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Article

Sub-sewershed Monitoring to Elucidate Down-the-Drain Pesticide Sources

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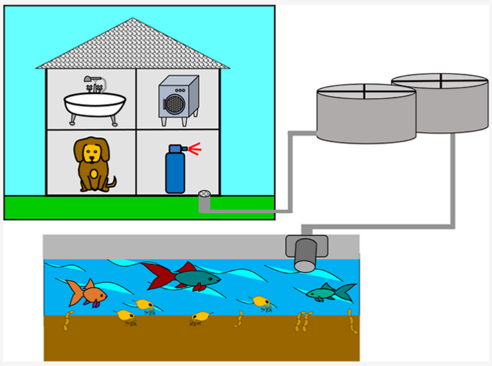

ABSTRACT: Pesticides have been reported in treated wastewater effluent at concentrations that exceed aquatic toxicity thresholds, indicating that treatment may be insufficient to adequately address potential pesticide impacts on aquatic life. Gaining a better understanding of the relative contribution from specific use patterns, transport pathways, and flow characteristics is an essential first step to informing source control measures. The results of this study are the first of their kind, reporting pesticide concentrations at sub-sewershed sites within a single sewer catchment to provide information on the relative contribution from various urban sources. Seven monitoring events were collected from influent, effluent, and seven sub-sewershed sites to capture seasonal variability. In addition, samples were collected from sites with the potential for relatively large mass fluxes of pesticides (pet grooming operations, pest control operators, and laundromats). Fipronil and imidacloprid were detected in most samples (>70%). Pyrethroids were detected in >50% of all influent and lateral samples. There were significant removals of pyrethroids from the aqueous process stream within the facility to below reporting limits. Imidacloprid and fiproles were the only pesticides that were detected above reporting limits in effluent, highlighting the importance of source identification and control for the more hydrophilic compounds. Single source monitoring revealed large contributions of fipronil, imidacloprid, and permethrin originating from a pet groomer, with elevated levels of cypermethrin at a commercial laundry location. The results provide important information needed to prioritize future monitoring efforts, calibrate down-the-drain models, and identify potential mitigation strategies at the site of pesticide use to prevent introduction to sewersheds.

KEYWORDS: *wastewater, pesticides, removal, influent, effluent, lateral*

■ INTRODUCTION

Pesticides, including pyrethroids, fipronil, and imidacloprid, have been reported in treated wastewater effluent at concentrations that exceed aquatic toxicity thresholds.[1] In arid regions, the discharge of treated effluent can dominate flow in streams and rivers and can contribute to estuarine environments with limited hydrodynamic exchange with the ocean, posing a potential risk to aquatic organisms. Limited data exist on the ability of wastewater treatment technologies to remove pesticides; however, available results suggest treatment may be insufficient to reduce pesticide concentrations to levels below aquatic toxicity thresholds.[1−3] Historically, the primary aim of wastewater treatment technologies was to remove bulk organic matter and pathogens and to reduce nutrients present in influent in the parts per million concentration range. The ability to reduce trace organic chemicals (TOrCs) present in the parts per billion to sub parts per trillion ranges has been an area of intense research over the past several decades. Advanced treatment technologies have been evaluated for their ability to reduce TOrC concentrations, with variable success.[4] However, the increased energy requirement and corresponding greenhouse gas emissions associated with advanced treatment technologies have also been documented.[5] Reducing toxicity related to pesticides may be better addressed through source control strategies than treatment.

The occurrence of pesticides within wastewater treatment facilities at concentrations of ecological concern has been established.[1−3] However, little information exists on pesticide transport within a sewershed. The use of patterns for a particular chemical may lead to small and continuous ubiquitous sources throughout a sewershed catchment or episodic, large volume pulses. For example, personal care products and pharmaceuticals may be discharged to the system by users throughout the day, in contrast to timed releases of industrial chemicals.[6] Large pulses from specific uses have been the focus of wastewater treatment plants' pre-treatment

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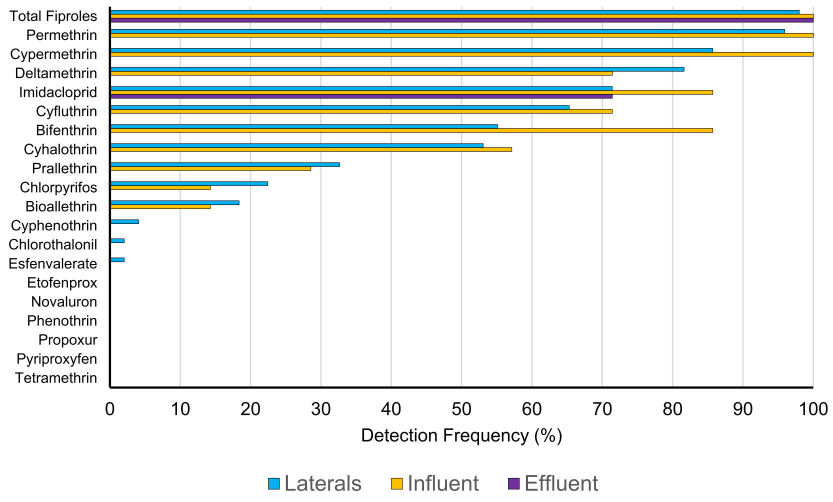

Figure 1. Detection frequency of pesticides in laterals, influent, and effluent. Summarizes all sampling sites over seven sampling events (laterals n = 49 and influent/effluent n = 7).

programs. For example, the US EPA codified pre-treatment standards to address the discharge of mercury from dental offices to WWTP (https://www.ecfr.gov/current/title-40/chapter-I/subchapter-N/part-441e). Advances in wastewater treatment technologies have been driven by the need to address continuous discharges such as personal care products, flame retardants, pharmaceuticals, and pesticides.[4,7,8] Generally, the variability of TOrC concentrations increases with decreasing catchment size.[9]

Sutton et al. (2019) provided a comprehensive conceptual model of potential sources and pathways for pesticides to enter wastewater catchments.[1] Every pesticide product used in California must be registered by both the United States Environmental Protection Agency (USEPA) and the California Department of Pesticide Regulation (CDPR), with permitted applications detailed within its label. For pyrethroids, there are additional California specific regulations imposed on professional use products during structural applications.[10] Thus, it is possible to determine which sources and pathways are possible on a chemical-by-chemical basis. This allows for a qualitative interpretation of measurements and prediction of the potential for high-use pulses to enter the sewershed. For example, source identification can be elucidated from isolating specific sewershed laterals, which are pipes that connect a structure to a municipal main sewer line. Elevated pesticide residues may be predicted at sewershed laterals originating from pet grooming facilities, pest control operators, or nurseries. However, quantitative information on relative contribution of these sources is limited. Teerlink et al. demonstrated the washing of dogs treated with spot-on fipronil products is a significant source of fipronil entering wastewater treatment plants.[11] Verifying and quantifying the relative contribution of other source pathways are key data gaps. Single source monitoring is a unique technique to isolate potential source contributions into the sewershed.

