

## SURFACE WATER AMBIENT MONITORING REPORT

### 1. Study highlights

- DPR Study Number 322
- Study Title Monitoring Pesticides in Wastewater Influent and Effluent
- Project Lead John Wheeler
- Email [John.Wheeler@cdpr.ca.gov](mailto:John.Wheeler@cdpr.ca.gov)
- 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: Nine counties throughout California (wastewater treatment plants participate anonymously; therefore, county names will not be provided).

Waterbody/Watershed: Twenty-eight wastewater treatment plants (WWTPs) discharging effluent into eight different waterbodies throughout California (twelve plants discharge into inland surface waters, thirteen plants discharge into marine/estuarine environments, and three plants primarily discharge into canals and/or percolation ponds for water reuse/groundwater recharge).

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- Land use type  Ag  Urban  Forested  Mixed  Other (sewershed)

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- Water body type

<input type="checkbox"/> Creek	<input type="checkbox"/> River	<input type="checkbox"/> Pond	<input type="checkbox"/> Lake
<input type="checkbox"/> Drainage Ditch	<input type="checkbox"/> Storm drain outfall	<input checked="" type="checkbox"/> Other	Wastewater

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- Objectives

Determine the presence and concentrations of selected pesticides in wastewater influent and effluent. Evaluate regional and seasonal variability in wastewater pesticide loading to WWTPs. Evaluate the influence of sewershed characteristics (e.g., population, contributing land use) on relative pesticide loading. Collect data to help elucidate pesticide transformation and removal efficacies within wastewater treatment systems.

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- Sampling period January 2024 – December 2024

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- Major findings

In the wastewater monitoring program, samples were analyzed for 37 compounds. Overall, detection frequencies (DFs) were much higher in influent than in effluent. Eight compounds had a DF of >25% in

influent, compared to only three in effluent. Classes of compounds analyzed include pyrethroids, fiproles (fipronil and degradates), organophosphates, neonicotinoids, carbamates, fungicides, isoxazolines, oxadiazines, and insect growth regulators.

**Pyrethroids.** Four of the pyrethroids analyzed had DFs >25% in influent: alpha-cypermethrin (99%), cypermethrin (93%), bifenthrin (44%), and etofenprox (39%). No pyrethroids were detected in effluent. Note: for isomeric compounds (e.g., cypermethrin), DFs for individual isomers may be higher than the DF for the “total” compound (sum of all isomers analyzed), due to differences in reporting limits.

**Fiproles.** Fipronil was detected in 85% of influent samples and 86% of effluent samples. All five of the fipronil degradates analyzed (fipronil amide, fipronil sulfide, fipronil sulfone, fipronil desulfinyl, and fipronil desulfinyl amide) had DFs <10% in influent and effluent. Fipronil concentrations exceeded the minimum freshwater chronic aquatic life benchmark in 79% of effluent samples, but did not exceed other available benchmarks. Fipronil desulfinyl and fipronil sulfone, although detected in effluent, did not exceed benchmarks.

**Organophosphates.** Two organophosphate compounds were analyzed in the wastewater monitoring program: chlorpyrifos and tetrachlorvinphos. Chlorpyrifos had a DF of 27% in influent and 6% in effluent, while tetrachlorvinphos had a DF of 1% in influent and 0% in effluent. Chlorpyrifos concentrations exceeded the minimum freshwater aquatic life benchmarks (both acute and chronic) in 6% of effluent samples, and exceeded the minimum marine acute aquatic life benchmark in 1% of effluent samples.

**Neonicotinoids.** Two neonicotinoid compounds were analyzed: imidacloprid and dinotefuran. Imidacloprid was detected in 98% of influent samples and 99% of effluent samples. Imidacloprid concentrations exceeded the minimum freshwater chronic aquatic life benchmark in 96% of effluent samples, and exceeded the minimum freshwater acute benchmark in 1% of effluent samples. Dinotefuran was detected in 100% of influent samples and 79% of effluent samples; however, no benchmarks were exceeded in effluent.

