June 16, 2023

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Subject: Draft Guidance to Registrants on Activities to Improve the Efficiency of Endangered Species Act Considerations for New Active Ingredient Registrations and Registration Review (Docket No. EPA-HQ-OPP-2023-0281)

Dear Brian Anderson:

On behalf of the Bay Area Clean Water Agencies (BACWA), we thank you for the opportunity to comment on the Endangered Species Assessment (ESA) draft Guidance to Registrants. BACWA's members include 55 publicly owned wastewater treatment facilities and collection system agencies serving 7.1 million San Francisco Bay Area residents. Every day, BACWA members' Publicly Owned Treatment Works (POTWs) treat millions of gallons of pesticide-containing wastewater that is then discharged to fresh or saltwater bodies, including local creeks and rivers, bays, and the Pacific Ocean. We take our responsibilities for safeguarding receiving waters seriously.

The Draft Guidance to Registrants neglects to address the indoor use of pesticides, which have a direct pathway to receiving waters and endangered species. We implore EPA to stop omitting indoor pesticide uses from its effort to improve the efficiency of Endangered Species Act considerations. There is overwhelming scientific evidence that pesticides used indoors pass through POTWs and appear in municipal wastewater effluent at levels that exceed EPA Office of Pesticide Program benchmarks and may harm aquatic ecosystems at many locations, including those where little effluent dilution is available.

We have attached our 2019 comment letter on the Draft Revised Method for National Level Endangered Species Risk Assessment Process for Biological Evaluations of Pesticides (Docket ID No. EPA–HQ–OPP–2019–0185), where we provide greater detail. We have also enclosed scientific references on indoor pesticides, urban pesticides, and pesticide prevalence in municipal wastewater for your use (see list of enclosures below).

Thank you for your consideration of our comments. If you have any questions, please contact

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Respectfully Submitted,

Lorien Fono, Ph.D., P.E.
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Enclosures:

1. BACWA Comment Letter to EPA on the Draft Revised Method for National Level Endangered Species Risk Assessment Process for Biological Evaluations of Pesticides (Docket ID No. EPA–HQ–OPP–2019–0185), August 15, 2019.
2. Sutton, R. et al. 2019. Occurrence and Sources of Pesticides to Urban Wastewater and the Environment. In Goh et al.; Pesticides in Surface Water: Monitoring, Modeling, Risk Assessment, and Management, ACS Symposium Series 1308; American Chemical Society: Washington, DC, 2019; pp 63-88.
3. Sadaria, A.M. et al. 2017. Passage of Fiproles and Imidacloprid from Urban Pest Control Uses Through Wastewater Treatment Plants in Northern California. Environmental Toxicology and Chemistry. 36 (6), 1473-1482.
4. Teerlink, J., et al. 2017. Fipronil washoff to municipal wastewater from dogs treated with spot-on products. Sci Total Environ 599-600: 960-966.
5. Markle, J. C. et al. 2014. Pyrethroid Pesticides in Municipal Wastewater: A Baseline Survey of Publicly Owned Treatment Works Facilities in California in 2013. In Jones et al. Describing the Behavior and Effects of Pesticides in Urban and Agricultural Settings; ACS Symposium Series 1168; American Chemical Society: Washington, DC, 2014; pp 177-194.
6. Shamim, M. et al. 2014. Conducting Ecological Risk Assessments of Urban Pesticide Uses. In Jones et al. Describing the Behavior and Effects of Pesticides in Urban and Agricultural Settings; ACS Symposium Series 1168; American Chemical Society: Washington, DC, 2014; pp 207-274.

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August 15, 2019

Tracy Perry
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Subject: Draft Revised Method for National Level Endangered Species Risk Assessment Process for Biological Evaluations of Pesticides (Docket ID No. EPA–HQ–OPP–2019–0185)

Dear Ms. Perry:

On behalf of the Bay Area Clean Water Agencies (BACWA), we thank you for the opportunity to comment on the Draft Revised Method for National Level Endangered Species Risk Assessment Process for Biological Evaluations (BEs) for pesticides. BACWA's members include 55publicly owned wastewater treatment (POTW) facilities and collection system agencies serving 7.1 million San Francisco Bay Area residents. We take our responsibilities for safeguarding receiving waters seriously and are very concerned about pesticides entering into wastewater systems through influent flows that may compromise effluent quality, biosolids reuse, and compliance with NPDES permit requirements.

BACWA is pleased that the EPA and the Fish and Wildlife Service (FWS) are cooperating to address endangered species in pesticide registration. As managers tasked with protecting the surface waters receiving our effluentand the species in these waters—including endangered species—we appreciate the effort being put forth to create a practical and effective coordinated system.

An effective pesticide consultation system is important for POTWs. The NPDES permits issued to BACWA's member agencies include requirements that effluent limits and receiving water limits protect the beneficial uses of waters of the State including protecting rare, threatened, or endangered species. Through these Clean Water Act (CWA) permits, water quality regulators make municipalities responsible for meeting Endangered Species Act (ESA) requirements.[1]

Since our member agencies do not have authority to control indoor or other upstream pesticide uses and have no practical control over subsequent discharges, we seek to ensure that the pesticides ESA Consultation process will lead to mitigations that will protect endangered species and their critical habitats. Because our responsibilities extend beyond endangered species to include all other beneficial uses in our receiving water, we also seek to ensure that Office of Pesticide Program's (OPP) pesticide Registration Review process will lead to mitigation that will protect all beneficial uses of surface waters (not just endangered species).

[1] For example, see City of Palo Alto Regional Water Quality Control Plant and Wastewater System Permit, Order No. R2-2014-0024 (June 11, 2014), Attachment F, Page F-11, Paragraph C.7.

Our goals in providing comments are to support EPA's efforts to develop a solid, functional BE process, and to ensure that both the BE process and EPA's Registration Review appropriately evaluate risks associated with urban pesticide use — and do so in a manner consistent with the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA), the ESA, and the CWA.

Overview of Comments

We agree with US EPA's assessment that the pilot BEs – including the one on malathion that we reviewed in detail and commented on – were unnecessarily complex and relatively inaccessible. Our primary concern is that both the pilot malathion BE and the proposed revised method for preparing BEs expressly exclude evaluation of environmental exposures due to indoor urban pesticide use and subsequent discharges to the sewer system. We recommend that US EPA integrate CWA compliance into BEs and the pesticides ESA Consultation process.

Based on remarks made at the June 10 public meeting, we understand that the draft method addresses only "conventional" pesticides and that other types of pesticides will be addressed in the future. When US EPA develops a process for reviewing antimicrobial pesticides, we would appreciate the opportunity to provide input, as antimicrobials are primarily used in methods that result in "down the drain"inputs to POTWs and, as a class, pose the greatest risk of interfering with the biological treatment processes that our treatment plants rely on.

Pesticides Used Indoors Must Be Addressed in BEs

On page 7 of the draft revised method for preparing BEs, Section 1a lists "indoor use" as an example of a pesticide use location with no environmental exposure pathway. This is not scientifically correct. As detailed in attached scientific papers, due to discharges associated with indoor pesticide uses, pesticides frequently occur in POTW effluent and biosolids. Endangered species may be exposed to these pesticides when effluents flow into surface waters that contain endangered species or in association with beneficial use of biosolids (such as its use for agricultural fertilizer).

Concentrations of at least half a dozen pesticides reported in undiluted POTW effluents exceed the US EPA OPP benchmarks for chronic exposure to aquatic invertebrates (Sutton et al 2019).[2] One indoor use – pet flea treatments – provides a clear and compelling demonstration that pesticides used indoors are washed directly (via pet washing, as measured by Teerlink et al 2017) and indirectly (via washing of human hands and other surfaces where pet flea control pesticides are transferred post-application) to the sewer system (see Sadaria et al 2016).

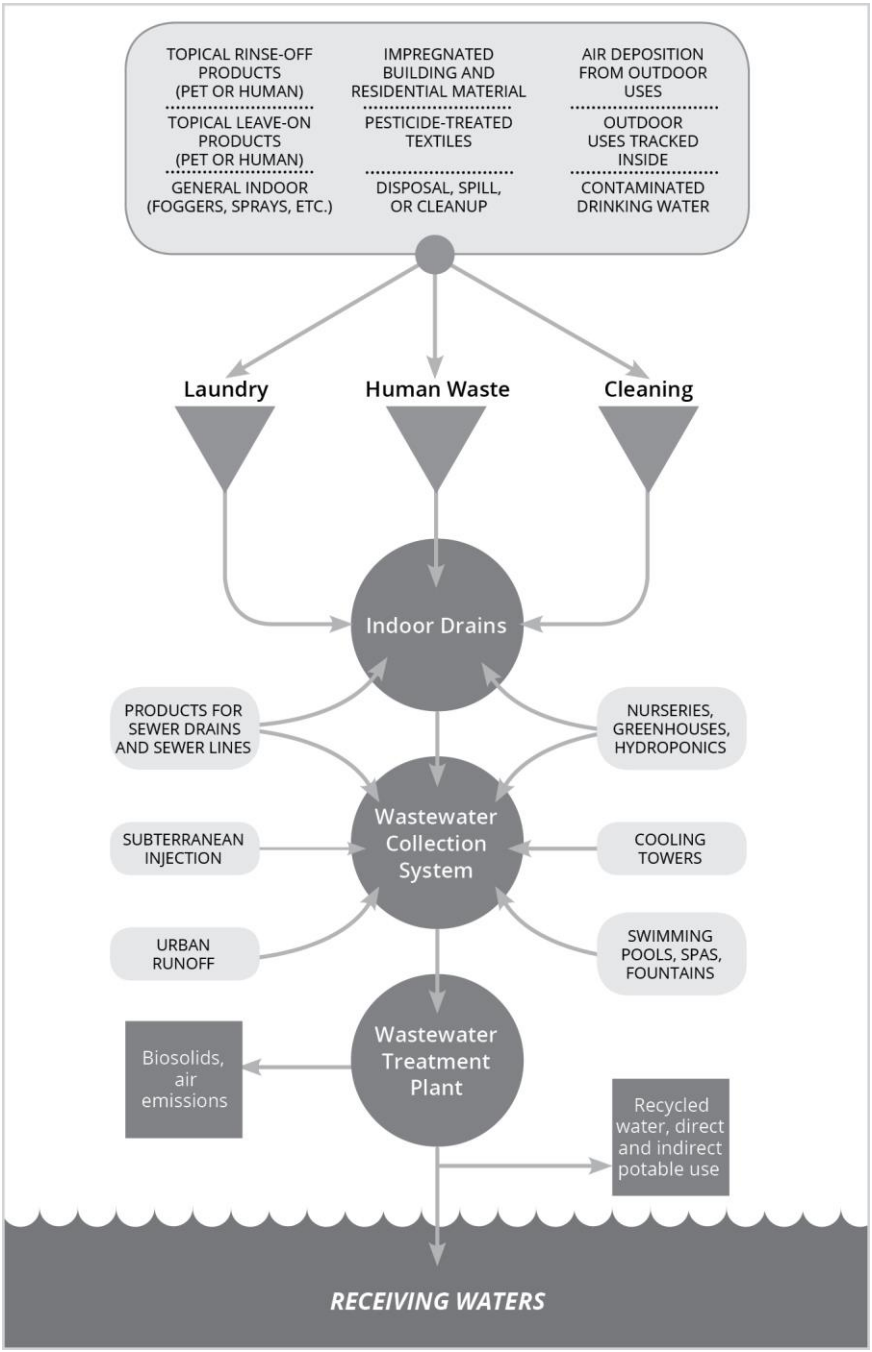
US EPA has been evaluating POTW discharges from indoor pesticide use in its pesticides risk assessments since the late 1990s. As described by a US EPA scientific team (Shamim et al 2014), US EPA uses simplified models like its Exposure and Fate Assessment Screening Tool (E-FAST) in combination with monitoring data and benchtop studies to estimate POTW effluent concentrations.