The goals of this study are to: (1) quantify pesticide residues in influent, effluent, and at the sub-sewershed scale; (2) characterize the variability in sewershed laterals to assess whether pesticides are introduced through large pulses or ubiquitous releases; (3) assess contribution from specialty sites with potential for increased pesticide discharge; and (4) investigate the relative contribution as a function of sewershed characteristics (e.g., residential, industrial, and commercial).

Sampling was conducted over a 9 month period to capture seasonal variability, with sampling events occurring on both weekdays and weekends across an entire municipal sewershed. It is recognized that evaluating the partitioning of hydrophobic TOrCs to biosolids is essential to fully understand the fate of contaminants in wastewater systems. However, this study will focus on the aqueous process stream.

■ MATERIALS AND METHODS

Study Site and Sampling. Samples were taken in the Palo Alto Regional Water Quality Control Plant (PAWT) between May 2016 and January 2017. PAWT is a tertiary treatment facility that employs a trickling filter, an activated sludge system, clarifiers, dual medium filtration, and ultraviolet disinfection prior to effluent discharge into the San Francisco Bay. The sewershed is classified as a separate sewer system, with storm water runoff directed into a different drainage system. The system serves approximately 236,000 residents, with a plant capacity of 148 megaliters per day (MLD) and an average of 68 MLD during dry weather flows. 24 h time-weighted composite samples were collected from influent, effluent, and seven sub-catchment locations. With the exception of one lateral location and the three specialty sites described below, all locations were instrumented with flow meters during the sampling periods (Table S5).

Three specialty sites were selected to investigate the potential for intensive pesticide release from a pet groomer, a pest control operation, and a laundromat. Sampling was conducted as close to the source as possible, with limited contribution from additional locations. Prior to sample collection, the sewer was physically cleaned from the structure to the monitoring location to eliminate sediment that may contribute residual pesticides.

All samples were collected with 15 min sampling intervals as 24 h time weighted composite samples using a combination of ISCO Model 2910, Hach Sigma 900 Max, and Sigma SD900 autosamplers, except for the June 2016 sample, which was collected at 30 min intervals.

Analytical Method Summary. A total of 25 target compounds were selected (Table S1) based on a shelf-survey

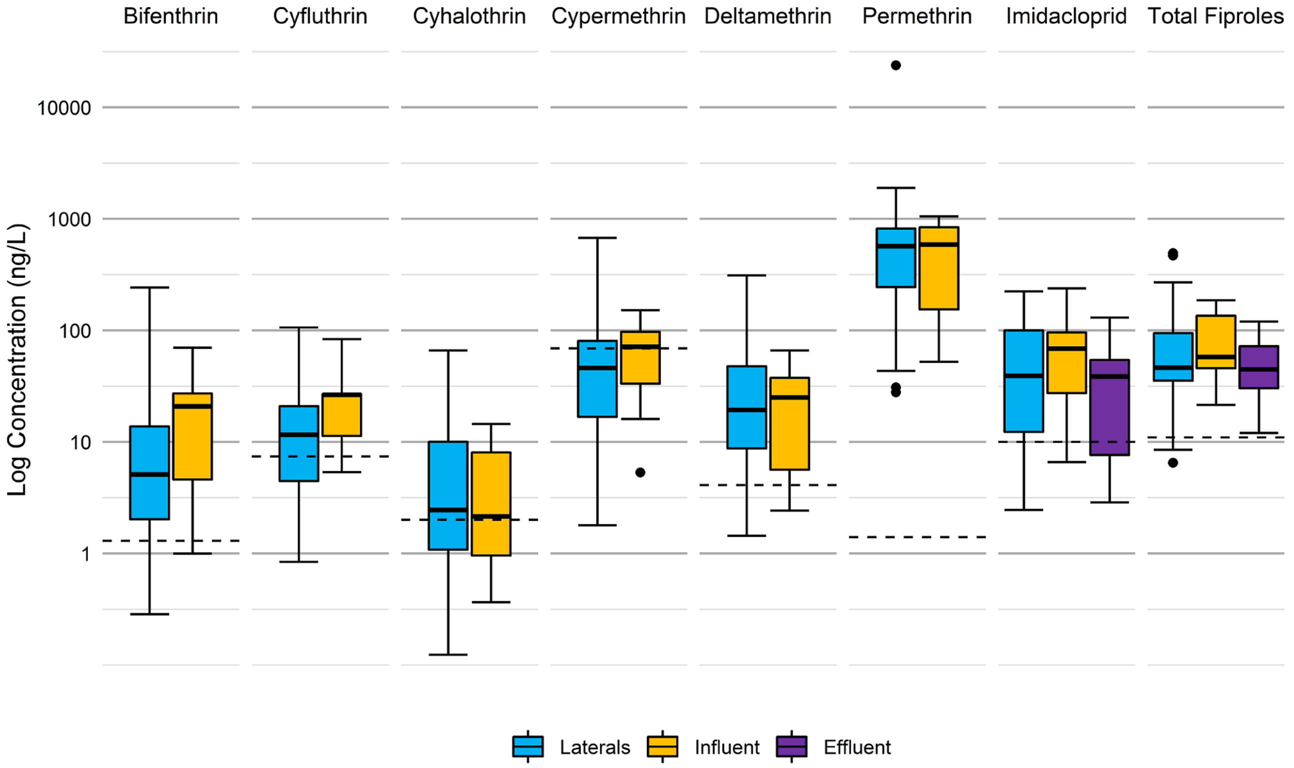

Figure 2. Box and whisker plot of pesticide concentrations with greater than 50% detection frequency in influent. Generated boxplots include data reported below LOQ using estimated values generated by CenBoxplot from the NADA package. Dotted lines indicate the US EPA chronic aquatic toxicity value for invertebrates. Total number of fiproles shows the fipronil benchmark. All pyrethroid concentrations were below RLs.

of products available directly to consumers, with consideration of toxicity.[12] Procedures for sample extraction and analysis were optimized for target compounds and derived from methods previously used to investigate pesticide occurrence in surface water samples;[3] key details including method validation are summarized here and methods are completely described in the Supporting Information (Tables S1–S4). Wastewater samples (200 mL of raw wastewater or 1 L of treated effluent) were filtered, spiked with a stable isotope-labeled surrogate solution, and passed over solid-phase extraction cartridges. Cartridges were dried and eluted first with ethyl acetate and then with methanol. Filters were extracted by sonication with hexane/acetone. Each extract was evaporated separately under nitrogen. Samples were analyzed using liquid and gas chromatography coupled with quadrupole time-of-flight mass spectrometers. LC−MS analysis of combined methanol/ethyl acetate/filter extracts was performed in the positive electrospray ionization mode and GC−MS analyses were performed on combined ethyl acetate/filter extracts in both negative chemical ionization and electron ionization modes.

