Department of Pesticide Regulation
Environmental Monitoring Branch
Surface Water Protection Program
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STUDY 322: Monitoring Pesticides in Wastewater: Influent, Effluent and Biosolids 2019–2020

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1.0 INTRODUCTION

The occurrence of pesticides in treated wastewater effluent at concentrations that exceed aquatic toxicity thresholds has been documented in California's wastewater treatment plants. Down-the-drain pesticide transport may result from direct application to drains or indirect transport from other indoor or outdoor applications. Residential indoor sources, such as foggers/sprays, topical applications to domestic pets, or pesticide treated textiles may enter the waste stream through activities including washing, bathing, or laundry. Similarly, transferring pesticides from outside applications on a person's clothing or shoes may also ultimately be transported down-the-drain through cleaning activities. Pyrethroids have been detected in treated wastewater effluent of California wastewater treatment plants (WWTPs) at concentrations that exceed acute toxicity thresholds for sensitive invertebrates [2]. A recent survey of eight WWTPs in the San Francisco Bay area found fipronil and imidacloprid in both influent and effluent samples, with little observed removal regardless of treatment capability [3]. These regional one-time surveys indicate the potential for pesticides within the sewershed to pass through WWTP and discharge to surface water and concentrations that exceed toxicity thresholds such as USEPA chronic aquatic life benchmarks. . In order to understand the potential risk posed by pesticide concentrations in wastewater effluent to California aquatic habitats, a more comprehensive analysis of representative pesticide loading into surface waters is warranted. Similar to urban and agricultural runoff, it is feasible that variances in regional pest pressures could result in differences in composition and magnitude of pesticide use, and subsequent transport to the wastestream [4]. WWTPs have a wide range of treatment capabilities before discharging effluent. These include facilities equipped with at least secondary treatment and many with additional tertiary processes. Final effluent may be additionally treated with a disinfectant such as UV radiation or chlorine prior to leaving the facility. Available studies suggest even with the highest level of treatment, pesticides such as pyrethroids, fipronil, and imidacloprid are present in effluent at concentrations that exceed toxicity thresholds; however, monitoring studies with consistent and robust analytical methods are not available. There is currently little understanding of the spatial and temporal variation of pesticides entering individual sewersheds. The monitoring effort described herein represents the initial steps in establishing a long-term monitoring network for pesticides in wastewater in order to characterize the potential aquatic risks associated with pesticides present in treated effluent. Subsequent year protocols will likely incorporate additional study objectives such as characterizing pesticide use patterns and sources within the sewershed.

2.0 OBJECTIVES

The overall goal of this project is to assess pesticide concentrations found in wastewater influent and effluent in California.. Specific objectives include:

1) Determine presence and concentrations of selected pesticides in wastewater influent, effluent, and biosolids;
2) Evaluate regional and seasonal differences in wastewater pesticide loading to WWTPs;
3) Evaluate magnitude of measured effluent concentrations relative to water quality or aquatic toxicity thresholds;
4) Evaluate influence of sewershed characteristics (i.e., population, contributing industry) on relative pesticide loading;

3.0 PERSONNEL

The study will be conducted by staff from the California Department of Pesticide Regulations (CDPR's) Environmental Monitoring Branch, Surface Water Protection Program (SWPP), under the general direction of Nan Singhasemanon, Environmental Program Manager. Key personnel are listed below:

Project Leader: Robert Budd, Ph.D.
Field Coordinator: Jason Carter, Ph.D.
Reviewing Scientist: Jennifer Teerlink, Ph.D.
Statistician: Dan Wang, Ph.D.
Laboratory Partner: UC Davis, Dr. Thomas Young's laboratory (Contract #18-C0159)
Collaborators: Wastewater Treatment Plants throughout California
Please direct questions regarding this study to Robert Budd, Research Scientist, at (916) 445-2505 or Robert.Budd@cdpr.ca.gov.