Available data suggest that typical municipal wastewater treatment processes do not reduce concentrations of some pesticides (e.g., imidacloprid), i.e., that these pesticides pass through POTWs (e.g., Sadaria et al 2016). While other pesticides have lower concentrations in effluent

[2] The "chronic" benchmark comparison is made because POTWs continuously discharge.

than in influent, this often reflects transfer into biosolids (e.g., pyrethroids – see Markle et al 2014).

The figure below, from Sutton et al. (2019) presents a well-documented conceptual model illustrating how pesticides used indoors flow to the sewer system, to POTWs, and ultimately into the environment via effluent, air emissions, and biosolids.



Clean Water Act Compliance Assessment Must Be an Integral Part of BEs and the Pesticide Endangered Species Act Consultation Process

CWA compliance is an integral part of endangered species and aquatic habitat protections. As mentioned above, through our CWA NPDES permits, water quality regulators effectively make municipalities responsible for meeting ESA requirements. Every day, BACWA members treat millions of gallons of wastewater that is then discharged to fresh or salt water bodies, including local creeks and rivers, bays, and the Pacific Ocean. In some cases, receiving waters may be effluent-dominated in that there is little to no dilution either because the receiving water is small or there is a lack of mixing at certain times due to thermal or saline stratification. These waterways provide crucial habitat to a wide array of aquatic species and waterfowl, including listed and non-listed endangered species.

Because local agencies in most states (including California) lack the statutory authority to regulate pesticide use in urban areas, it is essential that EPA and the Fish and Wildlife Service and National Marine Fisheries Service employ the pesticide consultation processes to assess and prevent urban water pollution as defined by the CWA and our NDPES permits. Since OPP controls pesticides labels, even our state pesticide regulatory agency cannot readily address pesticide water pollution and compliance with our NPDES permit if the pesticide discharges stem from consumer pesticide products. It is therefore essential that BEs, pesticide registration, and pesticide registration review processes adequately consider potential impacts to wastewater quality, so that such impacts to the beneficial uses of the receiving water are *prevented*.

If the pesticides ESA Consultation process fails to prevent toxic releases of pesticides to the aquatic environment, an undue burden to address the problem is placed on local governments. Often, there are few ways for a POTW to mitigate a toxic pollutant problem other than extremely costly treatment plant upgrades. In addition, wastewater facilities may be subject to additional requirements established as part of Total Maximum Daily Loads (TMDLs) set for the water bodies by U.S. EPA and state water quality regulatory agencies. The cost to wastewater facilities and other dischargers to comply with TMDLs can be up to millions of dollars per water body per pollutant.

Other comments:

1. **BEs must consider combined exposures from all pesticide uses in a watershed/sewershed.** The ESA requires consideration of "interrelated" and "interdependent" actions in every BE. POTWs often discharge to water bodies (e.g., San Francisco Bay) that also receive urban and agricultural runoff. Therefore, the evaluation of potential cumulative discharge of pesticides to POTWs as well as to water bodies where POTWs discharge needs to be evaluated in BEs.

2. **BEs must address all discharges to POTWs – not just those within 2,600 feet of the POTW.** The proposed 2,600-foot geographic limitation is inconsistent with sources of pesticides to POTWs. Wastewater collection systems may extend miles from the downstream POTW. All uses of a pesticide within the entire sewershed typically combine into a single POTW influent stream.

3. **BEs must evaluate all pesticide uses that US EPA is approving – not just historic usage.** When US EPA reviews a pesticide, it licenses each individual use of that pesticide as described on product labels. If US EPA restricts its analysis to select uses or geographic areas (the effect of the hindcasting usage data methodology proposed), it is effectively licensing uses that it is not evaluating, which is inconsistent with the ESA.

4. **BEs must use chronic invertebrate toxicity data.** The proposal to use only lethal toxicity (LC50) data for aquatic invertebrates deviates from the CWA regulation of aquatic ecosystems to protect food supplies for endangered species, which may include chronic toxicity testing of POTW effluent.

5. **Urban pesticide use estimates could be greatly improved with use of sales data collected annually by California Department of Pesticide Regulation (CDPR).** Each year, California DPR mandates reporting of pesticide product-specific sales. These data provide the quantity of active ingredients sold under every product brand-label combination. While CDPR considers its product-specific sales data as confidential, these data could be requested by US EPA and consolidated (e.g., by use category) before publishing in risk assessments.

Thank you for your consideration of our comments. If you have any questions, please contact BACWA's Project Managers:

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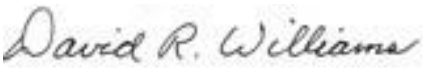

David R. Williams, P.E.
Executive Director
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Enclosures:

1. Sutton, R. et al. 2019. Occurrence and Sources of Pesticides to Urban Wastewater and the Environment. In Goh et al.; *Pesticides in Surface Water: Monitoring, Modeling, Risk Assessment, and Management*, ACS Symposium Series 1308; American Chemical Society: Washington, DC, 2019; pp 63-88.
2. Sadaria, A.M. et al. 2017. Passage of Fiproles and Imidacloprid from Urban Pest Control Uses Through Wastewater Treatment Plants in Northern California. *Environmental Toxicology and Chemistry*. 36 (6), 1473-1482.
3. Teerlink, J., et al. 2017. Fipronil washoff to municipal wastewater from dogs treated with spot-on products. *Sci Total Environ* 599-600: 960-966.

4. Markle, J. C. et al. 2014. Pyrethroid Pesticides in Municipal Wastewater: A Baseline Survey of Publicly Owned Treatment Works Facilities in California in 2013. In Jones et al. *Describing the Behavior and Effects of Pesticides in Urban and Agricultural Settings*; ACS Symposium Series 1168; American Chemical Society: Washington, DC, 2014; pp 177-194.
5. Shamim, M. et al. 2014. Conducting Ecological Risk Assessments of Urban Pesticide Uses. In Jones et al. *Describing the Behavior and Effects of Pesticides in Urban and Agricultural Settings*; ACS Symposium Series 1168; American Chemical Society: Washington, DC, 2014; pp 207-274.

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Chapter 5

Occurrence and Sources of Pesticides to Urban Wastewater and the Environment

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Municipal wastewater has not been extensively examined as a pathway by which pesticides contaminate surface water, particularly relative to the well-recognized pathways of agricultural and urban runoff. A state-of-the-science review of the occurrence and fate of current-use pesticides in wastewater, both before and after treatment, indicates this pathway is significant and should not be overlooked. A comprehensive conceptual model is presented to establish all relevant pesticide-use patterns with the potential for both direct and indirect down-the-drain transport. Review of available studies from the United States indicates 42 pesticides in current use. While pesticides and pesticide degradates have been identified in wastewater, many more have never been examined in this matrix. Conventional wastewater treatment technologies are generally ineffective at removing pesticides from wastewater, with high removal efficiency only observed in the case of highly hydrophobic compounds, such as pyrethroids. Aquatic life reference values can be exceeded in undiluted effluents. For example, seven compounds, including three pyrethroids, carbaryl, fipronil and its sulfone degradate, and imidacloprid, were detected in treated wastewater effluent at levels exceeding U.S. Environmental Protection Agency (US EPA) aquatic life benchmarks for chronic exposure to invertebrates. Pesticides

Goh et al.; Pesticides in Surface Water: Monitoring, Modeling, Risk Assessment, and Management
ACS Symposium Series; American Chemical Society: Washington, DC, 2019.

passing through wastewater treatment plants (WWTPs) merit prioritization for additional study to identify sources and appropriate pollution-prevention strategies. Two case studies, diazinon and chlorpyrifos in household pesticide products, and fipronil and imidacloprid in pet flea control products, highlight the importance of identifying neglected sources of environmental contamination via the wastewater pathway. Additional monitoring and modeling studies are needed to inform source control and prevention of undesirable alternative solutions.

Introduction

Pesticide pollution has long been recognized in agriculturally impacted surface waters. A growing body of work indicates pesticide pollution is common in urban waterways as well (*1–5*). This pollution has been directly linked to urban and agricultural runoff associated with rainfall (stormwater) and irrigation. There are abundant agricultural and urban runoff monitoring data, mechanistic field and laboratory transport studies, and robust modeling tools to predict the environmental fate of specific chemicals under various outdoor agricultural and urban application scenarios (*6–8*).

Much less is known about the occurrence of pesticides contained in treated municipal wastewater effluent discharging to surface waters. Unlike most urban or agricultural runoff, municipal wastewater is treated prior to discharge into receiving waters. Limited data exist on the efficacy of typical municipal wastewater treatment technologies for pesticide removal; however, available results suggest that these treatment processes — which were not designed to address trace chemical contaminants — are insufficient to reduce pesticide concentrations below aquatic toxicity thresholds (*9–11*).

