DEPARTMENT OF PESTICIDE REGULATION (DPR) Date: March 18, 2024

SURFACE WATER AMBIENT MONITORING REPORT

1. Study highlights

DPR Study Number: 322
Study Title: Monitoring Pesticides in Wastewater Influent and Effluent
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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: Seven counties throughout California (wastewater treatment plants participate anonymously).

Waterbody/Watershed: Twenty-four wastewater treatment plants discharging effluent into ten different waterbodies throughout California.

Objectives:

Determine the presence and concentrations of selected pesticides in wastewater influent and effluent. Evaluate regional and seasonal variability in wastewater pesticide loading to wastewater treatment plants (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.

Sampling period: August 2022 – December 2022

Major findings:

INSECTICIDES. In the wastewater monitoring program, samples were analyzed for 31 insecticide active ingredients and degradates. Overall, detection frequencies were much higher in influent than in effluent. Nineteen insecticides had a detection frequency (DF) of >50% in influent, compared to only five in effluent. Insecticide classes analyzed include pyrethroids, fiproles (fipronil and degradates), organophosphates, neonicotinoids, carbamates, and insect growth regulators.

Pyrethroids. Ten of the pyrethroids analyzed had DFs >50% in influent, with the highest being alpha-cypermethrin (100%), cypermethrin (100%), bifenthrin (95%), etofenprox (95%), and permethrin (95%). In effluent, all pyrethroids analyzed had DFs <5%.

Fiproles. Four of the fiproles analyzed had DFs >50% in influent, with the highest being fipronil (100%) and fipronil sulfone (100%), followed by fipronil amide (67%) and fipronil desulfinyl (56%). Detection frequencies in influent were much lower for fipronil desulfinyl amide (2%) and fipronil sulfide (2%). In effluent, three of the fiproles analyzed had DFs >50% (fipronil, 95%; fipronil sulfone, 95%; and fipronil desulfinyl, 72%). Much lower DFs were observed for fipronil amide (30%), fipronil sulfide (21%), and fipronil desulfinyl amide (0%) in effluent.

Organophosphates. Two organophosphate compounds were analyzed in the wastewater monitoring program: chlorpyrifos and tetrachlorvinphos. Chlorpyrifos had a DF of 51% in influent and 5% in effluent, while tetrachlorvinphos had a DF of 33% in influent and 19% in effluent.

Neonicotinoids. Imidacloprid is the only neonicotinoid that was analyzed in the wastewater monitoring program. This compound was ubiquitously detected (DF = 100%) in influent and effluent samples.

Carbamates. Propoxur is the only carbamate compound that was analyzed in the wastewater monitoring program. This compound had a DF of 53% in influent and 74% in effluent.

Insect Growth Regulators. Two insect growth regulators were analyzed in the wastewater monitoring program: novaluron and pyriproxyfen. Novaluron had a DF of 51% in influent and 7% in effluent, while pyriproxyfen had a DF of 84% in influent and 19% in effluent.

FUNGICIDES. Chlorothalonil is the only fungicide that was analyzed in the wastewater monitoring program. Chlorothalonil was not detected in any influent or effluent samples. However, this analyte proved difficult to analyze in influent, with 75% of spiked samples exhibiting percent recovery values outside the acceptable range (see section *4: Quality Control*).

CONCLUSIONS.

Pyrethroids are prevalent in influent (10 pyrethroids had DFs >50%), likely due to their widespread use in products with down-the-drain transport potential. However, they are largely absent from effluent (all analyzed pyrethroids had DFs <5%), likely due to sorption to solids before and during the treatment process.

Imidacloprid was detected in all influent and effluent samples analyzed, likely due to its widespread use in pet products and its high water solubility (514 mg/L).

Fiproles are prevalent in both influent (four fiproles had DFs >50%) and effluent (three fiproles had DFs >50%). Although detection frequencies vary, fipronil and fipronil sulfone tend to be the most prevalent fiproles in both sample matrices.

For future monitoring, SWPP staff should continue to recruit additional WWTPs to expand the geographic range of the study. Additionally, it may be beneficial to expand analytical capabilities to include additional pesticide active ingredients with potential for down-the-drain transport.

Recommendations for pesticides that need a DTSC ECL analytical method (from SWMP):

Sample analysis is performed by the Department of Toxic Substances Control's Environmental Chemistry Laboratory (DTSC ECL). Based on the availability of certain pesticide active ingredients (AIs) in products with potential for down-the-drain transport (e.g., pet products), SWPP staff have requested that the following pesticides be added to the analytical suite for this program: flumethrin, dinotefuran, S-indoxacarb, S-methoprene, and fluralaner. Currently, DTSC ECL staff are investigating whether it will be feasible to add these analytes to the analytical suite for this program. Future study reports may include data on these analytes.

2. Pesticide detection frequency

During the study period, a total of 43 influent samples and 43 effluent samples were collected. However, for some analytes, the sample count shown in Table 1 and/or Table 2 is less than 43 because some samples did not meet QC guidelines for the given analyte (see section 4: Quality Control). WWTPs participate anonymously; therefore, data will not be made publicly available. Contact the Project Lead to request further information.