**Carbamates.** Propoxur is the only carbamate compound that was analyzed. This compound was not detected in influent or effluent.

**Fungicides.** Chlorothalonil is the only fungicide that was analyzed in the wastewater monitoring program. This analyte proved difficult to analyze in influent. For the solids fraction of influent samples, none of the influent samples met QC guidelines (for all samples, chlorothalonil percent recovery values in spiked samples were outside the acceptable range). For this reason, it was not possible to determine a DF for chlorothalonil in influent. Chlorothalonil was not detected in any of the 71 effluent samples collected during 2025.

**Isoxazolines.** Fluralaner is the only isoxazoline compound that was analyzed. This compound was detected in 2% of influent samples and 3% of effluent samples.

**Oxadiazines.** S-Indoxacarb is the only oxadiazine compound that was analyzed. This compound was detected in 2% of influent samples and 0% of effluent samples.

**Insect Growth Regulators.** Three insect growth regulators were analyzed in the wastewater monitoring program: novaluron, pyriproxyfen, and S-methoprene. Pyriproxyfen had a DF of 5% in influent and 0% in effluent. The other two compounds were not detected in any influent or effluent samples.

## CONCLUSIONS.

Fiproles were detected in both influent and effluent, with the parent compound (fipronil) having the highest DFs (85% in influent, 86% in effluent). Fipronil exceeded the minimum freshwater chronic toxicity benchmark of 0.011 µg/L in 79% of effluent samples. Fipronil's degradates were not frequently detected (DF<10% in both influent and effluent).

Imidacloprid and dinotefuran were detected in most influent and effluent samples analyzed, likely due to their widespread use in products used indoors (e.g., pet products, indoor sprays, gel baits) and their high water solubility values (imidacloprid: 514 mg/L; dinotefuran: 39,800 mg/L). Imidacloprid concentrations exceeded the minimum freshwater chronic toxicity benchmark of 0.010 µg/L in 99% of effluent samples, and one sample exceeded the minimum freshwater acute toxicity benchmark of 0.385 µg/L. Despite having the highest median effluent concentration of all compounds analyzed (0.084 µg/L), dinotefuran did not exceed any aquatic life benchmarks in effluent samples. This is likely because the benchmark values for dinotefuran are much higher ( $\geq 395$  µg/L).

Pyrethroids are prevalent in influent (four pyrethroids had DFs  $>25\%$ ), due to their widespread use in products with down-the-drain transport potential. However, they were not detected in effluent samples (although they may have been present at levels below reporting limits) likely due to sorption to solids before and during the treatment process.

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- Recommendations for pesticides that need an analytical method:

Sample analysis is performed by the Department of Toxic Substances Control's Environmental Chemistry Laboratory (DTSC ECL). In early 2023, Surface Water Protection Program (SWPP) staff requested that the following compounds be added to the analytical suite for this program: flumethrin, dinotefuran, S-indoxacarb, S-methoprene, and fluralaner. This request was made based on the availability of these compounds in products with potential for down-the-drain transport (e.g., pet products). Beginning with wastewater samples collected in September 2023, DTSC ECL staff have successfully added these compounds to the analytical suite and have begun reporting their concentrations in both influent and effluent samples. In addition, in late 2024, SWPP staff requested that DTSC ECL staff work to reduce the reporting limits for pyrethroids in effluent. As of mid-2025, DTSC ECL has begun analyzing larger effluent volumes, which is expected to facilitate the reduction of reporting limits. Future study reports will likely reflect reduced reporting limits for some compounds.

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## **2. Pesticide detection frequency**

During the study period (January 2024 – December 2024), a total of 71 influent samples and 71 effluent samples were collected. However, for many analytes, the sample count shown in Table 1 and Table 2 is less than 71 because some samples did not meet QC guidelines for the given analyte (see section 4: Quality Control).