Treated wastewater effluent continuously discharged into surface waters represents an ongoing source of contaminants recalcitrant to removal. Treated wastewater effluent can dominate flow in streams and rivers in arid regions, as well as in estuarine environments with limited hydrodynamic exchange with the ocean (*12*). An understanding of the relative contribution of pesticides in wastewater effluent is essential to developing suitable management strategies for total pesticide loading to surface water.

The goal of this chapter is to provide a state-of-the-science review of the occurrence and fate of pesticide active ingredients ("pesticides") in wastewater influent and in effluent discharged to surface waters that serve as habitat for aquatic life. We do this through: (1) presenting a robust conceptual model of pesticide uses ("use patterns") available for down-the-drain transport; (2) summarizing all available journal-published monitoring data for current-use pesticides in United States (U.S.) wastewater treatment plants (WWTPs) influent and effluent; (3) presenting case studies that detail significant pesticide pathways; and (4) identifying gaps in monitoring and specific use patterns where research efforts should be focused. Other WWTP emissions and products (e.g., biosolids,

air emissions, recycled water) and other uses of treated effluent (e.g., for direct or indirect potable use) are acknowledged, but are beyond the scope of the monitoring data literature review provided.

This review focuses primarily on discharges to indoor drains that flow to separated municipal sewer systems designed to only carry indoor discharges; it does not address combined sewer systems that mix urban runoff with wastewater from indoor drains. While combined sewer systems are not uncommon in older urban areas of the U.S., most modern sanitary sewer systems do not provide significant drainage for urban runoff arising from precipitation events.

Pesticide-use patterns are strongly influenced by government regulation; therefore, the scope of this review was limited to the U.S., because of the relatively uniform regulatory structure in place. Of note, a significant proportion of U.S. monitoring data is from the state of California. For purposes of this review, we will not consider metals or antimicrobial pesticides (e.g., triclosan, triclocarban). Although there are pesticide products that contain metals as an active ingredient, additional nonpesticidal sources complicate the interpretation of available data. Similarly, antimicrobial active ingredients are present in products regulated as pesticides, as well as in personal care products regulated by agencies designed to protect human health. Compounds used both as pharmaceuticals and pesticides were also excluded, such as the blood thinner and rodenticide warfarin.

Regulatory Framework Relevant to Urban and Consumer Pesticide Applications

The U.S. Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) requires that all pesticide products are registered by the U.S. Environmental Protection Agency (US EPA) and places controls on the sale and use of pesticides. FIFRA requires pesticide manufacturers to submit supporting studies to demonstrate the efficacy and safety of proposed products. The US EPA then reviews the environmental fate and potential risks of pesticide products. Following federal registration, additional supporting studies may be required prior to registration in any particular state.

The US EPA includes municipal wastewater ("down-the-drain") modeling as a part of its pesticide registration evaluation and periodic reviews (*13*). The current US EPA model framework would benefit from an improved understanding of which pesticide-use patterns result in down-the-drain transport. Furthermore, information on the fraction of pesticide applied that are dislodged and reach indoor drains via specific-use patterns would improve modeling capabilities.

Product labels evaluated and approved by US EPA during pesticide registration, specify use patterns and application requirements. Pesticide labels are considered enforceable and regulators have the authority to assess fines and penalties for pesticides not applied according to label directions. State and local authorities can implement additional mitigation measures to address off-site pesticide transport through professional applicator permit conditions or through regulations.

Unlike professional applications, consumer use of pesticides, though widespread, has relatively limited regulation. This has crucial implications for the composition of wastewater, as consumer applications often dominate the pesticide-use patterns most likely to result in down-the-drain pesticide transport. It is not practical in such cases to enforce or to instruct individual consumers on safe pesticide use, the more difficult source reduction approach must be used to prevent and mitigate wastewater pesticide contamination. Gaining a robust understanding of pesticide-use patterns that result in down-the-drain transport and relative source contribution is necessary to develop successful source reduction measures.

Another U.S. law, the Clean Water Act also requires that states implement enforceable effluent pollutant limits on wastewater dischargers, including WWTPs. In California, where much of the monitoring data were developed, the State and Regional Water Quality Control Boards develop and implement these limits. Pesticides in wastewater effluent have posed a significant regulatory challenge for California water-quality regulators, particularly after a study found pyrethroids in the effluents of 28 of 31 municipal WWTPs, in some cases at concentrations higher than US EPA aquatic life benchmarks (*10*). For example, the Central Valley Regional Water Quality Control Board developed an amendment of a water-quality control plan to address the occurrence of pyrethroids in the entire Central Valley basin, including contributions from WWTPs (*14*).

WWTPs are legally responsible for limiting chemicals discharged to the environment; however, local municipal agencies like WWTPs cannot regulate the sale and use of pesticides in their service areas. California's Department of Pesticide Regulation (DPR), in partnership with the US EPA, has the regulatory authority over use and sale of pesticides in the state. Collaborative efforts between DPR and WWTPs to generate useful data to inform regulatory decisions are well underway.

A Conceptual Model of Pathways by Which Pesticide Sources Enter Wastewater Systems

A comprehensive conceptual model elucidates the multiple sources and pathways by which pesticides can enter municipal wastewater (Figure 1). The model must consider the entire region drained by the sewer system, also known as the *sewershed*. Refined conceptual models specific to particular pesticides or product types can be used to identify key sources whose control would most effectively reduce levels of pesticides in wastewater and receiving waters. Such models also enable enhanced evaluation of pesticide products during the registration process (*6*).

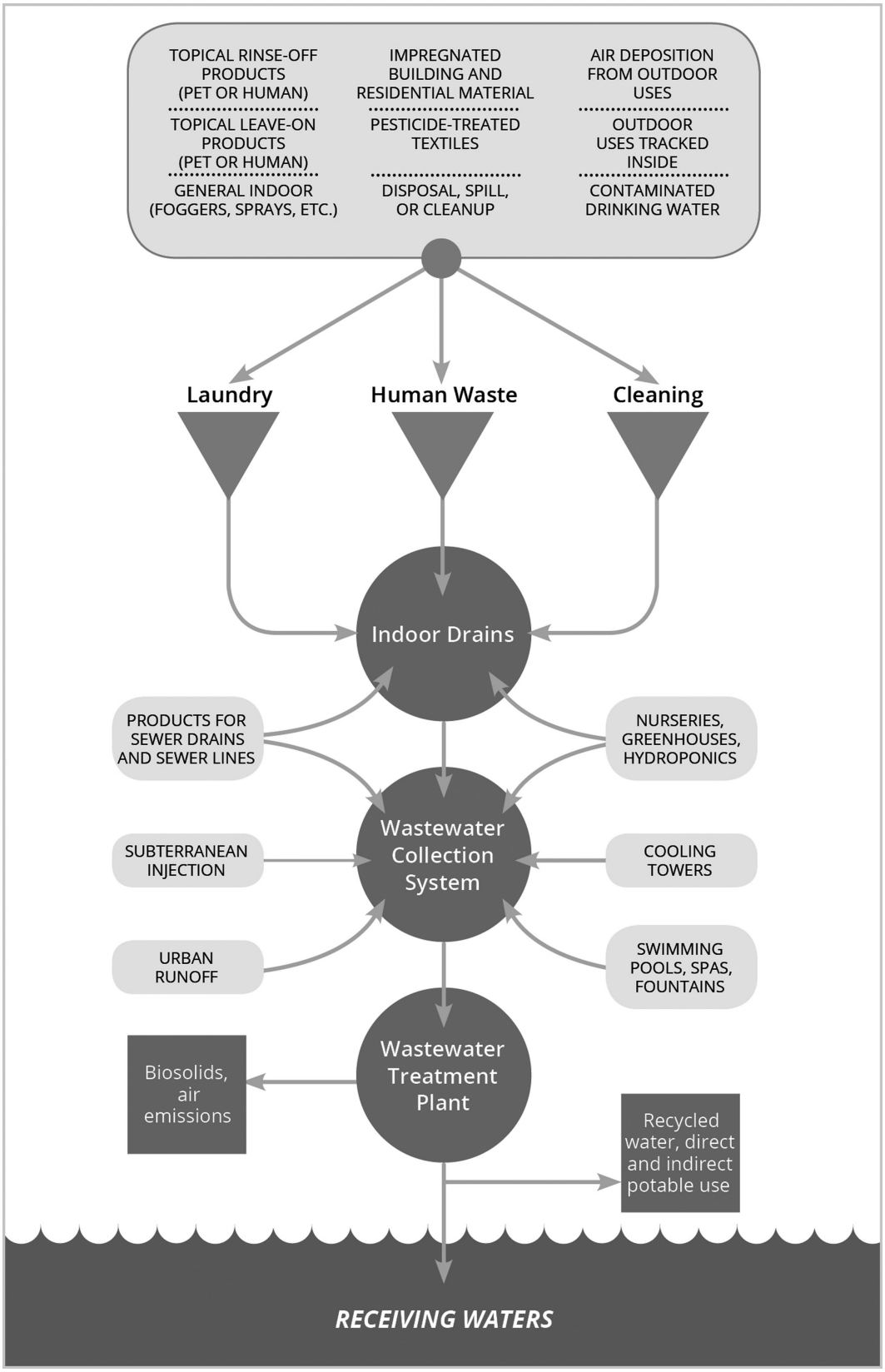

Figure 1. Conceptual model of sources of current-use pesticides to municipal wastewater. Black text is used to describe sources.

Readily identifiable and direct sources of pesticides to municipal wastewater are topical products intended to be rinsed down the drain, such as pesticidal shampoos. Examples for humans include over-the-counter shampoo treatments for lice (pediculicides) with pyrethrins or permethrin, or prescription-strength products with ivermectin, malathion, or spinosad. Examples for pets include flea and tick shampoos containing pyrethrins, permethrin, pyriproxyfen, and s-methoprene.