Data Analysis. Pesticide monitoring data are typically right-skewed in distribution.[13] It is also common to introduce bias in data sets utilizing targeted site selection in which previous information of the distribution is known.[14] Distribution histograms were created to confirm the skewness of the dataset. To offset the bias, all statistical analysis tests were conducted using R version 4.1 with NADA package macros for censored data as described by Helsel.[13] The Mann−Whitney test was used to determine significant differences in test concentrations. Significant differences in median values between multiple groups were evaluated using the Kruskall−Wallis test. Both statistical techniques account for multiple analytical reporting limits. An α of 0.05 was used as a level of significance in all statistical analysis tests. Descriptive statistics for left-censored data were calculated using the Kaplan−Meier method.

■ RESULTS AND DISCUSSION

Influent: What Is Entering the Waste Stream? The detection frequencies (DF) of pesticides in lateral and influent samples are summarized in Figure 1 and Table S6. Fipronil and its degradates, with concentrations summed to produce a total fiprole concentration, imidacloprid, and six pyrethroids (bifenthrin, cyfluthrin, cyhalothrin, cypermethrin, deltamethrin, and permethrin) were detected in more than 50% of influent and/or lateral samples (Figure 1). There were less frequent detections of some other pyrethroids [e.g., prallethrin (29% DF), bioallethrin (14%), cyphenothrin (4%), and esfenvalerate (2%)], as well as the fungicide chlorothalonil (2%). Chlorpyrifos was detected in 22% of sewer lateral samples at levels near detection limits. There is currently one registered chlorpyrifos pesticide product for use by professionals for cockroaches in sewers, which could result in a periodic, direct, low volume source into the sewershed. Etofenprox, novaluron, phenothrin, propoxur, pyriproxyfen, and tetramethrin were not detected in any sample, indicating their presence in this wastewater system is negligible.

Concentrations of the seven compounds (or compound groups in the case of fiproles) with DF above 50% in influent and lateral samples are summarized in Figure 2. Concentrations measured in municipal wastewater influent in this study are generally in good agreement with those available in the literature.[1] The maximum observed influent concentrations in this study are below the maximum values reported previously for all of the compounds in Figure 2 except cyfluthrin (83.6 vs 55 ng/L), fipronil amide (28.3 vs <0.3 ng/L), and fipronil sulfide (30.8 vs 5.2 ng/L).[1] The median concentrations in influent samples were lower than the highest reported median value reported by Sutton et al. for imidacloprid and most fiproles, but were consistently higher than previously reported median concentrations for fipronil amide, fipronil sulfide, and all of the pyrethroid insecticides.[1] For several compounds the values were only slightly higher (2.5% for bifenthrin, 86.8% for permethrin), but for others, the values were substantially larger than those of the highest previously reported median, ranging from 2.6 times higher for cypermethrin to 9.0 times larger for fipronil amide. Previous influent collected at the study facility found similar total fiprole concentrations (11% RPD), but much higher imidacloprid concentrations (37% RPD) than those of the current study.[2] This might indicate differences in spatial and/or temporal use patterns. Previous studies encompassed a large spatial distribution of facilities within the United States, while the current study focused on one facility during multiple time periods.

In general, concentration variability was larger in lateral samples than in influent samples (Figure 2). This could be a result of sub-sewershed pulses that when combined have a more consistent signal.

Effluent: What Is Entering Surface Waters? Effluent concentrations for the pyrethroid insecticides in wastewater effluent were all below the limits of quantification, despite being frequently measured in influent (Figure 1). The LOQs varied by sampling events but had median values of 1 ng/L (bifenthrin), 2 ng/L (cyfluthrin), 3 ng/L (deltamethrin), 5 ng/L (cypermethrin), and 25 ng/L (permethrin). Fiproles and imidacloprid were the only pesticides detected above LOQs in effluent samples at 100 and 71% frequency, respectively (Table S6). The median values in wastewater effluent were below the low end of the median range reported from other peer-reviewed literature for imidacloprid and fipronil (20 and 7% lower, respectively), and 48−275% higher than those reported for the fipronil degradates.[1]

Although the present study was not designed to directly determine removal (e.g., influent and effluent sampling times were coincident rather than lagged by average hydraulic residence time), the comparison of influent and effluent concentrations is still useful in adding to the body of knowledge regarding the treatability of pesticides within the waste stream. The percent change in the concentration between influent and effluent was calculated as

$$\%\ \text{change} = \frac{\text{effluent} - \text{influent}}{\text{influent}} \times 100$$

The minimum percent change was determined by using the maximum value of the result or LOQ; therefore, the actual removal efficiencies could be higher than those reported here.

The median percent removal for pyrethroids was >90% for bifenthrin, cypermethrin, cyfluthrin, permethrin, and cyhalothrin and ≥80% for deltamethrin, prallethrin, and bioallethrin (Table 1). Weston et al. observed similar removal of pyrethroids from the aqueous process stream within a Sacramento, CA WWTP, with >84% removal of bifenthrin, cyhalothrin, cypermethrin, and permethrin during six monitoring events.[3] It is important to note that the method detection limits were above U.S. EPA aquatic toxicity thresholds for some samples; thus, a non-detect in effluent samples does not confirm a lack of potential toxicity for any sample of permethrin, three samples of deltamethrin, and one of bifenthrin (Table S7). All other effluent samples were below their respective minimum aquatic benchmarks, indicating a significant reduction in potential ecological risk.