Upon receipt in the laboratory, influent samples are filtered. The filtrate and solid fractions then undergo separate extraction and analysis procedures. Effluent samples are not filtered in the laboratory, because suspended solids concentrations in effluent are already very low due to wastewater treatment processes. In the

laboratory, pesticides are extracted from aqueous media (i.e., effluent and influent filtrate) using solid phase extraction, and from the suspended solids fraction of influent using Soxhlet extraction. The extracts are analyzed by gas chromatography with quadrupole time-of-flight mass spectrometry (GC-QTOF) and liquid chromatography with triple quadrupole mass spectrometry (LC-QQQ), and are quantified using non-extracted isotopically labeled internal standards.

In Table 1 (below), a pesticide is considered to be detected in a given influent sample if the pesticide was detected in either the filtrate or solid fraction (or both). Similarly, pesticide concentrations for each influent sample are calculated as the sum of concentrations detected in the filtrate and solid fractions (if the pesticide is detected in both fractions); if the pesticide is detected in only one fraction, the concentration measured in that fraction is used.

WWTPs participate anonymously; therefore, data will not be made publicly available. Contact the Project Lead to request further information about the study.

Table 1. Pesticide detections and concentrations in influent (filtrate and/or solids)

Pesticide	Sample Count	Number of Detections	Detection frequency (%)	Minimum Reporting Limit (µg/L)	Median (µg/L)	90 <sup>th</sup> Percentile (µg/L)
alpha-Cypermethrin	71	70	99	0.003	0.015	0.042
beta-Cyfluthrin	71	16	23	0.008	< 0.007	0.012
Bifenthrin	71	31	44	0.031	< 0.031	0.080
Chlorpyrifos	71	19	27	0.016	< 0.016	0.060
Cyfluthrin	71	8	11	0.016	< 0.016	0.016
Cypermethrin	71	66	93	0.016	0.040	0.138
Cyphenothrin	71	0	0	0.078	N/A	N/A
Deltamethrin	71	0	0	0.078	N/A	N/A
Dinotefuran	71	71	100	0.016	0.098	0.188
Esfenvalerate	59	0	0	0.031	N/A	N/A
Etofenprox	71	28	39	0.016	< 0.016	0.073
Fenpropathrin	71	0	0	0.031	N/A	N/A
Fipronil	71	60	85	0.016	0.034	0.066
Fipronil amide	71	5	7	0.016	< 0.016	< 0.016
Fipronil desulfinyl	71	0	0	0.016	N/A	N/A
Fipronil desulfinyl amide	71	1	1	0.016	N/A	N/A
Fipronil sulfide	71	1	1	0.016	N/A	N/A
Fipronil sulfone	71	2	3	0.016	< 0.016	< 0.016
Flumethrin	63	0	0	0.031	N/A	N/A
Fluralaner	63	1	2	0.016	N/A	N/A
gamma-Cyhalothrin	65	3	5	0.010	< 0.010	< 0.010
Imidacloprid	63	62	98	0.016	0.069	0.106
lambda-Cyhalothrin	71	1	1	0.031	N/A	N/A

Pesticide	Sample Count	Number of Detections	Detection frequency (%)	Minimum Reporting Limit (µg/L)	Median (µg/L)	90 <sup>th</sup> Percentile (µg/L)
Novaluron	60	0	0	0.016	N/A	N/A
Permethrin	67	0	0	0.390	N/A	N/A
Phenothrin	71	0	0	0.779	N/A	N/A
Prallethrin	71	0	0	0.016	N/A	N/A
Propoxur	71	0	0	0.016	N/A	N/A
Pyrethrin 1	70	0	0	0.031	N/A	N/A
Pyriproxyfen	59	3	5	0.016	< 0.016	< 0.016
S-Bioallethrin	71	0	0	0.016	N/A	N/A
S-Indoxacarb	63	1	2	0.016	N/A	N/A
S-Methoprene	51	0	0	0.063	N/A	N/A
Tau-Fluvalinate	71	0	0	0.016	N/A	N/A
Tetrachlorvinphos	71	1	1	0.016	N/A	N/A
Tetramethrin	63	0	0	0.016	N/A	N/A

