	0	0.02	0	13	FC	0	0
S-Metolachlor	50	1	0.02	2	8	NVA	0	0
Simazine	50	1	0.02	2	2.24	NVA	0	0
Tebufenozide	2	0	0.02	0	11	FC	0	0
Thiobencarb	2	0	0.02	0	1	IC	0	0
Trifloxystrobin	50	1	0.02	2	2.76	IC	0	0
Trifluralin	50	5	0.05	10	1.9	FC	0	0

*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. Complete data set in Appendix.

Pesticide	Number of samples	Number of detections	Detection frequency (%)	LC ₅₀ (µg/g OC)*	Detection frequency of sediments ≥ 1 TU*
Bifenthrin	16	7	44	0.52	12.5
Cyfluthrin	16	1	6	1.08	0
Cypermethrin	16	2	13	0.38	6.3
Esfenvalerate	16	3	19	1.54	6.3
Fenpropathrin	16	0	0	1.6	0
Lambda-cyhalothrin	16	4	25	0.45	12.5
Permethrin	16	6	38	10.83	0

*Sediment Toxicity Units (TUs) are calculated using the formula, use TU = C/1000/LC₅₀/%TOC, where C = concentration (µg/kg dry weight), LC₅₀ (µg/kg) 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; Ding et al. 2011, Arch. Environ. Toxicol. 61:83–92; 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 LC₅₀.

3. Tracking Benchmark Exceedances (BME) or Sediment Toxicity (TU)

Table 3. For further data analysis: pesticides that have $\geq 10\%$ aquatic benchmark exceedances [BME] [Table 1] or ≥ 1 sediment toxicity units [TU] [Table 2]) for 3 consecutive years are recommended for further detailed data analysis (Ambient Urban Monitoring Methodology SOP METH014)

BME (for pesticides with $\geq 10\%$ BME) or Sediment TUs (for pesticides with ≥ 1 Sediment TU) (all sites) for the past 3 years							
Pesticide	Water	Sediment	Current year (i)	i - 1	i - 2	Last written evaluation (reference)	Further data analysis (Y/N)
Bifenthrin	x		28	38	46	None	Y
Chlorpyrifos	x		4	11	6	2012	N
Lambda-cyhalothrin	x		28	28	29	None	Y
Imidacloprid	x		94	95	89	2012	Y
Malathion	x		18	13	15	None	Y
Methomyl	x		16	20	31	None	Y
Permethrin	x		20	38	32	None	Y
Bifenthrin		x	12.5	NA	NA	None	N
Lambda-cyhalothrin		x	12.5	NA	NA	None	N

4. QC

Table 4. Laboratory Quality Control (QC) Summary

QC Type	Water Samples		Sediment Samples	
	Total Number	Number of QC out of control	Total Number	Number of QC out of control
Lab Blanks	231	0	16	0
Matrix Spikes/Duplicates	231	0	16	0
Laboratory Control Spikes/Duplicates	0	Enter No.	Enter No.	Enter No.
Blind Spikes	25	4	Enter No.	Enter No.
Surrogate Spikes	Enter No.	Enter No.	Enter No.	Enter No.
Other QC: Describe	Enter No.	Enter No.	Enter No.	Enter No.
Explain out of control QC and interpretation of data:	Blind spikes for four analytes from two sampling events were out of the recovery control limits. Bifenthrin spike in the sample set of May had a recovery of 125.6%, which is above the upper recovery control limit by 7%. Despite the higher recovery, bifenthrin was not detected in any of the samples in May. Ethalfluralin, benfluralin and prodiamine blind spikes during the September sampling event had 0% recoveries. As the matrix spikes for the three analytes were within the recovery control limits, it is likely that the low recoveries resulted from lab errors. The monitoring results for the four analytes in May and September sampling events were included in this summary report because their matrix spikes were within the QC control limits.			

5. Supporting Information (SI)

The following SI is available upon request, please contact the author.

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Appendix I. Study protocol

Appendix II. Sampling site information and pictures

Appendix III. Water quality data

Appendix IV. Sediment monitoring data

Appendix V. Water monitoring data

Appendix VI. Aquatic toxicity data

Appendix VII. Analytical and toxicity test methods