Table 1. Estimated Percent Aqueous Process Stream Removal of Pesticides Based on Effluent and Influent Concentrations[a]

pesticide	observations	range	average	median
bifenthrin	6	78−96	≥91%	≥94%
cypermethrin	7	6−98	≥78%	≥93%
cyfluthrin	5	87−98	≥92%	≥92%
permethrin	7	52−99	≥88%	≥92%
cyhalothrin	4	53−97	≥83%	≥91%
deltamethrin	5	65−92	≥85%	≥89%
prallethrin	2	82−84	≥83%	≥83%
bioallethrin	1	80	≥80%	≥80%
chlorpyrifos	1	53	≥53%	≥53%
imidacloprid	6	10−62	≥41%	46%
total fiproles	7	(−)44−87	24%	33%
fipronil	7	(−)17−82	21%	21%
fipronil-sulfide	5	32−77	≥56%	62%
fipronil-sulfone	6	(−)68−50	4%	17%
fipronil amide	6	(−)20−88	≥37%	≥38%
fipronil-desulfinyl amide	2	(−)41−63	11%	11%
fipronil-desulfinyl	4	(−)347−(−)108	(−)264%	(−)300%

[a] (−) indicates effluent concentrations higher than influent concentrations. Only pesticides with observed influent and/or effluent detections calculated. The LOQ used for effluent in cases with concentrations below the LOQ. ≥ indicates the estimated removal based on LOQ values. Range values represent conservative estimates for pesticides with all effluent concentrations ≤ LOQ.

Removal of the neonicotinoid imidacloprid was less complete, with a median removal value of 46% (10−62%). Two previous studies have demonstrated that imidacloprid is incompletely removed by typical municipal wastewater treatment operations.[2,15] In Sadaria et al. (2016), monitoring of eight San Francisco Bay Area municipal wastewater treatment plants observed negligible removal of imidacloprid (7%).[2] Sadaria et al. (2016) monitored a single plant over 5 days and found statistically insignificant aqueous removal of imidacloprid throughout the tertiary facility, with mean effluent concentrations <13% lower than influent concentrations .[15] The amount of imidacloprid remaining in treated effluent in the current study is still of ecological concern because on five out of seven monitoring dates, the imidacloprid in the effluent exceeded the 10 ng/L aquatic toxicity benchmark by factors of 1.03 to 13.

Addressing the removal of fipronil during wastewater treatment operations is more complex since five different fipronil degradation products were routinely detected in this study and they are formed by different environmental processes (photodegradation, aerobic biodegradation, anaerobic degradation, and hydrolysis). With a median reduction of 21% for the parent compound between influent and effluent concentrations, this indicates moderate transference to byproducts or sorption and subsequent settling within the facility (Table 1). The median total fiprole removal was 33%, which was similar to Sadaria et al. (2016), who observed a 35% reduction in the total fiprole concentration from the median

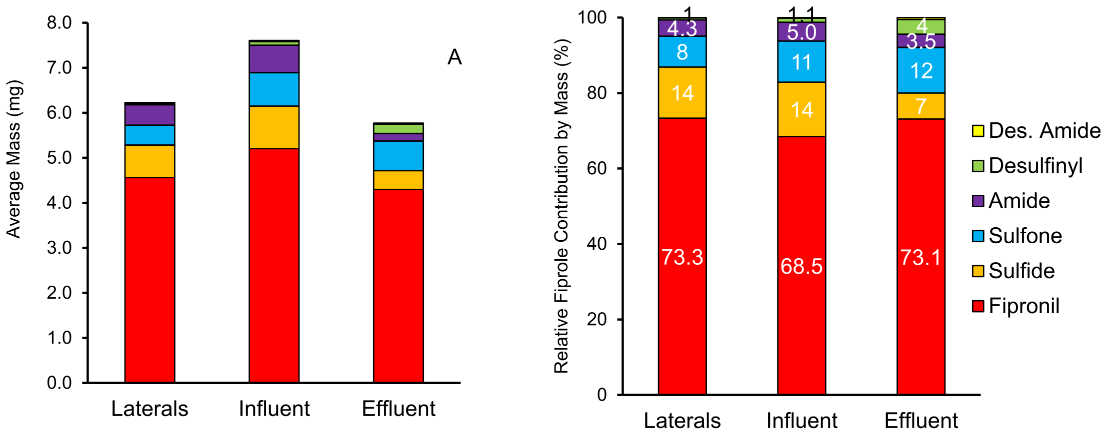

Figure 3. (A) Average mass (μg) of fiproles by event (24 h sampling period) for laterals, influent, and effluent. (B) Relative contributions (%) of fiprole masses for laterals, influent, and effluent samples. Individual lateral mass summed for each sampling date prior to averaging.

influent (83.6 ng/L; $n = 8$) to the median effluent (53.6 ng/L; $n = 8$).[2] Regardless, the incomplete removal/transference of fipronil poses a potential ecological risk to sensitive aquatic species, with all seven effluent concentrations of the parent chemical exceeding the 11 ng/L aquatic benchmark value.

Influent total fiprole loads were highly variable, ranging from 2 to over 20 g/d. The parent compound contributed the majority of fiprole loading throughout the sewershed. Of the degradates, sulfone and sulfide had the largest average contributions to fiprole loading in influent and effluent, each ranging from 7 to 14% of the total mass loads (Figure 3). On average, the desulfinyl and amide forms combined contributed less than 8% of the total fiprole loads. Findings regarding fiprole speciation in municipal wastewater in this study are largely consistent with the work of Sadaria et al. (2016), who found that the amide and desulfinyl forms were minor contributors to overall speciation, with concentrations frequently below detection limits in influent, while the sulfone and sulfide forms were always detectable in influent samples. The primary qualitative difference between our results and those of Sadaria et al. (2016) is that for most of the plants they studied, fipronil sulfone concentrations were much higher than fipronil sulfide concentrations; in our study, the two species were nearly equal in concentration and loading; reasons for this discrepancy are not immediately clear.[2] Fipronil sulfide consistently had the highest percent decrease in concentrations of all fiproles, while desulfinyl effluent concentrations increased by an average of 264% from incoming influent concentrations. This may suggest the aerobic metabolic and photolytic processes have a stronger influence of fiprole speciation than anaerobic metabolism within the treatment train.