Chlorothalonil is not shown in the table because there were no influent samples which met QC guidelines for this compound. The values in the “Sample Count” column reflect the number of samples which met QC guidelines for the given analyte. The values in the “Number of Detections” and “Detection Frequency” columns include observations qualified as “D” (detection), but do not include observations qualified as “T” (trace). Median and 90th percentile values were estimated using the Kaplan-Meier method to include censored observations (non-detects and “trace” observations) using the *NADA2* package in RStudio. When there are <2 non-censored observations for a given pesticide, the Kaplan-Meier method is unable to estimate summary statistics (as indicated by “N/A”).

Table 2. Pesticide detections and concentrations in effluent

Pesticide	Sample Count	Number of Detections	Detection frequency (%)	Minimum Reporting Limit (µg/L)	Median (µg/L)	90 <sup>th</sup> Percentile (µg/L)
alpha-Cypermethrin	55	0	0	0.004	N/A	N/A
beta-Cyfluthrin	63	0	0	0.004	N/A	N/A
Bifenthrin	55	0	0	0.016	N/A	N/A
Chlorothalonil	71	0	0	0.008	N/A	N/A
Chlorpyrifos	71	4	6	0.008	< 0.008	< 0.008
Cyfluthrin	63	0	0	0.008	N/A	N/A
Cypermethrin	55	0	0	0.008	N/A	N/A
Cyphenothrin	63	0	0	0.100	N/A	N/A
Deltamethrin	55	0	0	0.040	N/A	N/A
Dinotefuran	71	71	100	0.008	0.084	0.168
Esfenvalerate	59	0	0	0.040	N/A	N/A
Etofenprox	63	0	0	0.020	N/A	N/A
Fenpropathrin	71	0	0	0.040	N/A	N/A
Fipronil	71	61	86	0.008	0.022	0.043

Pesticide	Sample Count	Number of Detections	Detection frequency (%)	Minimum Reporting Limit (µg/L)	Median (µg/L)	90 <sup>th</sup> Percentile (µg/L)
Fipronil amide	71	5	7	0.008	< 0.008	< 0.008
Fipronil desulfinyl	71	3	4	0.008	< 0.008	< 0.008
Fipronil desulfinyl amide	71	0	0	0.016	N/A	N/A
Fipronil sulfide	71	0	0	0.008	N/A	N/A
Fipronil sulfone	71	5	7	0.008	< 0.008	< 0.008
Flumethrin	43	0	0	0.040	N/A	N/A
Fluralaner	71	2	3	0.008	< 0.008	< 0.008
gamma-Cyhalothrin	55	0	0	0.005	N/A	N/A
Imidacloprid	71	70	99	0.008	0.069	0.100
lambda-Cyhalothrin	55	0	0	0.016	N/A	N/A
Novaluron	71	0	0	0.008	N/A	N/A
Permethrin	43	0	0	0.401	N/A	N/A
Phenothrin	55	0	0	0.401	N/A	N/A
Prallethrin	71	0	0	0.008	N/A	N/A
Propoxur	71	0	0	0.008	N/A	N/A
Pyrethrin 1	23	0	0	0.016	N/A	N/A
Pyriproxyfen	71	0	0	0.008	N/A	N/A
S-Bioallethrin	71	0	0	0.008	N/A	N/A
S-Indoxacarb	63	0	0	0.008	N/A	N/A
S-Methoprene	55	0	0	0.032	N/A	N/A
Tau-Fluvalinate	40	0	0	0.008	N/A	N/A
Tetrachlorvinphos	71	0	0	0.008	N/A	N/A
Tetramethrin	71	0	0	0.008	N/A	N/A

The values in the “Sample Count” column reflect the number of samples which met QC guidelines for the given analyte. The values in the “Number of Detections” and “Detection Frequency” columns include observations qualified as “D” (detection), but do not include observations qualified as “T” (trace). Median and 90th percentile values were estimated using the Kaplan-Meier method to include censored observations (non-detects and “trace” observations) using the *NADA2* package in RStudio. When there are <2 non-censored observations for a given pesticide, the Kaplan-Meier method is unable to estimate summary statistics (as indicated by “N/A”).