Other topical pesticide products may not be designed specifically for rinse-off application, but nevertheless enter municipal wastewater through bathing and cleaning activities. For example, after human dermal application of insect repellents containing *N*,*N*-diethyl-*m*-toluamide (DEET), the compound is washed from the skin while bathing and enters the municipal wastewater system. DEET has been widely detected in both wastewater influent and effluent (*15*).

Topical spot-on or spray pesticide products for flea and tick control are commonly applied to pets; pesticides include fipronil, imidacloprid, s-methoprene, pyriproxyfen, pyrethrins, permethrin and other pyrethroids, etofenprox, dinotefuran, indoxacarb, spinetoram, and selamectin (*16–18*). These pesticides enter municipal wastewater through multiple pathways including pet bathing (*19*), transfer to humans via petting (*20–25*) followed by washing and bathing; and transfer to pet bedding (*23–26*), interior surfaces, and house dust (*27–30*), followed by cleaning and laundering activities that result in down-the-drain discharges. Commercial pet grooming facilities are likely to discharge notable levels of pesticides from products used to treat pets (*19*).

Bathing, residential cleaning, and laundry activities are expected to result in pesticide discharge to municipal wastewater from a variety of other urban applications, including: (1) indoor pest-control products such as sprays, foggers, and crack and crevice treatments; (2) pesticide-impregnated construction and building materials; and (3) pesticide-treated clothing, pet bedding, and other textiles. Disposal of indoor-use pesticides, including improper cleanup of accidental spills by either professional applicators or consumers, likely results in larger sporadic discharges to wastewater. Commercial laundry facilities serving professional pesticide applicators or agricultural workers may also release larger loads of pesticides to the municipal sewer system.

Pesticides more generally associated with outdoor uses and urban runoff can also make their way into wastewater via transport indoors followed by washing, cleaning, and laundry activities. Pesticides in outdoor-use products can be tracked indoors via shoes, clothing, and skin (*27*, *31*), with higher levels observed for professional pesticide applicators and agricultural workers (*28*, *31*, *32*). Indoor contamination can also result from air deposition of volatile or spray pesticide applications from nearby outdoor settings (*33*).

Another potential indirect source of pesticides to wastewater is human waste contaminated via pesticide ingestion and via other indoor or occupational exposures. Some pesticides have been observed in human urine (*34*); however, due to lack of data, this indirect pathway is only suspected for other pesticides.

Contaminated drinking water can be a source of pesticides to municipal wastewater systems. Pesticides applied in the vicinity of both surface water and groundwater supplies can result in broad, low-level environmental contamination.

Because conventional drinking water treatment technologies were not designed to remove pesticides, these compounds may persist in finished drinking water. For example, recent studies in the U.S. have documented neonicotinoid insecticides (*35*) (clothianidin, imidacloprid, and thiamethoxam) and herbicides (*36*) (atrazine and metolachlor) in finished drinking water. While such findings have implications for human exposure to pesticides, they can also contribute to the presence of these compounds in wastewater.

Additional sources of pesticides to wastewater include herbicides designed to be flushed through sewer drains and sewer lines to kill roots penetrating pipes; products to control bacteria and algae in swimming pools, hot tubs, spas, and decorative fountains or water features draining to the municipal sewer system; specialized biocides used in cooling towers; insecticides and fungicides used in hydroponic cultivation, particularly for cannabis; and pesticides used at plant nurseries, including large chain retailers with nursery departments. More diffuse sources of pesticides traveling via urban stormwater runoff or subsurface flows can also infiltrate wastewater collection systems via cracks or leaks in sewer pipes, even when flows are not deliberately directed to sewers. Infiltration is suspected to provide an indirect, underground point of entry for other outdoor urban applications of pesticidal products (including injected termiticides). A sewer system's vulnerability to infiltration increases with deterioration of pipes, typically a function of infrastructure age.

All pesticides entering municipal wastewater collection systems are subjected to wastewater treatment. Conventional treatment technologies are designed primarily to handle human waste and food waste compounds present at relatively high concentrations, and often have limited efficacy in eliminating unique pesticide compounds present at nanogram/liter (ng/L) concentrations. Any contamination that does not partition to solids or degrade during treatment is discharged to receiving waters via treated wastewater effluent.

Monitoring data are sparse for many of the products or use patterns emphasized in this conceptual model. For example, many sources are associated with nonprofessional or consumer applications; unfortunately, consumer pesticide use practices are poorly characterized. Door-to-door surveys suggest widespread pesticide use in residences (*37*), and surveys of store shelves indicate ready access to an evolving array of pesticides in consumer-use products (*38*). Other sources of pesticides that are both poorly understood and may increase in use over time include those associated with construction and building materials, textiles such as clothing or mattresses, and hydroponic cannabis-growing operations. These gaps in understanding limit our ability to identify the most significant sources of pesticides found in wastewater.

Comprehensive Review of Available Current-Use Pesticide Influent and Effluent Data for the United States

Municipal wastewater has long been recognized as a pathway for discharge to receiving waters of contaminants derived from pharmaceuticals, personal care and cleaning formulations, and other consumer products; however, relatively few

studies have evaluated this pathway for pesticides in current-use pesticides. This dearth of data is not surprising given that, prior to this publication, there has been no comprehensive conceptual model describing the potential pathways by which pesticides enter wastewater.

Presented here is a compilation of data from peer-reviewed publications describing the occurrence of current-use pesticides in influent and effluent (Table 1). The data compilation was limited to the U.S., and metals, antimicrobials, and pesticides also used as pharmaceuticals were excluded, as they may be derived from multiple additional sources not governed by pesticide regulation. Wastewater treatment processes vary from plant to plant. In this review we did not distinguish the type or level of treatment for specific monitoring results. In the U.S., municipal WWTPs utilize primary and secondary treatment at a minimum while advanced or tertiary treatment is common in densely populated city centers.

This extensive review of the scientific literature revealed wastewater influent and/or effluent detections for 20 insecticides and degradates, one insect repellent, 18 herbicides and degradates, two fungicides, and one wood preservative. The literature review found no detections for 39 additional pesticides and degradates. This review found information on a total of 81 pesticides in wastewater, which represents a small fraction of the hundreds of pesticides registered for use in the U.S. While information on a limited number of additional pesticide analytes may be available in grey literature, this does not alter the fact that there is a substantial shortage of data on current-use pesticides.

Some studies provide paired influent and effluent data that can be used to estimate removal efficiency of conventional wastewater treatment technologies. High levels of removal, 80–100% reductions observed following treatment, were only seen in studies of pyrethroids and high removals did not occur in all sampled WWTPs (*9*, *10*). This is not unexpected, as conventional wastewater treatment is focused on nutrient and pathogen removal, rather than removal or degradation of low levels of bioactive compounds with wide-ranging physicochemical properties. For some compounds, paired influent and effluent data are not available, preventing an estimate of removal efficiency.

Table 1. Occurrence of Pesticides in Wastewater Influent and Effluent in the U.S.

Pesticides & Degradates	*Inf./Eff.*	*Range (ng/L)*[a]	*Median (ng/L)*[b]	*DF (%)*	*No. of Samples*	*No. of Facilities*	*References*
2,4-D	Eff.	<100–1890	<100	3	102	52	(*39*)
2,4-DB	Eff.	<610–7440	<610	10	102	52	(*39*)
2,4-Dichlorophenol*	Eff.	<19–470	<19	62	102	52	(*39*)
Acetamiprid	Inf.	3–4.7	3.2	100	5	1	(*40*)
	Eff.	0.6–5.7	1.3–1.7	76	17	13	(*40*)
Acetamiprid-N-desmethyl*	Inf.	<0.6	<0.6	0	5	1	(*40*)
	Eff.	1.1–1.6	1.2	100	5	1	(*40*)
Acetochlor	Eff.	<0.89–240	1.3	61	38	3	(*41–43*)
Atrazine	Inf.	1–67	2–18.4	100	19	4	(*44–46*)
	Eff.	<7–390	<7–29	82	67	16	(*41–44*, *46*, *47*)
Bifenthrin	Inf.	<0.1–74	7.7–20.3	96	80	32	(*9*, *10*)
	Eff.	<0.1–14.1	<1–10.3	71	92	34	(*9*, *10*, *48*, *49*)
Carbaryl	Eff.	<0.49–663	<41	9	140	55	(*39*, *41–43*)
Chlorpropham	Eff.	<7.7–72.4	<7.7	3	102	52	(*39*)
Chlorpyrifos	Inf.	<1–81.9	15.2	85	13	1	(*9*)
	Eff.	<1–24.1	<1–3	40	30	5	(*9*, *41*, *42*, *49*)

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Table 1. (Continued). Occurrence of Pesticides in Wastewater Influent and Effluent in the U.S.

Pesticides & Degradates	*Inf./Eff.*	*Range (ng/L)*[a]	*Median (ng/L)*[b]	*DF (%)*	*No. of Samples*	*No. of Facilities*	*References*
Clothianidin	Inf.	<0.9–666	18	80	5	1	(*40*)
	Eff.	<0.9–347	12.5–45.3	47	17	13	(*40*)
Cyfluthrin	Inf.	<0.8–55	<1–8.85	74	80	32	(*9*, *10*)
	Eff.	<0.2–4	<1–0.3	42	90	34	(*9*, *10*, *49*)
Cypermethrin	Inf.	<0.8–200	18–27.3	99	80	32	(*9*, *10*)
	Eff.	<0.167–17	<1–1.3	56	90	34	(*9*, *10*, *49*)
DEET[c]	Inf.	413–42,300	413–10,100	100	18	4	(*44*, *45*, *50*)
	Eff.	<5–13,600	25–675	85	171	69	(*39*, *43*, *44*, *50–53*)
Deltamethrin	Inf.	<1.6–210[d]	<3.33	42	67	31	(*10*)
	Eff.	<0.2–2.7	<1	15	81	34	(*10*, *49*)
Diazinon	Eff.	<5–150	<5–38	64	25	22	(*41*, *42*, *47*, *51*)
Dicamba	Eff.	<300–760	<300	3	102	52	(*39*)
Dichlorprop	Eff.	<300–370	<300	1	102	52	(*39*)
Diuron	Eff.	<4–775	<4	46	102	52	(*39*)
Esfenvalerate	Inf.	<1.6–360[d]	<1.67–2.3	46	67	31	(*10*)
	Eff.	<0.167–3.7	<1	27	81	34	(*10*, *49*)
Fenpropathrin	Inf.	<0.8–130 [e]	<1.67	4	67	31	(*10*)