Sub-sewershed Evaluation. This study was not designed to quantify the magnitude of concentrated pulses that would require high-frequency grab samples; however, the variability within the sewershed can highlight potential concentrated sources.[9] For each pesticide, a Kruskall–Wallis test was conducted to identify statistically significant ($p < 0.05$) differences by lateral sampling locations ($n = 9$). While pesticides were ubiquitous throughout the sewershed, significant differences in concentrations were noted. Cypermethrin ($p = 0.004$) and prallethrin ($p < 0.000$) concentrations varied significantly by site. This result appears to be largely a function of the consistently high concentrations observed at one lateral sampling site (Table S8). In addition to cypermethrin and prallethrin concentrations, the highest median concentrations were observed within the same lateral for bifenthrin, bioallethrin, cyhalothrin, deltamethrin, and permethrin. It is unclear what factor is driving the elevated pyrethroid concentrations found within this lateral. However, the overlying area is composed primarily of residential land (79%), consisting primarily of land zoned for high-density residential parcels (Figure S1). This lateral had the highest percent of residential zoning of the laterals with available land use data. This could indicate indoor pesticide use is more concentrated within high-density residential areas, leading to a higher pesticide loading.

Temporal Variability. A similar approach was undertaken to evaluate seasonal differences in lateral concentrations by the sampling event. Several pesticide concentrations were observed to vary significantly by the sampling event, including bifenthrin, cyfluthrin, cyhalothrin, cypermethrin, permethrin, chlorpyrifos, imidacloprid, and fiproles (Table S9). For the pyrethroids, there is a general trend of lower mass loading in May and June sampling, with a dramatic increase for July–January (Figure 4). Maximum mass loads of most pyrethroid insecticides were in the range of 1–10 g/d except for permethrin, which had a maximum load an order of magnitude larger. The mass loading of fipronil and its derivatives followed a pattern similar to that for bifenthrin, cyfluthrin, and deltamethrin, with very low loads in May and June, increased loads in July–November, and distinctly higher loads in January. Loads for imidacloprid followed a nearly inverse trend compared to the other active ingredients, with maximum loads in May/June, moderate loads during July–September, and very low loads in the cooler months (November, January).

The significant increase in fiprole and several pyrethroid concentrations observed during the January 2017 event could be attributed to storm water runoff unintentionally entering the waste stream. The influent flow rate in January (111 MLD) was significantly higher than the upper end of the 95% confidence interval around the influent flow rate (Figure S2). The large increase in influent flow was caused by a significant storm system that delivered 7.1 cm of precipitation (based on the nearest California Irrigation Management Information System site) over the period Jan 7–10, 2017. The wastewater treatment plant operation staff reported that the sewer flows were significant enough to lift off manhole covers at various locations across the system during this storm. This suggests an influx of pesticide loads into the waste stream from surface runoff, despite the system typically receiving negligible

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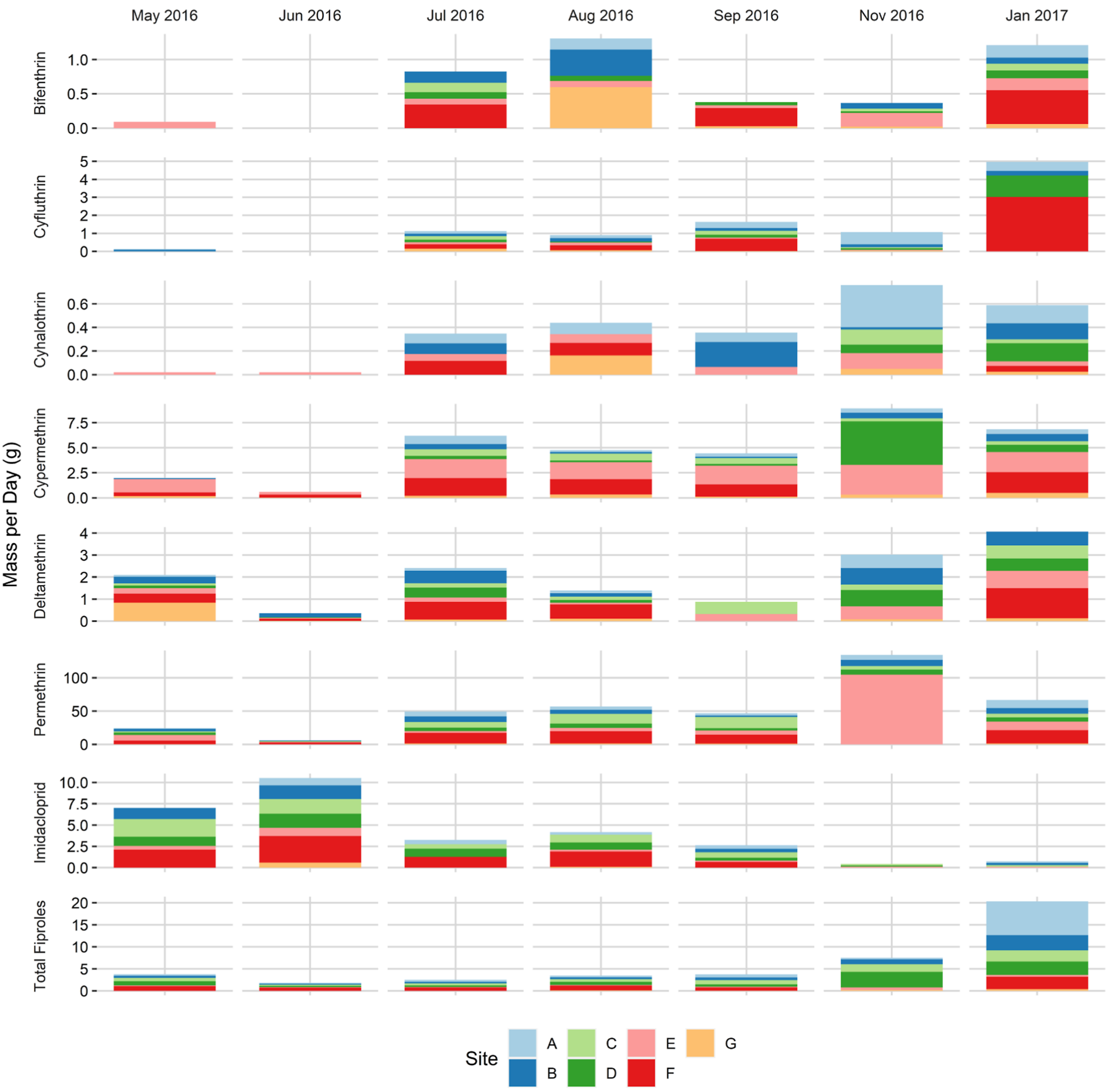

Figure 4. Mass loading of frequently detected pesticides as a function of the sampling date.

contributions from outdoor sources. Pyrethroids and fiproles are commonly detected pesticides found in California urban surface waters at concentrations that could account for the increased signal. While imidacloprid is also often detected in urban runoff, it is more hydrophilic than pyrethroids and fiproles.[16−18] Thuyet et al. (2012) observed concentrations of imidacloprid inoculated on concrete falling below detection levels within 7 days, while fipronil concentrations remained high after four simulated rain events on day 14.[19] It is possible that the residual concentrations of imidacloprid on the landscape had been depleted during previous storm systems (Figure S4).

