

1. Study highlights

- Study Number: 304
- Title: Surface Water Monitoring for Pesticides in Agricultural Areas in the Central Coast and Southern California, 2017
- Author: Xin Deng

- Study area: County: Imperial, Monterey, Santa Barbara, Santa 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: type

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

- Sampling period: March, 2017 – October, 2017

- Pesticides monitored:
 Abamectin, Carbaryl, Chlorantraniliprole, Chlorpyrifos, Diazinon, Diflubenzuron, Dimethoate, Indoxacarb, Imidacloprid, Malathion, Methomyl, Methoxyfenozide, Bifenthrin, Cyfluthrin, Cypermethrin, Fenpropathrin, (Es)fenvalerate, λ-Cyhalothrin, Permethrin, Atrazine, Bensulide, Benfluralin, Diuron, Ethalfluralin, Oryzalin, Pendimethalin, Prodiamine, Prometryn, Trifluralin, Oxyfluorfen, Simazine, S-Metolachlor, Azoxystrobin, Cyprodinil, Pyraclostrobin, Quinoxyfen, Trifloxystrobin

- Major findings:

INSECTICIDES. 19 insecticidal active ingredients (A.I.) were monitored in 2017. The most frequently detected A.I.s were imidacloprid (95%), chlorantraniliprole (87%), methomyl (82%) and methoxyfenozide (80%). Bifenthrin was the most frequently detected pyrethroid (42%), followed by permethrin (38% DF), λ -cyhalothrin (28%), cypermethrin (16%), fenpropathrin (8%), (es)fenvalerate (6%) and cyfluthrin (4%). Insecticides with moderate detection frequencies were chlorpyrifos (13%), dimethoate (20%), malathion (18%) and indoxacarb (15%). Carbaryl and diflubenzuron were detected in low frequencies at 6% and 3%, respectively. Abamectin and diazinon were not detected in any of the samples. Insecticides with concentrations exceeding their lowest U.S. EPA aquatic life benchmarks (BM) in high frequencies were imidacloprid (95%), bifenthrin (38%), permethrin (38%), λ -cyhalothrin (28%) and methomyl (20%). The recent updates of the BM values had lowered the lowest imidacloprid BM from 1.05 to 0.01 $\mu\text{g/L}$, which resulted in BM exceedances for all the samples with detectable concentrations. BM exceedances for chlorpyrifos, dimethoate, and malathion were within 9–13%. BM exceedances for chlorantraniliprole, diflubenzuron, dimethoate were in low frequencies (2–4%). There were no BM exceedances for carbaryl, indoxacarb, methoxyfenozide and fenpropathrin.

HERBICIDES AND FUNGICIDES. 13 herbicides and 5 fungicides were monitored in 2017. A.I.s with high detection frequencies were bensulide (82%), atrazine (75%), azoxystrobin (71%), prometryn (59%), pyraclostrobin (54%) and oxyfluorfen (33%). Those with moderate detection frequencies include cyprodinil (22%) and diuron (14%). A.I.s that had low detection frequencies were pendimethalin (7%) trifluralin (4%) and quinoxifen (3%). No detections were reported for the rest of the herbicides and fungicides. Prometryn, bensulide, and oxyfluorfen were the three herbicides that were detected at concentrations exceeding their lowest BM at 4, 7 and 9%, respectively.

TOXICITY. Water samples collected at Sal_Davis (Salinas River at Davis Road, Salinas) and Sal_Haro (Tembladero Slough at Haro Street, Castroville) on April 18 and May 15 were tested for toxicity by UC Davis Granite Canyon Marine Pollution Laboratory.

10-day toxicity tests with *Hyalella azteca* were conducted on samples from both sites on April 18 and May 15. Only one sample from the Sal_Haro site on April 18 significantly reduced *Hyalella* survivals but no effects were observed from any other samples. The 10-day *Chironomus dilutus* survival test was only conducted on April 18 on samples from both sites. No effects on survival and growth were observed (see complete data sets in Appendix V).

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- Recommendations for pesticides that need a CDE analytical method (from Surface Water Monitoring Prioritization Model):
Fenhexamid, Fenamidone, Fludioxonil, Spinetoram
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2. Pesticide detection frequency