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Pesticides & Degradates	*Inf./Eff.*	*Range (ng/L)*[a]	*Median (ng/L)*[b]	*DF (%)*	*No. of Samples*	*No. of Facilities*	*References*
	Eff.	<0.167–0.8	<1	2	81	34	(*10*, *49*)
Fipronil	Inf.	<20–146	30–70.5	66	41	33	(*11*, *54*)
	Eff.	<0.5–340	30–104	67	57	40	(*11*, *41*, *42*, *54*, *55*)
Fipronil amide*	Inf.	<0.3	<0.3	0	8	8	(*11*)
	Eff.	<0.3–19.8	1.25–6.7	95	21	13	(*11*, *55*)
Fipronil desulfinyl*	Inf.	<0.5–5.5	<0.8	19	16	8	(*11*)
	Eff.	<0.5–30.8	<0.8–9.4	56	32	15	(*11*, *41*, *42*, *55*)
Fipronil sulfide*	Inf.	<0.5–5.2	1.95–2.05	81	16	8	(*11*)
	Eff.	<0.5–52.2	<5–8.4	81	32	15	(*11*, *41*, *42*, *55*)
Fipronil sulfone*	Inf.	<0.5–31.2	8–23.1	94	16	8	(*11*)
	Eff.	<0.5–79.1	<5–30.7	88	32	15	(*11*, *41*, *42*, *55*)
Fluridone	Eff.	<7.7–27	<7.7	1	102	52	(*39*)
Glyphosate	Eff.	<100–2000	<100	27	11	10	(*47*)
Imazapyr	Eff.	<40–17,200	<40	9	102	52	(*39*)
Imidacloprid	Inf.	30–306	51.4–161	100	21	17	(*11*, *40*)
	Eff.	18.5–305	48.3–164	100	25	21	(*11*, *40*)[f]
Lambda-cyhalothrin	Inf.	<0.8–72	2.4–16	78	80	32	(*9*, *10*)

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Table 1. (Continued). Occurrence of Pesticides in Wastewater Influent and Effluent in the U.S.

Pesticides & Degradates	*Inf./Eff.*	*Range (ng/L)*[a]	*Median (ng/L)*[b]	*DF (%)*	*No. of Samples*	*No. of Facilities*	*References*
	Eff.	<0.167–5.5	<1	41	90	34	(*9*, *10*, *49*)
Mecoprop	Eff.	<0.28–72	4	80	35	1	(*43*)
Metolachlor	Eff.	<0.9–98	<6–75	74	38	3	(*41–43*)
Pentachloro-phenol	Eff.	<100–300	<100	2	102	52	(*39*)
Permethrin	Inf.	30–3800	180–315	100	80	32	(*9*, *10*)
	Eff.	<1–170	<1–21.4	64	90	34	(*9*, *10*, *49*)
Prometon	Eff.	<4–64	<10	4	105	54	(*39*, *41*, *42*)
Propiconazole	Eff.	<20–9020	<20	3	102	52	(*39*)
Simazine	Eff.	<4–56	<4	1	105	54	(*39*, *41*, *42*)
Terbuthylazine	Eff.	<4–61	<4	1	102	52	(*39*)

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Pesticides & Degradates	*Inf./Eff.*	*Range (ng/L)*[a]	*Median (ng/L)*[b]	*DF (%)*	*No. of Samples*	*No. of Facilities*	*References*
Thiabendazole	Eff.	24–27	25.5	100	2	2	(*52*)
Triclopyr	Eff.	<300–3900	<300	11	102	52	(*39*)

Inf. = Influent; eff. = effluent. DF = detection frequency. MDL = method detection limit. * indicates compound is a degradate [a] If minimum is nondetect, the lowest MDL is reported. [b] Range of medians reported by the studies. [c] (*15*) conducted a broader review on DEET and reported a maximum concentration of 8480 and 14,000 ng/L, and a DF of 100% (sample size = 71) and 88.1% (sample size = 310) in influent and effluent, respectively, in wastewater treatment plants in the US. [d] The maximum concentration is substantially greater than the second largest value (29 and 29 ng/L for deltamethrin and esfenvalerate, respectively.) [e] There are three detections out of 67 samples: 360, 100, and 1.3 ng/L. [f] (*39*) sampled effluent from 52 WWTPs in Oregon and analyzed for imidacloprid. DF was 9.8% (10 out of 102 samples) at MDL=20 ng/L with a median (median of detections) of 237 ng/L and maximum of 387 ng/L. The study was not included in the table because the MDL was relatively high, which resulted in a considerably lower DF, compared to other studies. Pesticides analyzed but not detected [MDL, ng/L]: alachlor [5], azinphos-methyl [50], α-hexachlorohexane [5], benfluralin [10], butylate [4], carbofuran [20], cis-permethrin [6], cyanazine [18], dacthal [3], dieldrin [9], dinotefuran [32.6], disulfoton [20], EPTC [2], ethalfluralin [9], ethoprophos [5], fipronil desulfinyl amide [9], fonofos [3], linuron [35], malathion [27], metribuzin [6], molinate [2], napropamide [7], parathion [10], parathion-methyl [15], pebulate [4], pendimethalin [22], phorate [11], propachlor [10], propanil [11], propargite [20], propyzamide [4], tebuthiuron [16], terbacil [34], terbufos [17], thiacloprid [0.1], thiamethoxam [0.3], thiobencarb [5], tri-allate [2], trifluralin [9] (*40–42*).

Relative Ecotoxicity of Pesticides in Effluent

For those pesticides for which effluent monitoring data exist, compounds found at concentrations exceeding aquatic toxicity thresholds are typically prioritized for source identification and management action. The continuous discharge of treated municipal wastewater effluent containing pesticides at such levels suggests a potential for harm, particularly to sensitive aquatic species in highly impacted ecosystems, such as effluent-dominated streams.

Pesticides—particularly insecticides—in WWTP effluent can exceed aquatic toxicity based reference values. For example, observed WWTP pesticide effluent concentrations (Table 1) exceeded the following US EPA chronic invertebrate aquatic life pesticide benchmarks (*56*): the pyrethroids bifenthrin (1.3 ng/L), lambda-cyhalothrin (2 ng/L), and permethrin (1.4 ng/L); carbaryl (500 ng/L); fipronil (11 ng/L) and its degradate, fipronil sulfone (37 ng/L); and imidacloprid (10 ng/L). Other pesticides detected in effluent at levels above 50% of the lowest available US EPA aquatic life pesticide benchmark include: the pyrethroids cyfluthrin (7.4 ng/L) and deltamethrin (4.1 ng/L); chlorpyrifos (40 ng/L); diazinon (170 ng/L); and imazapyr (24,000 ng/L).

While identifying effluent pesticide levels exceeding reference values is useful for prioritization, this alone is not proof of harm. The potential for adverse impacts on aquatic species depends not only on discharged pesticide concentrations, but also on site-specific factors in the receiving waters. Such factors include: (1) dilution; (2) the presence of the pesticide in question in other discharges (e.g., urban stormwater runoff); (3) the presence of other contaminants that may cause additive, synergistic, or antagonistic effects (e.g., related pesticides and pharmaceuticals); and (4) the presence of substances that alter bioavailability or toxicity (e.g., dissolved organic carbon). Processes such as biodegradation and partitioning in receiving waters can also have long-term implications for the potential for adverse impacts to wildlife.

Gaps in available ecotoxicity data must also be acknowledged, as a lack of understanding of potential risks could lead to unexpected impacts. For example, relatively few studies of pesticide toxicity relevant to saltwater species and estuarine or marine receiving waters are available. Fewer ecotoxicity studies are available for pesticide degradates, metabolites, and transformation products (e.g., disinfection byproducts) relative to parent compounds. Additionally, few reference values (e.g., US EPA pesticide aquatic life benchmarks) have been developed to specifically address these compounds.

Nevertheless, the presence of a pesticide in effluent at levels exceeding reference values (e.g.,US EPA pesticide aquatic life benchmarks and other aquatic toxicity thresholds) signals the need for a closer examination of its sources, uses, and pathways to wastewater.

Case Studies Illustrating Use of WWTP Monitoring Data and Conceptual Models

Compound-specific conceptual models can guide targeted examinations of: (1) the relative quantities of the identified active ingredient in available pesticide

products; (2) the pathways of transport relevant to these products; and (3) the relative contributions of different types of wastewater discharge to the sewer system, including residential and key commercial or industrial facilities. Two case studies that illustrate this approach can provide evidence to guide management actions designed to reduce the presence of pesticides in surface water.

Case Study: Diazinon and Chlorpyrifos

Toxicity testing in the late 1980s found that effluent from the Central Contra Costa Sanitary District WWTP (Martinez, California) was acutely toxic to *Ceriodaphnia dubia.* In accordance with the Clean Water Act and the California Porter Cologne Act, the San Francisco Regional Water Quality Control Board required toxicity identification evaluations (TIEs) to determine the cause of the toxicity. The TIE studies suggested that the combination of two organophosphate pesticides, diazinon and chlorpyrifos, was causing the effluent toxicity. At the time, these pesticides were commonly found in products available directly to consumers, including lawn and garden products, indoor pest control products, and flea and tick treatments for pets (*57*).

DPR partnered with Central Contra Costa Sanitary District to conduct wastewater sampling to better understand potential sources. Sampling included influent and subsewershed sites (i.e., residential areas and commercial locations). Commercial sampling focused on sites expected to introduce higher relative pesticide loads to the wastewater catchment, including pet groomers, kennels, and pest-control businesses. Diazinon and chlorpyrifos were detected in all 37 influent daily-composite samples, with mean values of 310 and 190 ng/L, respectively. Pesticide concentrations reported in residential sewage ranged from ND–4300 and ND–1200 ng/L for diazinon and chlorpyrifos, respectively. Commercial sampling locations contained the highest measured concentrations: 20,000 ng/L of diazinon in sewage from a kennel, and 38,000 ng/L of chlorpyrifos in sewage from a pet groomer.