There were a few instances where a particular lateral sampling event corresponded with an elevated mass flux, indicating a use or event that resulted in the large flux of pesticides. In some cases, single samples collected within a lateral represented a disproportionate amount of loading compared to all sampling events, including cyfluthrin (31%, site F on Jan 2017), fipronil (20%, site A on Jan 2017), fipronil amide (36%, site B on Jan 2017), fipronil desulfinyl amide (64%, site B on Jan 2017), and permethrin (27%, site E on Nov 2016). Except for permethrin, the instances of high fluxes within the laterals occurred during the January 2017 storm event, in which there was evidence of urban runoff entering the system.

To evaluate whether sample timing has any effect on observed concentrations, sampling events were grouped based on the day of the week in which they were collected. Samples collected during the weekend included the June and September sampling events, while the May, July, August,

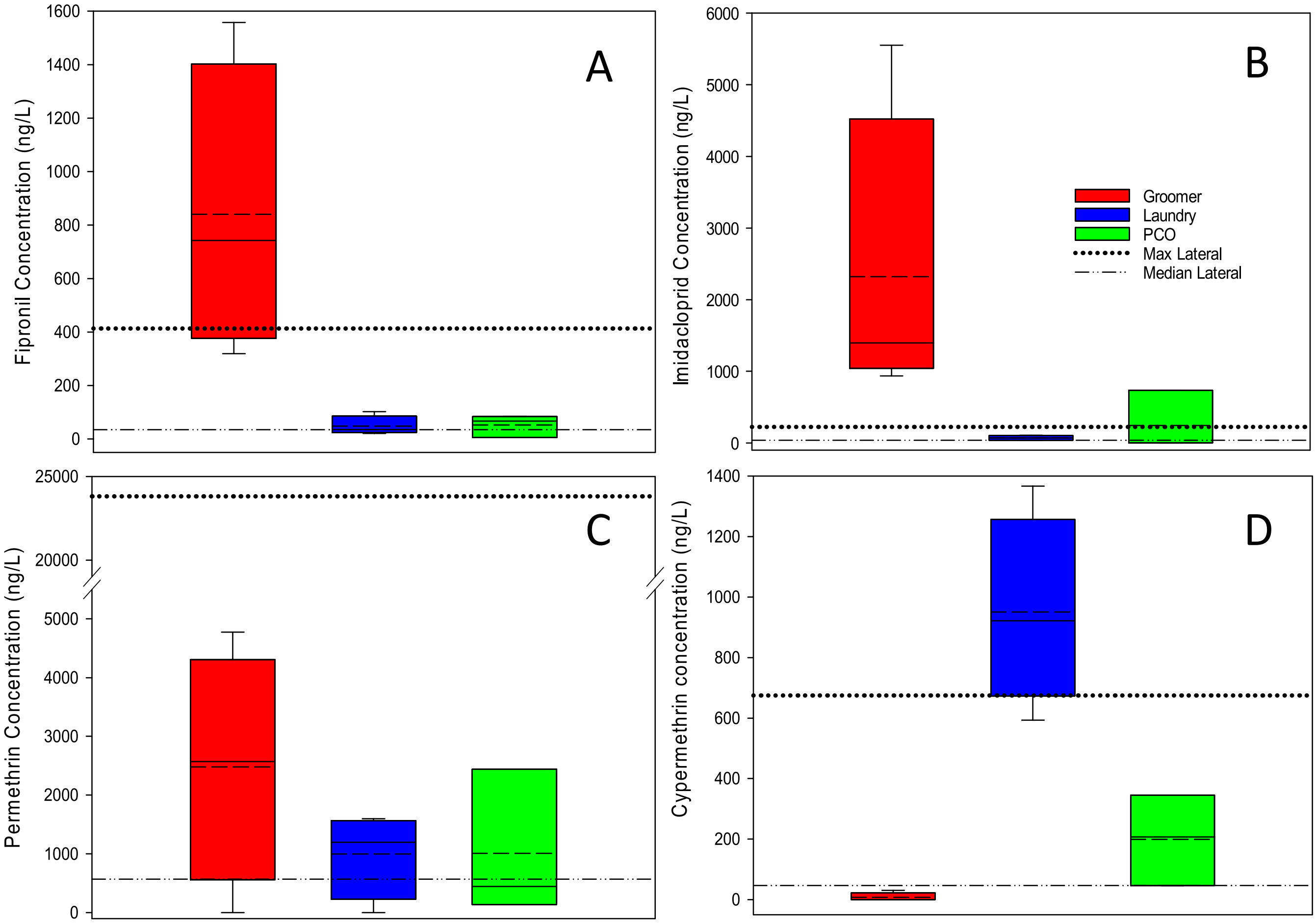

Figure 5. Concentration box plots of (A) fipronil, (B) imidacloprid, (C) permethrin, and (D) cypermethrin at groomer (red), laundry (blue), and PCO (green) sub-sewershed monitoring locations. Dashed line in the box represents the mean concentration.

October, and January events occurred during the weekday (Table S5). While there were not enough data to perform a robust statistical analysis, there were no obvious trends based on timing. Most pesticide concentrations were slightly higher during the weekday; however, average bifenthrin and imidacloprid concentrations were higher during the weekend (Figure S3).

Potential Sources: What Are the Major Contributors. Sutton et al. present a comprehensive conceptual model that describes potential pesticide sources and associated pathways that can introduce pesticides to wastewater influent.[1] Evidence provided by single source monitoring data in conjunction with an evaluation of registered product use types for individual active ingredients detected in influent samples can provide a line of evidence to identify significant source pathways for pesticides entering the waste stream. The information gained during this analysis is utilized to further refine the conceptual model of transport pathways from urban sources into the waste stream (Figure S5).