Table 3. Benchmark exceedance frequencies for pesticides in effluent

Pesticide	Sample Count	Detection frequency (%)	Minimum Freshwater Acute Benchmark Exceedance Frequency (%)	Minimum Freshwater Chronic Benchmark Exceedance Frequency (%)	Minimum Marine Acute Benchmark Exceedance Frequency (%)	Minimum Marine Chronic Benchmark Exceedance Frequency (%)
Chlorpyrifos	71	6	6	6	1	0
Dinotefuran	71	100	0	0	0	N/A
Fipronil	71	86	0	79	0	0
Fipronil desulfinyl	71	4	0	0	0	0
Fipronil sulfone	71	7	0	0	0	0
Imidacloprid	71	99	1	96	0	0

The values in the “Sample Count” column reflect the number of samples which met QC guidelines for the given analyte. The values in the “Detection Frequency” column include observations qualified as “D” (detection), but do not include observations qualified as “T” (trace). Benchmarks are used as a screening tool for relative toxicity (benchmark exceedances in effluent do not necessarily indicate exceedances in receiving water). In the benchmark exceedance columns, “N/A” indicates that no benchmark of the given type (e.g., marine chronic) was available for the analyte. Pesticides and degradates without any benchmarks available are omitted from this table. In addition, pesticides and degradates with no detections in effluent are omitted from this table.

### **3. Tracking Exceedances of Aquatic Life Benchmarks**

For further data analysis: pesticides that have a >10% aquatic life benchmark exceedance frequency for three consecutive years are recommended for further detailed data analysis if no analysis has been completed in the past five years. In the next study report (for samples collected in 2025), data from calendar years 2023 through 2025 will be analyzed; aquatic life benchmark exceedances for that time period will be tracked and tabulated.

### **4. Quality Control**

Table 4. Laboratory Quality Control (QC) summary

Sample Matrix	QC Type	Total QC Count	Number of QC Out of Control
Influent (Filtrate)	Lab Blank	259	0
Influent (Filtrate)	Matrix Spike	259	32
Influent (Solids)	Lab Blank	259	0
Influent (Solids)	Matrix Spike	259	39
Effluent	Lab Blank	259	0
Effluent	Matrix Spike	259	36

Samples were analyzed for 37 analytes. A lab blank and a matrix spike were performed and analyzed in each analytical batch of samples. The values shown in the “Total QC Count” column in Table 4 (above) reflect the total sum of the number of analytes that were analyzed in each batch. There were no analyte detections in lab blanks. In the matrix spike samples, spiked analytes are measured, and the percent recovery is calculated for each analyte. In cases where the percent recovery was outside of the acceptable range, the data from that analyte in that same analytical batch were considered unacceptable and were not used.

In addition to the quality control measures described above, DTSC ECL staff also analyze laboratory control samples. Preliminary data indicate that percent recoveries for all analytes in laboratory control samples are within acceptable ranges; however, DTSC ECL staff continue to collect and review these data in their efforts to establish control limits. Future monitoring reports may include more information regarding the laboratory control samples.

### **5. Data: water quality, aquatic toxicity, and analytical chemistry results**

WWTPs participate anonymously; therefore, data from individual facilities will not be made publicly available. Instead, data will only be shared in aggregated (e.g., DFs across all participant facilities) and anonymized format, as shown in this report. In addition, the identities (and identifying characteristics such as discharge coordinates) of participant facilities will not be made publicly available.