Mass balance calculations determined that the overall mass contribution from residential sewage dominated the total pesticide mass entering the WWTP. Although the residential sewage concentrations were much lower, due to the higher residential flow rate, the residential contribution (82%) greatly exceeded the commercial contributions (6%) (*57*). This subsewershed study highlighted the need to understand pesticide sources, pathways, and relative contributions to establish a robust conceptual model and inform effective mitigation solutions.

As noted previously, the US EPA conducts registration reviews for actively-registered products. As a part of the re-registration review process in the early 2000s, concerns over human health arose for both pesticides. In 2000, registrants voluntarily agreed to terminate almost all indoor residential uses of chlorpyrifos in 2001, and all indoor residential uses of diazinon in 2002 (*58*, *59*).

Limited available long-term monitoring data suggest a general reduction in chlorpyrifos and diazinon WWTP influent concentrations as a result of this near complete phase-out of their indoor uses. Weston et al. (*9*). reported a median of 15.2 ng/L for chlorpyrifos in influent from another California WWTP sampled 2010–2012, representing an order of magnitude reduction from 1996

results. Similarly, the median diazinon influent concentration reported in a US EPA WWTP survey conducted in 2005–2008 was <10 ng/L (*60*). Conducting long-term monitoring in parallel with mitigation measure implementation would ensure that source control measures do indeed result in reduced chemical loading.

Of note, the data presented in Singhasemanon et al. (*57*) were not included in Table 1, as they primarily represent contributions from products no longer in current use. Current consumer insecticidal product replacements now typically contain active ingredients such as pyrethroids, and more recently fipronil and imidacloprid. Unfortunately, the use reduction of organophosphates has coincided with an increase in pyrethroid occurrence in wastewater influent. As noted previously, effluent levels of pyrethroids, as well as newer replacements fipronil and imidacloprid, now exceed US EPA aquatic life benchmarks.

Case Study: Fipronil and Imidacloprid in Pet Flea and Tick Treatments

To keep homes and pets free of fleas and ticks, treatment of dogs and cats with pesticides has been common for several decades. Shortly before the phase-out of most pet flea shampoos in the early 2000s, a new class of spot-on flea control products for pets entered the market. Fipronil and imidacloprid are common active ingredients in these popular topical products (*18*).

While occurrence data for both fipronil and its degradates (collectively fiproles) and imidacloprid in WWTP influent and effluent are sparse, these compounds are typically detected in available studies (Table 1). In one such study, the per capita influent loads for fiproles (54 ± 9 nmol/person/d, mean ± standard deviation) and imidacloprid (190 ± 80 nmol/person/d) for 7 Northern California WWTPs had low load variability, suggesting ubiquitous, low-level contributions from sources within the service areas (*11*). The authors outlined a conceptual model specific to fiproles and imidacloprid, that included all potential sources to wastewater, and the means by which pesticides derived from these sources might enter wastewater (*11*); these sources are a subset of those included within the comprehensive conceptual model provided in Figure 1.

Comparison of per capita pesticide loads in influent with active ingredient concentrations in individual pesticide applications suggested that widespread use of spot-on or spray flea control products might be the primary source of fiproles in wastewater (*11*). An estimate of influent fiprole load per fipronil-treated dog was found to be consistent with levels of the active ingredient in spot-on or spray products. Other potential sources, including use of crack-and-crevice treatments, outdoor pesticide applications tracked indoors, contaminated drinking water, and episodic discharges from spills, cleanup, or improper disposal, were found unlikely to be major contributors. The similarity of use patterns for imidacloprid suggested it was likely to be transported via comparable pathways (*11*).

Sadaria et al. (*11*) found multiple pathways by which fipronil and imidacloprid derived from flea control products can enter wastewater: (1) bathing of treated pets by professional groomers or pet owners in the home; (2) washing human hands contaminated via pet contact; (3) human waste following ingestion of trace levels of the pesticide as a result of pet contact; and (4) cleaning and laundering of residential surfaces, including pet bedding, that came into contact

with pets or contaminated house dust. A subsequent study examined fiproles in rinsate from bathing fipronil-treated dogs 2, 7, or 28 days after treatment (*19*). Results confirmed pet bathing as a direct pathway of fiproles derived from spot-on products to municipal wastewater, with fiproles detected in 100% of samples and levels generally decreasing with increasing time from application (*19*). Additional calculations suggested washing 25% of fipronil-treated dogs in a service area within 7 days of treatment could account for the entire fiprole load of the sewershed, indicating spot-on products containing fipronil are likely to be an important fiprole source (*19*). While comparable data are not available for imidacloprid, the compound's higher solubility could result in significant wash off during pet bathing. In addition, targeted sampling of wastewater discharged from a pet-grooming operation confirmed the release of fipronil, pyrethroids, and imidacloprid to the wastewater catchment (*19*).

Additional evidence supports other pathways identified in the conceptual model. As noted previously, fipronil and imidacloprid in spot-on products can be readily transferred to humans via petting (*20*, *21*, *23*, *25*). Pesticides transferred to the hands of companions may enter wastewater via washing, or via unintentional ingestion followed by elimination. The human waste pathway is known to be relevant for imidacloprid, as it has been detected in human urine (*34*), but has not been investigated for fipronil (*61*).

Pesticide active ingredients in flea treatment also commonly appear in house dust. Fipronil and degradates were observed in nearly every sample of house dust examined in two studies of homes in Texas and California (*29*, *30*). While fipronil in house dust may also be derived from indoor- and outdoor-use products for non-flea pests such as ants, reported concentrations were more than 20 times higher in residences housing a dog treated with a spot-on fipronil product relative to those without treated pets (*29*). Imidacloprid was also detected in house dust from 32 of 38 California houses sampled (*30*).

Spot-on products containing each of these pesticides have also been observed to transfer to pet bedding (*23*, *26*). Cleaning and laundering are known to transfer contaminants associated with house dust and textiles to the wastewater system (*62*), and can be expected to transfer fipronil and imidacloprid as well.

Levels of these pesticides in wastewater before and after treatment indicate both fiproles and imidacloprid are relatively persistent, with little removal occurring via common WWTP treatment technologies (*11*, *40*, *54*). As noted previously, concentrations in effluent commonly exceed US EPA aquatic life benchmarks (*56*). Flea control products containing these pesticides may therefore pose risks to surface waters receiving discharges of municipal effluent, particularly when dilution of that effluent is limited.

Regional actions informed by these recent studies have already begun. The Bay Area Clean Water Agencies (BACWA), a joint powers authority that includes municipalities and special districts providing sanitary sewer services to more than 6.5 million people in the San Francisco Bay Area, has prioritized engagement with state and federal agencies to address the impacts of flea control pesticides, including providing comments to US EPA highlighting the need to include pet products in models used in pesticide risk assessment and regulation (*63*, *64*).

BACWA has distributed consumer education materials and findings from recent studies (*11*, *19*), which have also been highlighted via local media.

Priority Data Gaps

Available monitoring data, although sparse, highlight the need to address pesticide loading to surface water from WWTP effluent. Existing studies indicate that some pesticides (pyrethroids, fipronil, imidacloprid, and carbaryl) exceed aquatic life reference values and suggest the potential for harm to aquatic ecosystems, particularly to sensitive aquatic species in highly impacted ecosystems, such as effluent-dominated streams and estuaries. These and any other pesticides exceeding aquatic life reference values are high priorities for additional study to identify sources and appropriate pollution prevention strategies.

Developing strategies that continue to provide protection from pests while reducing overall pesticide loading will require a robust, quantitative understanding of use patterns and subsequent down-the-drain transport. Pesticide-specific customization of the comprehensive conceptual model (Figure 1) is an essential first step to build the knowledge to develop effective mitigation solutions. Refining this conceptual model for specific active ingredients can elucidate key data gaps, inform monitoring designs, and ultimately inform effective mitigation measures.

In the case of chlorpyrifos and diazinon, a conceptual understanding of potential sources based on registered uses led to a focused investigation of subsewershed contributions, characterizing sewage concentrations and loadings from residential and commercial sites (*57*). Study calculations to fill this data gap revealed low-level, ubiquitous residential sources to be of greater importance than large mass pulses (*57*). This case study illustrates how cooperative relationships between wastewater agencies and pesticide regulators are needed to ensure necessary data are obtained to inform potential mitigation.

A refined conceptual model (*11*) identified the need to confirm suggested contamination pathways, an important data gap in the case of fipronil- and imidacloprid-based flea and tick control. A study of the most direct contamination pathway (e.g., bathing treated animals in locations discharging to the sewer) suggested it is likely to provide significant mass transfer (*19*). However, presence of flea control active ingredients on pet bedding (*23*, *26*), pet owners (*20*, *21*, *23*, *25*), and house dust (*29*, *30*) indicate true source control at the site of application may be needed to significantly reduce down-the-drain transport.

Further WWTP influent and effluent monitoring is necessary to document occurrence or absence of additional as yet unexamined pesticides. More than 1000 pesticides are currently registered. The pesticide market continually shifts to adapt to changing needs and to produce alternatives to replace pesticides or product types most heavily scrutinized by federal and state regulators. Pesticides with the use patterns identified in the conceptual model, particularly those where parent compounds or degradates have relatively high aquatic toxicity, should be the highest priority for monitoring effluent discharged to surface waters that serve

as habitat for aquatic life. Long-term monitoring to evaluate spatial and seasonal patterns and to track temporal trends resulting from mitigation or regulatory actions would fill additional data gaps for these prioritized pesticides.

There is also a need to identify and screen for degradates and metabolites of pesticides, including degradates formed during wastewater treatment (e.g., disinfection byproducts). The degradation products of some pesticides are known, but very few have been measured in WWTP influent and effluent. In some cases, degradate aquatic toxicity is comparable to, or greater than, the toxicity of the parent compounds. Identifying potentially harmful degradates is an area of intensive research that often utilizes high-resolution mass spectrometry to search for both known degradates and previously unidentified transformation products (*30*, *65*). However, these techniques may not be sufficiently sensitive to rule out the presence of pesticides at ppt levels.