Among possible pathways, there is a growing body of evidence that topical pet products can contribute significantly to pesticide loading within the waste stream.[2,11,21] Fipronil, imidacloprid, and permethrin have been identified as the most common active ingredients within spot-on pet products by mass.[11] Of these three AIs, fipronil has the fewest registered uses in California and is primarily used in spot-on pet and structural pest control products. Structural applications are not expected to be a significant pathway for fipronil into municipal wastewater, as all registered uses are either outdoors or into structural voids within the structure. As previously discussed, the extreme precipitation event during January may have provided a temporary direct pathway for fipronil in surface runoff to enter the sewershed within the separate sewer system. Imidacloprid and pyrethroids, including permethrin, are registered for many uses in California besides topical pet products. These include products intended as indoor area sprays, bed bug control, and total release foggers, which may have the ability to transfer pesticides down the drain through direct contact and washing activities.[20,21]

Previous work directly measured fiproles released during routine bathing of treated dogs and concluded that spot-on fipronil products are a significant source of fiproles to wastewater.[11] It was estimated that if just 25% of pet owners washed animals 7 days after application in locations plumbed to sewers, this could account for the entire per-capita mass loading observed in the San Francisco Bay area. While the previous study focused on fipronil, it is reasonable to assume that the same transport principles would apply to the other active ingredients. This hypothesis is supported by samples collected at the sub-sewershed locations. Fiprole and imidacloprid concentrations collected at the pet groomer location were significantly elevated above the maximum observed concentrations at the main lateral locations (Figure 5), providing direct evidence that topical pet products can be a significant source of these active ingredients to the waste stream. While lower than the maximum observed concentration, the median groomer sub-sewershed permethrin concentration was approximately five times higher than the associated median concentration in the laterals, highlighting topical pet products as an important source for all three active ingredients. 25 percent of currently registered residential products containing deltamethrin are also pet products.[21] However, all are formulated as pet collars. Given that all deltamethrin concentrations in the groomer samples were below the median lateral concentrations, this suggests that the use of this product type results in minimal transference from the pet to wastewater.

Elevated median concentrations were observed at the commercial laundry sub-sewershed site compared to lateral concentrations for every monitored pesticide (Table S10). The median concentration of cypermethrin observed at the laundry sub-sewershed site was significantly greater than the maximum concentration found within any lateral sample (Figure 5). An analysis of sales data of residential indoor-use products that were identified in previous store surveys revealed the mass of cypermethrin sold was approximately an order of magnitude larger than the next highest active ingredient.[22] This is in agreement with an extensive analysis of product use and sales data designed to identify products with down-the-drain potential.[23] Over 80% of identified products containing cypermethrin available to consumers are labeled for indoor use only, with 45% of products formulated as total release foggers. Keenan (2009) found that upward of 30% of cypermethrin mass was available for transfer from various indoor horizontal surfaces after discharging fogger products indoors.[24] Cypermethrin is not currently present in topical personal care products, supporting the hypothesis that indirect transfer from surface applications to clothing prior to washing activities represents a pathway for this active ingredient (Figure S5).[20,21]

An extensive shelf survey of available pesticide products to homeowners was conducted at retail locations during a similar time frame (Mar−May 2017) and in regional proximity to the monitored sewershed. The survey identified 140 products containing 66 individual active ingredients, including those found within influent samples. Cypermethrin (19) was identified in the largest number of products for indoor residential use, followed by deltamethrin (14), prallethrin (10), permethrin (8), cyhalothrin (8, γ and λ combined), imidacloprid (7), and bifenthrin (2).[22] The prevalence of these active ingredients within a wide range of readily available indoor use products suggests transport from a variety of potential application sources. However, foggers may be the most influential of indoor application types for providing transferable mass to the sewershed. In an assessment of dispersion factors on horizontal surfaces, there was an observed 100% dispersion for fogger applications, followed by perimeter sprays (50%), crack and crevice treatments (15%), and spot applications (2%).[25] Although cyfluthrin (cyfluthrin and β-cyfluthrin combined) was identified in 14 homeowner products in regional store surveys, only four of these are registered for indoor applications, and cyfluthrin was not identified in any pet product. However, two cyfluthrin products are used to control bed bugs.[12,22] The potential for bed bug control products to contribute pesticides down the drain after residential use is unclear.

The median concentrations of bifenthrin, cypermethrin, and fipronil were slightly elevated at the pest control operator's sub-sewershed location, with median bifenthrin concentrations upward of 8 times the median lateral concentration. However, all concentrations were generally low. Considering this location type would typically have professional-grade pest control products containing a higher percentage of active ingredients than are typically available to homeowners, this suggests that regulations on cleaning equipment and containers are working. However, future sampling efforts should isolate commercial laundry services in which pest control operator uniforms may be washed.

Implications. Pyrethoids, fiproles, and imidacloprid were prevalent in wastewater influent throughout the study period. There was significant removal of pyrethroids from the aqueous process stream within the facility to below reporting limits. Although the associated ecological risks were unable to be determined in all instances, this study suggests that treated wastewater may not be a significant source of pyrethroids to receiving surface waters. On the other hand, fiproles and imidacloprid were present in effluent at levels of potential ecological concern, suggesting the WWTP should be considered when evaluating total pesticide loading to surface waters, particularly for these more hydrophilic compounds within the sewershed. The speciation within the facility suggests photolytic and aerobic digestion are more influential drivers for fiprole transference than anaerobic metabolism.

Using the single source monitoring data from this study in conjunction with information gained by evaluating registered product labels, we are able to validate both transport pathways and detected pesticides in the development of a refined conceptual model for pesticides entering the waste stream (Figure S5). Elevated levels of active ingredients found at the pet groomer location further support the hypothesis that topical pet products are a significant source of pesticide loads to wastewater. All pesticide concentrations of samples collected at the laundry and the pest control operator were elevated above the respective median lateral for each pesticide. The elevated level of cypermethrin above lateral concentrations provides evidence that applications of total release foggers may serve as a major source for pesticides to transfer down the drain. This also indicates that pesticides in registered products for home pest control have the ability to be transferred from the application point down the drain, likely through laundering/cleaning of materials that come into contact with the treated surface. Information gained in this study may be utilized to inform down-the-drain evaluations as part of future pesticide registration processes to help predict the relative contributions of pesticides entering the waste stream to surface water loadings.

Future Needs. While the data from this study provide much needed evidence of pesticide occurrence and associated sources within wastewater, data gaps in understanding the full impacts of this pollutant class as a down-the-drain concern remain. Target analytes in this study consisted predominantly of insecticides. Future monitoring should expand to include other chemistries to evaluate the potential risk from other product types. Large-scale evaluations of monitoring data are required to determine the spatial extent of pesticides in the waste stream and to assess whether regional differences in concentrations exist. Long-term monitoring data are necessary to evaluate temporal trends and verify the seasonal variability observed during this study. It is critical to determine removal efficacies resulting from various treatment technologies to identify important parameters responsible for removal. Also, a more comprehensive evaluation of the fate of pesticides within a facility is warranted, including the sorption to the biosolid fraction, to provide a mass balance of chemical transport pathways for future modeling efforts. Lastly, assessing contributing source transport pathways not evaluated in this document is necessary to build a more complete model for pesticides entering the waste stream.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.2c07443.