4.0 STUDY PLAN

4.1 Site Selection. Monitoring sites are chosen based on the need to collect the necessary data to address study objectives. Volunteer WWTPs throughout California were identified through direct contact with plant management and technical staff. Participating WWTPs span a wide range of comparative parameters, including region, size (measured in gallons treated per day), treatment capability (secondary or tertiary), final treatment (disinfectant), and point of discharge (surface waters or marine) (Table 1). Additional sample locations may be included as participation in the program increases.

4.2 Pesticides for Analysis. SWPP conducted a retail store survey to identify pesticide products and associated active ingredients available directly to the consumer with potential for down-the-drain transport including pet products [5]. SWPP used the results from the survey to create a preliminary list of target analytes. Analytical methods were developed for a select list of pesticides during a previous collaborative project (Contract # 14-C0103) with UC Davis. Developed analytical methods (Table 2) were used to analyze samples collected during a yearlong monitoring study at a California wastewater treatment plant. In addition to the targeted analytical methods, non-target and suspect screening approaches were used on all samples to identify any pesticides consistently present and in need of further quantification. There were no additional pesticides of concern identified at this time. A subsequent retail store survey further confirmed that the established targeted analytical methods sufficiently capture pesticides currently available for homeowner purchase and use [6]. The analytical method for analysis of biosolids is currently under development and will target a comparable list of analytes, with a focus on hydrophobic pesticides that partition to the solid phase of treated wastewater.

4.3 Sample Collection.

All influent, effluent, and biosolid samples will be collected and shipped by the participating WWTPs to UC Davis using sampling bottles, coolers, and prepaid shipping labels provided by CDPR. CDPR will coordinate sampling events to ensure all samples are collected within a similar time frame, allowing for analysis of all sites as a single batch. Collection methods will follow methods consistent with individual plant collection protocols using 24-hour composite (either flow-weighted or time-weighted) for all influent and effluent samples. Influent and effluent samples will be collected in 1-L amber bottles per monitoring event. Influent and effluent sampling will be conducted up to four times at each of the participating WWTPs (Table 3). Influent samples will be collected after the preliminary filtration and before primary treatment. Effluent samples will be collected at the end stage of physical treatment, but may be taken prior to the disinfection step. Dewatered biosolids will be collected at each location once during the course of the study. All samples will be shipped on ice within 24 hrs of collection using CDPR-provided coolers and shipping labels to Dr. Thomas Young at the University of California at Davis for analysis. Additional water quality parameters and details specific to collected sample (i.e., daily flow data) may be provided by individual WWTPs. A chain-of-custody record will be completed and accompany each sample.

5.0 CHEMICAL ANALYSIS

Water and biosolid samples will be analyzed for pesticides by Dr. Thomas Young at the University of California at Davis according to the methods developed under CDPR Contracts 14-C0103 and 18-C0159 [9].

6.0 DATA ANALYSIS AND REPORTING

Each participating plant will receive the pesticides results from their plant as quickly as they are made available. CDPR will not associate final results with specific plant locations and identities without express written consent of the participating plant. Otherwise, all pesticide results will be presented in an anonymized format.

We will use various nonparametric and parametric statistical methods to analyze all of the data generated during this study including site information, general water quality measurements, and pesticide analytical data. The data collected from this project may be used to develop or calibrate down-the-drain pesticide model.

Environmental pesticide monitoring data are typically heavily skewed and contain a number of results that are below limits of quantification (LOQs). Statistical analysis of datasets with multiple RLs may violate the normality and equal-variance assumptions of parametric procedures (e.g., ANOVA and *t*-tests). In order to appropriately address the characteristics of the sample data, a more generic and distribution-free approach, such as non-parametric statistics, will be used in this study. Helsel (2012) illustrated the application of non-parametric procedures to skewed and censored environmental data. We will primarily reference Helsel (2012) as a general guideline for data analysis of this study. The data will be analyzed by using the R statistical program (R Core Team, 2014), specifically the Nondetects And Data Analysis for environmental data (NADA) package for R (http://cran.r-project.org/web/packages/NADA/NADA.pdf), and Minitab (http://www.minitab.com/en-us/).