Focused investigations of specific sources and sites within sewersheds are needed to better understand pesticide contributions from use patterns identified in the conceptual model. Several suspected high-use indoor pesticides sources are poorly understood and merit prioritization. For example, irrigation water from nursery operations discharging to wastewater collection systems (including stores that temporarily hold plants before sale) has received little study. Legalization of cannabis cultivation in many states may lead to an increase in hydroponic indoor growing systems and associated pesticide applications. Intensive use of pesticides such as for bed bug mitigation and subsequent cleaning activities is another identified data gap. While professional pest control operators are a highly-regulated group intimately familiar with pesticide handling requirements, the laundering of uniforms used during application is likely a concentrated source to wastewater. Similarly, the commercial laundering of uniforms for large groups (e.g., the military) whose clothing has come in contact with pesticides is likely to introduce large pulses of pesticides to sewer systems. Finally, to inform mitigation and predictive modeling of pesticide discharges, it is important to gain a better understanding of the fraction of certain pesticide uses that is dislodgeable and available for transport down the drain, including impregnated building and construction materials, foggers, and sprays.

Developing advanced engineering solutions to expand the capacity of wastewater treatment to reduce trace organic chemicals, present in the ppb to sub-ppt concentrations, has been an area of intense research over the past 20 to 30 years (*66*). However, due to the diverse chemical properties of pesticides, source control is more likely to provide financially feasible and effective mitigation, rather than implementing costly and potentially ineffective upgrades that add wastewater treatment technologies for removal of specific pesticides.

Enhanced understanding of compound-specific removal in wastewater treatment will improve our ability to prevent and manage risk. Available data provide some insights, but are too sparse to reflect the diverse design and operations of WWTPs. Use of additional or alternative treatment technologies, such as reverse osmosis or advanced oxidation, may also impact concentrations of pesticides and transformation products and such data can inform improved predictive modeling.

Addressing data gaps concerning pesticide wastewater treatment removal efficiency and incorporating this information into currently used risk evaluation modeling tools, such as the US EPA Exposure and Fate Assessment Screening Tool (E-FAST) (*13*), could inform development of effective mitigation solutions and could prevent future registration of products that pose a risk to surface water through down-the-drain transport. The E-FAST model relies on removal predictions based solely on physical and chemical properties rather than chemical-specific removal studies. This approach can introduce inaccuracies in modeling. For example, Parry and Young (*67*) measured the distribution of pyrethroids in secondary treated effluent and found additional settling time would not result in improved removal efficiency. The observed association between pyrethroids and dissolved organic matter present in wastewater may account for the over-predicted removal of pyrethroids by the E-FAST model (*68*). Predictive modeling must also recognize long-term trends, such as expected decreases in per capita water use which may result in increases in contaminant concentrations in influent.

Conclusion

Pesticide contamination of aquatic ecosystems occurs via WWTP effluent discharges as well as via agricultural and urban runoff. This state-of-the-science review of the occurrence of pesticides in wastewater derived primarily from indoor, down-the-drain inputs indicates that, for some pesticides, continuous discharges of WWTP effluent have the potential to adversely impact vulnerable aquatic biota. Protecting the quality of water resources that receive these effluent discharges is essential, particularly in regions with effluent-dominated streams, or embayments with limited hydrodynamic exchange with the ocean.

Addressing the data gaps identified in this review will improve the ability to prevent and manage these risks. The knowledge gained will not only allow for informed mitigation solutions, but also enhanced evaluation of pesticide products prior to registration and use. Pollution prevention is a key strategy to improve water quality for municipal wastewater pathways.

Acknowledgments

The Regional Monitoring Program for Water Quality in San Francisco Bay provided support for the preparation of this review (San Francisco Estuary Institute Contribution No. 880). The authors thank P.L. Tenbrook for assistance with development of the conceptual model, N. Singhasemanon for a thorough review, and R. Askevold for graphic design. Reviews by B. Arnold, J. Davis, D. Lin, D. Muir, P. Trowbridge, and the anonymous reviewers led to significant improvements.

Disclaimer

The views expressed herein are those of the authors and do not necessarily reflect those of the California Department of Pesticide Regulation.

References

1. Gilliom, R. J.; Barbash, J. E.; Crawford, C. G.; Hamilton, P. A.; Martin, J. D.; Nakagaki, N.; Nowell, L. H.; Scott, J. C.; Stackelburg, P. E.; Thelin, G. P.; Wolock, D. M. *The Quality of our Nation's Waters—Pesticides in the Nation's Streams and Ground Water, 1992-2001*; U.S. Geological Survey Circular 1291; Reston, VA, 2006.
2. Lao, W. J.; Tsukada, D.; Greenstein, D. J.; Bay, S. M.; Maruya, K. A. Analysis, Occurrence, and Toxic Potential of Pyrethroids, and Fipronil in Sediments from an Urban Estuary. *Environ. Toxicol. Chem.* **2010**, *29*, 843–851.
3. Ensminger, M.; Budd, R.; Kelley, K.; Goh, K. 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**, 1–14.
4. Stone, W. W.; Gilliom, R. J.; Ryberg, K. R. Pesticides in U.S. Streams and Rivers: Occurrence and Trends During 1992-2011. *Environ. Sci. Technol.* **2014**, *48*, 11025–11030.
5. Hladik, M.; Kolpin, D. W. First National-scale Reconnaissance of Neonicotinoid Insecticides in Streams Across the USA. *Environ. Chem.* **2015**, *13*, 12–20.
6. Luo, Y.; Deng, X.; Xie, Y.; Singhasemanon, N.; Goh, K. S. Improved Modeling Approaches for Pesticide Registration Evaluation for Surface Water Protection in California. In *Pesticides in Surface Water: Monitoring, Modeling, Risk Assessment, and Management*; Goh, K. S.; Gan, J., Young, D. F., Luo, Y. , Eds.; ACS Symposium Series 1308; American Chemical Society: Washington, DC, 2019; Chapter 13.
7. Deng, X.; Wagner, S.; Wang, D.; Luo, Y.; Goh, K. S. Pesticide Detections, Benchmark Exceedances, and Temporal Trends in Surface Water California's Imperial, Salinas, and Santa Maria Valleys. In *Pesticides in Surface Water: Monitoring, Modeling, Risk Assessment, and Management*; Goh, K. S.; Gan, J., Young, D. F., Luo, Y. , Eds.; ACS Symposium Series 1308; American Chemical Society: Washington, DC, 2019; Chapter 8.
8. Domagalski, J. Agricultural Chemical Concentrations and Loads in Rivers Draining the Central Valley, California: Before, During, and After an Extended Drought. In *Pesticides in Surface Water: Monitoring, Modeling, Risk Assessment, and Management*; Goh, K. S.; Gan, J., Young, D. F., Luo, Y. , Eds.; ACS Symposium Series 1308; American Chemical Society: Washington, DC, 2019; Chapter 17.
9. Weston, D. P.; Ramil, H. L.; Lydy, M. J. Pyrethroid Insecticides in Municipal Wastewater. *Environ. Toxicol. Chem.* **2013**, *32*, 2460–2468.

10. Markle, J. C.; van Buuren, B. H.; Moran, K.; Barefoot, A. C. Pyrethroid Pesticides in Municipal Wastewater: A Baseline Survey of Publicly Owned Treatment Works Facilities in California in 2013. In *Describing the Behavior and Effects of Pesticides in Urban and Agricultural Settings*; ACS Symposium Series 1168; American Chemical Society: Washington, DC, 2014; pp 177–194.
11. Sadaria, A. M.; Sutton, R.; Moran, K. D.; Teerlink, J.; Brown, J. V.; Halden, R. U. Passage of Fiproles and Imidacloprid from Urban Pest Control Uses Through Wastewater Treatment Plants in Northern California, USA. *Environ. Toxicol. Chem.* **2017**, *36*, 1473–1482.
12. Brooks, B. W.; Riley, T. M.; Taylor, R. D. Water Quality of Effluent-Dominated Ecosystems: Ecotoxicological, Hydrological, and Management Considerations. *Hydrobiologia* **2006**, *556*, 365–379.
13. Shamim, M.; Meléndez, J.; Sappington, K.; Ruhman, M. Conducting Ecological Risk Assessments of Urban Pesticide Uses. In *Describing the Behavior and Effects of Pesticides in Urban and Agricultural Settings*; ACS Symposium Series 1168; American Chemical Society: Washington, DC, 2014; pp 207–274.
14. CVRWQCB (Central Valley Regional Water Quality Control Board). *Proposed Amendments to the Water Quality Control Plan for the Sacramento River and San Joaquin River Basins for the Control of Pyrethroid Pesticides Discharges, Final Staff Report*; Rancho Cordova, CA, 2017.
15. Merel, S.; Snyder, S. A. Critical Assessment of the Ubiquitous Occurrence and Fate of the Insect Repellent *N,N*-diethyl-*m*-toluamide in Water. *Environ. Int.* **2016**, *96*, 98–117.
16. Halos, L.; Beugnet, F.; Cardoso, L.; Farkas, R.; Franc, M.; Guillot, J.; Pfister, K.; Wall, R. Flea Control Failure? Myths and Realities. *Trends Parasitol.* **2014**, *30*, 228–233.
17. Siak, M.; Burrows, M. Flea Control in Cats: New Concepts and the Current Armoury. *J. Feline Med. Surg.* **2013**, *15*, 31–40.
18. DPR (California Department of Pesticide Regulation). *California Product/ Label Database Queries & Lists*; Sacramento, CA, 2018.
19. 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.
20. Jennings, K. A.; Canerdy, T. D.; Keller, R. J.; Atieh, B. H.; Doss, R. B.; Gupta, R. C. Human Exposure to Fipronil from Dogs Treated with Frontline. *Vet. Hum. Toxicol.* **2002**, *44*, 301–303.
21. Craig, M. S.; Gupta, R. C.; Candery, T. D.; Britton, D. A. Human Exposure to Imidacloprid from Dogs Treated with Advantage. *Toxicol. Mech. Methods* **2005**, *15*, 287–291.
22. Gupta, R. C.; Masthay, M. B.; Canerdy, T. D.; Acosta, T. M.; Provost, R. J.; Britton, D. M.; Atieh, B. H.; Keller, R. J. Human Exposure to Selamectin from Dogs Treated with Revolution: Methodological Consideration for Selamectin Isolation. *Toxicol. Mech. Methods* **2005**, *15*, 317–321.
23. Bigelow Dyk, M.; Liu, Y.; Chen, Z.; Vega, H.; Krieger, R. I. Fate and Distribution of Fipronil on Companion Animals and in their Indoor