> Details of analytical methods, analytical results, effluent exceedances, statistical analysis, landuse evaluation, flow distribution, and the conceptual model (PDF)

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Notes

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■ REFERENCES

(1) Sutton, R.; Xie, Y.; Moran, K. D.; Teerlink, J.Occurrence and sources of pesticides to urban wastewater and the environment. *Pesticides in Surface Water: Monitoring, Modeling, Risk Assessment, and Management*; ACS Publications, 2019; pp 63−88.

(2) Sadaria, A.; Sutton, R.; Moran, K.; Teerlink, J.; Brown, J.; Halden, R. Passage of fiproles and imidacloprid from urban pest control uses through wastewater treatment plants in northern California, USA. *Environ. Toxicol. Chem.* **2016**, *36*, 1473−1482.

(3) Weston, D. P.; Ramil, H. L.; Lydy, M. J. Pyrethroid Insecticides in Municipal Wastewater. *Environ. Toxicol. Chem.* **2013**, *32*, 2460−2468.

(4) Bellona, C.; Drewes, J. E.; Xu, P.; Amy, G. Factors affecting the rejection of organic solutes during NF/RO treatment-a literature review. *Water Res.* **2004**, *38*, 2795−2809.

(5) Pesqueira, J. F. J. R.; Pereira, M. F. R.; Silva, A. M. T. Environmental impact assessment of advanced urban wastewater treatment technologies for the removal of priority substances and contaminants of emerging concern: A review. *J. Cleaner Prod.* **2020**, *261*, 121078.

(6) Teerlink, J.; Hering, A. S.; Higgins, C. P.; Drewes, J. E. Variability of trace organic chemical concentrations in raw wastewater at three distinct sewershed scales. *Water Res.* **2012**, *46*, 3261−3271.

(7) Harris-Lovett, S.; Lienert, J.; Sedlak, D. L. Towards a New Paradigm of Urban Water Infrastructure: Identifying Goals and Strategies to Support Multi-Benefit Municipal Wastewater Treatment. *Water* **2018**, *10*, 1127.

(8) Marron, E. L.; Mitch, W. A.; von Gunten, U. v.; Sedlak, D. L. A Tale of Two Treatments: The Multiple Barrier Approach to Removing Chemical Contaminants During Potable Water Reuse. *Acc. Chem. Res.* **2019**, *52*, 615−622.

(9) Ort, C.; Lawrence, M. G.; Rieckermann, J.; Joss, A. Sampling for Pharmaceuticals and Personal Care Products (PPCPs) and Illicit Drugs in Wastewater Systems: Are Your Conclusions Valid? A Critical Review. *Environ. Sci. Technol.* **2010**, *44*, 6024−6035.

(10) CDPR. *California Code of Regulations Section 6970. Surface Water Protection in Outdoor Nonagricultural Settings*. 2012. Available at. https://www.cdpr.ca.gov/docs/legbills/calcode/040501.htm.

(11) Teerlink, J.; Hernandez, J.; Budd, R. Fipronil washoff to municipal wastewater from dogs treated with spot-on products. *Sci. Total Environ.* **2017**, *599−600*, 960−966.

(12) Werf, R. V.; Aldana, A.; Teerlink, J.; Budd, R.*Retail Store Survey of Consumer-Use Indoor Pesticide Products*; CDPR: Sacramento, CA, 2014.

(13) Helsel, D. R.*Statistics for Censored Environmental Data Using Minitab and R*, 2nd ed.; John Wiley and Sons: New York, 2012; p 344.

(14) Budd, R.*Study 270 Ambient Surface Water and Mitigation Monitoring in Urban Areas in Southern California*; CDPR: Sacramento, CA, 2018.

(15) Sadaria, A. M.; Supowit, S. D.; Halden, R. U. Mass balance assessment for six neonicotinoid insecticides during conventional wastewater and wetland treatment: nationwide reconnaissance in United States wastewater. *Environ. Sci. Technol.* **2016**, *50*, 6199−6206.

(16) Budd, R.*Study 270 Urban Monitoring in Southern California Watersheds*; CDPR: Sacramento, CA, 2019.

(17) Ensminger, M.*Study 299 Pesticide Monitoring in Urban Areas of Northern California*; CDPR: Sacramento, CA, 2021.

(18) Ensminger, M. P.; Budd, R. B.; Kelley, K. C.; Goh, K. S. Pesticide occurrence and aquatic benchmark exceedances in urban surface waters and sediments in three urban areas of California, USA, 2008−2011. *Environ. Monit. Assess.* **2013**, *185*, 3697.

(19) Thuyet, D. Q.; Jorgenson, B. C.; Wissel-Tyson, C.; Watanabe, H.; Young, T. M. Wash off of imidacloprid and fipronil from turf and concrete surfaces using simulated rainfall. *Sci. Total Environ.* **2012**, *414*, 515−524.

(20) USEPA. PPLS Database. United States Environmental Protection Agency Pesticide Product and Label System. 2022. Available at: https://ordspub.epa.gov/ords/pesticides/f?p=PPLS:1 (accessed March 1, 2021).

(21) CDPR. CDPR PLDA. California Department of Pesticide Regulation. California Product Label Database Application. 2022.

Available at: https://apps.cdpr.ca.gov/docs/label/labelque.cfm (accessed March 1, 2021)..

(22) Budd, R.; Peters, K.*Survey of Pesticide Products Sold in Retail Stores in Northern California*; CDPR: Sacramento, CA, 2017.

(23) Xie, Y.; Budd, R.; Teerlink, J.; Luo, Y.; Singhasemanon, N. Assessing pesticide uses with potentials for down-the-drain transport to wastewater in California. *Sci. Total Environ.* **2021**, *773*, 145636.

(24) Keenan, J. J.; Vega, H.; Krieger, R. I. Potential exposure of children and adults to cypermethrin following use of indoor insecticide foggers. *J. Environ. Sci. Health, Part B* **2009**, *44*, 538−545.

(25) Keenan, J. J.; Ross, J. H.; Sell, V.; Vega, H. M.; Krieger, R. I. Deposition and spatial distribution of insecticides following fogger, perimeter sprays, spot sprays, and crack-and-crevice applications for treatment and control of indoor pests. *Regul. Toxicol. Pharmacol.* **2010**, *58*, 189−195.