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

Pesticide	Sample Count	Number of Detections	Detection frequency (%)	Minimum Method Detection Limit (µg/L)
alpha-Cypermethrin	43	43	100	0.001
beta-Cyfluthrin	43	23	53	0.002
Bifenthrin	43	41	95	0.014
Bioallethrin	43	0	0	0.002
Chlorothalonil	24	0	0	0.003
Chlorpyrifos	43	22	51	0.006
Cyfluthrin	43	23	53	0.004
Cyhalothrin	43	26	60	0.007
Cypermethrin	43	43	100	0.006
Cyphenothrin	43	1	2	0.014
Deltamethrin	43	30	70	0.018
Esfenvalerate	43	0	0	0.009
Etofenprox	43	41	95	0.003
Fenpropathrin	43	9	21	0.011
Fipronil	43	43	100	0.002
Fipronil amide	43	29	67	0.004
Fipronil desulfinyl	43	24	56	0.001
Fipronil desulfinyl amide	43	1	2	0.004
Fipronil sulfide	43	1	2	0.003
Fipronil sulfone	43	43	100	0.002
gamma-Cyhalothrin	43	34	79	0.002

Pesticide	Sample Count	Number of Detections	Detection frequency (%)	Minimum Method Detection Limit (µg/L)
Imidacloprid	43	43	100	0.001
Novaluron	43	22	51	0.001
Permethrin	43	41	95	0.100
Phenothrin	43	0	0	0.680
Prallethrin	43	10	23	0.002
Propoxur	43	23	53	0.001
Pyrethrin 1	43	4	9	0.013
Pyriproxyfen	43	36	84	0.004
Tau-Fluvalinate	43	0	0	0.003
Tetrachlorvinphos	43	14	33	0.001
Tetramethrin	43	15	35	0.001

The values in this table include samples for which the solids and/or filtrate fraction of the influent met QC guidelines (see section 4: Quality Control) and include "trace" observations below the reporting limit but above the method detection limit.

Table 2. Pesticide detections in effluent

Pesticide	Sample Count	Number of Detections	Detection frequency (%)	Minimum Method Detection Limit (µg/L)
alpha-Cypermethrin	33	0	0	0.001
beta-Cyfluthrin	42	0	0	0.002
Bifenthrin	33	0	0	0.014
Bioallethrin	43	0	0	0.002
Chlorothalonil	43	0	0	0.003
Chlorpyrifos	43	2	5	0.006
Cyfluthrin	42	0	0	0.004
Cyhalothrin	33	0	0	0.007
Cypermethrin	42	0	0	0.006
Cyphenothrin	43	0	0	0.014
Deltamethrin	33	0	0	0.018
Esfenvalerate	33	0	0	0.009
Etofenprox	42	1	2	0.003
Fenpropathrin	43	0	0	0.011
Fipronil	43	41	95	0.002
Fipronil amide	43	13	30	0.004
Fipronil desulfinyl	43	31	72	0.001
Fipronil desulfinyl amide	43	0	0	0.004
Fipronil sulfide	43	9	21	0.003
Fipronil sulfone	43	41	95	0.002
gamma-Cyhalothrin	33	0	0	0.002

Pesticide	Sample Count	Number of Detections	Detection frequency (%)	Minimum Method Detection Limit (µg/L)
Imidacloprid	43	43	100	0.001
Novaluron	43	3	7	0.001
Permethrin	33	0	0	0.100
Phenothrin	33	0	0	0.680
Prallethrin	43	0	0	0.002
Propoxur	43	32	74	0.001
Pyrethrin 1	23	1	4	0.013
Pyriproxyfen	43	8	19	0.004
Tau-Fluvalinate	33	0	0	0.003
Tetrachlorvinphos	43	8	19	0.001
Tetramethrin	43	0	0	0.001

The values in this table include samples which met QC guidelines (see section 4: Quality Control) and include "trace" observations below the reporting limit but above the method detection limit.

3. Tracking Pesticide Concentrations Over Time

While the wastewater monitoring program was initiated as a pilot study in 2019, full-scale monitoring did not begin until August 2022. Therefore, a detailed analysis of pesticide concentration trends over time is not provided in this study report. Future study reports will include such an analysis, likely beginning with the 2024 report (at which point, three years' worth of data will be available).

4. Quality Control

Table 3. Laboratory Quality Control (QC) summary

Sample Matrix	Number of Analytical Batches	QC Type	Number of Analytes	Total QC Count	Number of QC Out of Control
Influent (Filtrate)	4	Lab Blank	32	128	3
		Matrix Spike	32	128	2
Influent (Solids)	4	Lab Blank	32	128	3
		Matrix Spike	32	128	6
Effluent	5	Lab Blank	32	160	0
		Matrix Spike	32	160	23

There were a total of eight analytical batches of influent samples analyzed (split into four batches each of filtrate and solids), and five effluent batches. 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 3 (above) reflect the number of analytical batches for the sample matrix, multiplied by the total number of analytes in the study (32).

In lab blanks, there were a total of six analyte detections which occurred during analysis of influent samples: three during the analysis of the aqueous fraction (filtrate) and three during the analysis of the solids fraction. In cases where an analyte was detected in a lab blank, the data from that analyte in that same analytical batch were considered unacceptable and were not used.

In the matrix spike samples, spiked analytes are measured, and the percent recovery is calculated for each analyte. DTSC ECL staff provided analyte-specific acceptable ranges of percent recovery. For chlorpyrifos, cyphenothrin, phenothrin, and pyrethrin 1, the acceptable range is 30-170% recovery. For all other analytes, the acceptable range is 50-150% recovery. These values may change over time as DTSC ECL staff continue to collect and review data. In cases where the percent recovery was either too low or too high, the data from that analyte in that same analytical batch were considered unacceptable and were not used.

5. Data: water quality 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., detection frequencies 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.