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

Pesticide	Number of samples	Number of detections	Reporting Limit (µg/L)	Detection frequency (%)	Lowest USEPA benchmark (BM) (µg/L)*	Number of BM exceedances	BM exceedance frequency (%)
Abamectin	35	0	0.02	0	0.17 IA	0	0
Carbaryl	35	2	0.02	6	0.5 IC	0	0
Chlorantraniliprole	55	48	0.02	87	4.4 IC	1	2
Chlorpyrifos	55	7	0.02	13	0.04 IC	6	11
Diazinon	51	0	0.02	0	0.105 IA	0	0
Diflubenzuron	36	1	0.02	3	0.00025 IC	1	3
Dimethoate	55	11	0.02	20	0.5 IC	5	9
Indoxacarb	39	6	0.02	15	75 IC	0	0
Imidacloprid	55	52	0.02	95	0.01 IC	95	95
Malathion	55	10	0.02	18	0.049 IC	7	13
Methomyl	55	45	0.02	82	0.7 IC	11	20
Methoxyfenozide	55	44	0.02	80	6.3 IC	0	0
Bifenthrin	50	21	0.001	42	0.0013 IC	19	38
Cyfluthrin	50	2	0.002	4	0.0074 IC	1	2
Cypermethrin	50	8	0.005	16	0.069 IC	2	4
(Es)fenvaleerate	50	3	0.005	6	0.017 IC	2	4
Fenpropathrin	50	4	0.005	8	0.064 IC	0	0
λ-Cyhalothrin	50	14	0.002	28	0.002 IC	14	28
Permethrin	50	19	0.002	38	0.0014 IC	19	38
Atrazine	4	3	0.02	75	1 NVA	0	0
Benfluralin	55	0	0.05	0	1.9 FC	0	0
Bensulide	55	45	0.02	82	11 IC	4	7
Diuron	35	5	0.02	14	2.4 NVA	0	0
Ethalfuralin	55	0	0.05	0	0.4 FC	0	0
Oryzalin	55	0	0.02	0	13 VA	0	0
Oxyfluorfen	55	18	0.05	33	0.29 NVA	5	9
Pendimethalin	55	4	0.05	7	5.2 NVA	0	0
Prodiamine	55	0	0.05	0	1.5 IC	0	0
Prometryn	51	30	0.02	59	1.04 NVA	2	4
Simazine	36	0	0.02	0	2.24 NVA	0	0
S-Metolachlor	51	0	0.02	0	8 NVA	0	0
Trifluralin	55	2	0.05	4	1.9 FC	0	0
Azoxystrobin	51	36	0.02	71	44 IC	0	0
Cyprodinil	51	11	0.02	22	8 IC	0	0
Pyraclostrobin	51	28	0.02	54	1.5 NVA	0	0
Quinoxifen	36	1	0.02	3	13 FC	0	0

Trifloxystrobin	35	0	0.02	0	2.76	IC	0	0
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*FA, fish acute; FC, fish chronic; IA, invertebrate acute; IC, invertebrate chronic; NA, non-vascular acute; VA, vascular acute

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

Table 2. 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							Last written evaluation (reference)	Further data analysis (Y/N)
Area	Pesticide	Water	Sediment	Current year (i)	i - 1	i - 2		
The Central Coast and Imperial County	Bifenthrin	x		38	46	47	None	Y
	Chlorpyrifos	x		11	6	12	2012	N
	Imidacloprid	x		$\geq 95^*$	$\geq 89^{**}$	$\geq 81^{**}$	2012	Y
	λ -Cyhalothrin	x		28	29	33	None	Y
	Malathion	x		13	15	17	None	Y
	Methomyl	x		20	31	22	None	Y
	Permethrin	x		38	32	27	None	Y

* “ \geq ” is indicated because the reporting limit is above lowest imidacloprid BM. Trace detections may be above the BM. “NR” indicates ‘no record’.

**BMEs were calculated based on the most recent BM value (0.01 $\mu\text{g/L}$) updated by the US EPA in November 2017. The BMEs were 21% and 7% in 2015 and 2016, respectively, based on the previous BM value of 1.05 $\mu\text{g/L}$.

4. QC

Table 3. 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	276	0	Enter No.	Enter No.
Matrix Spikes/Duplicates	276	0	Enter No.	Enter No.
Laboratory Control Spikes/Duplicates	0	0	Enter No.	Enter No.
Blind Spikes	27	5	Enter No.	Enter No.
Surrogate Spikes	16	0	Enter No.	Enter No.
Other QC: Describe	0	0	Enter No.	Enter No.
Explain out of control QC and interpretation of data:	<p>A total of five blind spikes were out of the recovery control limits. Trifluralin, pendimethalin and oxyfluorfen spikes in May samples had recovery percentages above their upper recovery control limits by 4%, 13.5% and 5.3%, respectively. Despite the exceedances, trifluralin and pendimethalin had no detections in any of the samples in May. Oxyfluorfen was detected in 5 of the 10 samples and 2 samples exceeded the lowest US EPA aquatic life benchmark for oxyfluorfen. While the higher recoveries for trifluralin and pendimethalin were unlikely to affect the analytical results, it's possible that the detections and concentrations for oxyfluorfen were overestimated. Pyraclostrobin and methomyl spikes in June samples exceeded their lower recovery control limits, resulting in 0% recovery for pyraclostrobin and 42% for methomyl. However, pyraclostrobin and methomyl were detected in 4 of 6 samples and 5 of 6 samples, respectively. As the matrix spikes for both compounds were within the recovery control limits, it's likely that the low recoveries were resulted from lab errors. The monitoring results for the 5 compounds in May and June sampling events were included in this summary report because their matrix spikes were within the QC control limits.</p>			

5. Supporting Information

Index of Supporting Information

Appendix I. Study protocol

Appendix II. Sampling site information and pictures

Appendix III. Water quality data

Appendix IV. Water monitoring data

Appendix V. Aquatic toxicity data

Appendix VI. Analytical methods