Based on the study objectives, preliminary analysis, and data availability, we propose the following statistical procedures for data analysis (Table 4).

1) Explanatory data analysis will be performed to summarize the characteristics of the sample data. Plots such as boxplots, histograms, probability plots, and empirical distribution functions will be produced to explore any potential patterns implied by the data.
2) Hypothesis tests will be conducted to compare the concentration between groups of interest. Non-parametric procedures will be used to compute the statistics for hypothesis testing. Data with multiple reporting limits will be censored at the highest limit before proceeding if the test procedure allows only one RL.

Collected data will be summarized in a data report and potentially peer-review journal articles. Participating plants will be granted the opportunity (minimum of 30 days) to review written reports or journal articles prior to publication.

7.0 TIMELINE

Field Sampling: May 2019–May 2020
Chemical Analysis: May 2019–July 2020
Summary Report: December 2020

Table 1. Summary of participating WWTPs in monitoring study.

Facility Treatment	Discharge Point	Number of Plants	Plant Capacity (MGD)*
Secondary	Ocean	12	7.6–450
	Fresh Water	2	6.7–60
Tertiary	Ocean	2	8.5–20
	Fresh Water	7	15–100
	Recycled	2	2
Total		**25**	**2-450**

*Millions of gallons per day (MGD)

Table 2. Pesticides to be monitored for in wastewater influent and effluent, with their respective reporting limit (RL).

Pesticide	Source Type	LOQ (ng/L)	
		Influent	**Effluent**
Bifenthrin	GC NCI	1	0.4
Chlorpyrifos	GC NCI	0.5	0.1
Cyfluthrin	GC NCI	2	1
Cyhalothrin	GC NCI	0.5	0.2
Cypermethrin	GC NCI	5	1
Deltamethrin	GC NCI	5	4
Esfenvalerate	GC NCI	1	1
Fipronil-desulfinyl	GC NCI	0.2	0.04
Fipronil-sulfide	GC NCI	0.2	0.04
Fipronil-sulfone	GC NCI	0.2	0.2
Permethrin	GC NCI	10	10
Chlorothalonil	GC NCI	100	20
Novaluron	GC NCI	2	1
Prallethrin	GC NCI	0.5	0.2
Phenothrin	GC NCI	100	20
Cyphenothrin	GC NCI	1	0.4
Fipronil amide	GC NCI	0.5	0.2
Fipronil-desulfinyl amide	GC NCI	0.5	0.2
Bioallethrin	GC NCI	0.2	0.1
Fipronil	GC NCI	1	0.4
Propoxur	LC ESI +	5	1
Pyriproxyfen	LC ESI +	25	5
Imidacloprid	LC ESI +	10	2

Table 3. Estimated wastewater sample allocation with three to four discrete sampling events for influent and effluent and one biosolids event.

# WWTP	Event 1	Event 2	Event 3	Event 4	Total Samples
Influent					
Up to 50	1	1	1		Up to 90
Effluent					
Up to 50	1	1	1		Up to 90
Biosolids					
Up to 32	1				Up to 30

Table 4. Non-parametric procedures frequently used for comparing paired data, two samples and three or more samples.

Data	Non-Parametric Procedure
Paired data	*Wilcoxon signed-rank test* for uncensored data *Sign test* (modified for ties) for censored data with one RL *Score tests* for censored data with multiple RLs (the PPW test and the Akritas test)
Two samples	*Wilcoxon rank-sum (or Mann-Whitney) test* or *Kolmogorov-Smirnov test* for censored data with one RL *Score tests* for censored data with multiple RLs (the *Gehan test* and generalized *Wilcoxon test*)
Three or more samples in one-way layout	*Kruskal-Wallis test* (for unordered alternative) or *Jonckheere-Terpstra test* (for ordered alternative) for censored data with one RL *Generalized Wilcoxon score test* for censored data with multiple RLs *Multiple comparison* to detect which group is different
Three or more samples in two-way layout	*Friedman's test* (for unordered alternative) or *Page's test* (for ordered alternative) for censored data with one RL Multiple comparison to detect which group is different

References

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