Residences Following Spot-on Flea Treatments. *J. Environ. Sci. Health, Part B* **2012**, *47*, 913–924.
24. Driver, J. H.; Ross, J. H.; Guerino, F.; Wrzesinski, C. Measurement of the Temporal Transferability of Indoxacarb to Cotton Gloves from Spot-on Treated Dogs. *J. Toxicol. Environ. Health, Part A* **2014**, *77*, 696–704.
25. Case, K. M.; Vega, N. M.; Gupta, R. C.; Lasher, M. A.; Canerdy, T. D. Safety Evaluation of Parastar Plus in Dogs and Assessment of Transferable Residue of Fipronil and Cyphenothrin from Dogs to Humans. *Front. Vet. Sci.* **2016**, *3*, 89.
26. Jacobs, D. E.; Hutchinson, M. J.; Stanneck, D.; Mencke, N. Accumulation and Persistence of Flea Larvicidal Activity in the Immediate Environment of Cats Treated with Imidacloprid. *Med. Vet. Entomol.* **2001**, *15*, 342–345.
27. Colt, J. S.; Lubin, J.; Camann, D.; Davis, S.; Cerhan, J.; Severson, R. K.; Cozen, W.; Hartge, P. Comparison of Pesticide Levels in Carpet Dust and Self-reported Pest Treatment Practices in Four US Sites. *J. Expo. Anal. Environ. Epidemiol.* **2004**, *14*, 74–83.
28. Obendorf, S. K.; Lemley, A. T.; Hedge, A.; Kline, A. A.; Tan, K.; Dokuchayeva, T. Distribution of Pesticide Residues within Homes in Central New York State. *Arch. Environ. Contam. Toxicol.* **2006**, *50*, 31–44.
29. Mahler, B. J.; Van Metre, P. C.; Wilson, J. T.; Musgrove, M.; Zaugg, S. D.; Burkhardt, M. R. Fipronil and its Degradates in Indoor and Outdoor Dust. *Environ. Sci. Technol.* **2009**, *43*, 5665–5670.
30. Moschet, C.; Anumol, T.; Lew, B. M.; Bennett, D. H.; Young, T. M. Household Dust as a Repository of Chemical Accumulation: New Insights from a Comprehensive High-Resolution Mass Spectrometric Study. *Environ. Sci. Technol.* **2018**, *52*, 2878–2887.
31. Simcox, N. J.; Fenske, R.A.; Wolz, S.A.; Lee, I.C.; Kalman, D.A. Pesticides in household dust and soil: Exposure Pathways for Children of Agricultural Families. *Environ. Health Perspect.* **1995**, *103*, 1126–1134.
32. Fenske, R. A.; Lu, C.; Negrete, M.; Galvin, K. Breaking the Take Home Pesticide Exposure Pathway for Agricultural Families: Workplace Predictors of Residential Contamination. *Am. J. Ind. Med.* **2013**, *56*, 1063–1071.
33. Deziel, N. C.; Friesen, M. C.; Hoppin, J. A.; Hines, C. J.; Thomas, K.; Freeman, L. E. A Review of Nonoccupational Pathways for Pesticide Exposure in Women Living in Agricultural Areas. *Environ. Health Perspect.* **2015**, *123*, 515–524.
34. Ueyama, J.; Harada, K. H.; Koizumi, A.; Sugiura, Y.; Kondo, T.; Saito, I.; Kamijima, M. Temporal Levels of Urinary Neonicotinoid and Dialkylphosphate Concentrations in Japanese Women Between 1994 and 2011. *Environ. Sci. Technol.* **2015**, *49*, 14522–14528.
35. Klarich, K. L.; Pflug, N. C.; DeWald, E. M.; Hladik, M. L.; Kolpin, D. W.; Cwiertny, D. M.; LeFevre, G. H. Occurrence of Neonicotinoid Insecticides in Finished Drinking Water and Fate During Drinking Water Treatment. *Environ. Sci. Technol. Lett.* **2017**, *4*, 168–173.
36. Glassmeyer, S. T.; Furlong, E. T.; Kolpin, D. W.; Batt, A. L.; Benson, R.; Boone, J. S.; Conerly, O.; Donohue, M. J.; King, D. N.; Kostich, M. S.; Mash, H. E.; Pfaller, S. L.; Schenck, K. M.; Simmons, J. E.; Varughese, E.

A.; Vesper, S. J.; Villegas, E. N.; Wilson, V. S. Nationwide Reconnaissance of Contaminants of Emerging Concern in Source and Treated Drinking Waters of the United States. *Sci. Total Environ.* **2017**, *581–582*, 909–922.
37. Budd, R.; Ensminger, M.; Wang, D.; Goh, K. S. Monitoring Fipronil and Degradates in California Surface Waters, 2008-2013. *J. Environ. Qual.* **2015**, *44*, 1233–1240.
38. Vander Werf, R.; Aldana, A.; Teerlink, J.; Budd, R. *Retail Store Survey of Consumer-Use Indoor Pesticide Products, 2014*; California Department of Pesticide Regulation, Environmental Monitoring Branch: 2015.
39. Hope, B. K.; Pillsbury, L.; Boling, B. A State-wide Survey in Oregon (USA) of Trace Metals and Organic Chemicals in Municipal Effluent. *Sci. Total Environ.* **2012**, *417*, 263–272.
40. 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.
41. Barber, L. B.; Keefe, S. H.; Brown, G. K.; Furlong, E. T.; Gray, J. L.; Kolpin, D. W.; Meyer, M. T.; Sandstrom, M. W.; Zaugg, S. D. Persistence and Potential Effects of Complex Organic Contaminant Mixtures in Wastewater-Impacted Streams. *Environ. Sci. Technol.* **2013**, *47*, 2177–2188.
42. Barber, L. B.; Keefe, S. H.; Kolpin, D. W.; Schnoebelen, D. J.; Flynn, J. L.; Brown, G. K.; Furlong, E. T.; Glassmeyer, S. T.; Gray, J. L.; Meyer, M. T. *Lagrangian Sampling of Wastewater Treatment Plant Effluent in Boulder Creek, Colorado, and Fourmile Creek, Iowa, during the Summer of 2003 and Spring of 2005−Hydrological and Chemical Data*; U.S. Geological Survey Open-File Report 2011-1054; Reston, VA, 2011.
43. Fairbairn, D. J.; Arnold, W. A.; Barber, B. L.; Kaufenberg, E. F.; Koskinen, W. C.; Novak, P. J.; Rice, P. J.; Swackhamer, D. L. Contaminants of Emerging Concern: Mass Balance and Comparison of Wastewater Effluent and Upstream Sources in a Mixed-use Watershed. *Environ. Sci. Technol.* **2015**, *50*, 36–45.
44. Mohapatra, S.; Huang, C.-H.; Mukherji, S.; Padhye, L. P. Occurrence and fate of pharmaceuticals in WWTPs in India and Comparison with a Similar Study in the United States. *Chemosphere* **2016**, *159*, 526–535.
45. 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.
46. Vatovec, C.; Phillips, P.; Van Wagoner, E.; Scott, T.-M.; Furlong, E. Investigating Dynamic Sources of Pharmaceuticals: Demographic and Seasonal use are More Important than Down-the-Drain Disposal in Wastewater Effluent in a University City Setting. *Sci. Total Environ.* **2016**, *572*, 906–914.
47. Kolpin, D. W.; Thurman, E. M.; Lee, E. A.; Meyer, M. T.; Furlong, E. T.; Glassmeyer, S. T. Urban Contributions of Glyphosate and its Degradate AMPA to Streams in the United States. *Sci. Total Environ.* **2006**, *354*, 191–197.

48. Parry, E.; Lesmeister, S.; Teh, S.; Young, T. M. Characteristics of Suspended Solids Affect Bifenthrin Toxicity to the Calanoid Copepods *Eurytemora Affinis* and *Pseudodiaptomus Forbesi*. *Environ. Toxicol. Chem.* **2015**, *34*, 2302–2309.
49. Weston, D. P.; Lydy, M. J. Urban and Agricultural Sources of Pyrethroid Insecticides to the Sacramento-San Joaquin Delta of California. *Environ. Sci. Technol.* **2010**, *44*, 1833–1840.
50. Snyder, S. A.; Wert, E. C.; Rexing, D. J.; Zegers, R. E.; Drury, D. D. Ozone Oxidation of Endocrine Disruptors and Pharmaceuticals in Surface Water and Wastewater. *Ozone Sci. Eng.* **2006**, *28*, 445–460.
51. Glassmeyer, S. T.; Furlong, E. T.; Kolpin, D. W.; Cahill, J. D.; Zaugg, S. D.; Werner, S. L.; Meyer, M. T.; Kryak, D. D. Transport of Chemical and Microbial Compounds from Known Wastewater Discharges: Potential for Use as Indicators of Human Fecal Contamination. *Environ. Sci. Technol.* **2005**, *39*, 5157–5169.
52. Meador, J. P.; Yeh, A.; Young, G.; Gallagher, E. P. Contaminants of Emerging Concern in a Large Temperate Estuary. *Environ. Pollut.* **2016**, *213*, 254–267.
53. Nelson, E. D.; Do, H.; Lewis, R. S.; Carr, S. A. Diurnal Variability of Pharmaceutical, Personal Care Product, Estrogen and Alkylphenol Concentrations in Effluent from a Tertiary Wastewater Treatment Facility. *Environ. Sci. Technol.* **2010**, *45*, 1228–1234.
54. Heidler, J.; Halden, R. U. Fate of Organohalogens in US wastewater Treatment Plants and Estimated Chemical Releases to Soils Nationwide from Biosolids Recycling. *J. Environ. Monit.* **2009**, *11*, 2207–2215.
55. McMahen, R. L.; Strynar, M. J.; McMillan, L.; DeRose, E.; Lindstrom, A. B. Comparison of Fipronil Sources in North Carolina Surface Water and Identification of a Novel Fipronil Transformation Product in Recycled Wastewater. *Sci. Total Environ.* **2016**, *569*, 880–887.
56. US EPA (United States Environmental Protection Agency) Office of Pesticide Programs Aquatic Life Benchmarks and Ecological Risk Assessments for Registered Pesticides. https://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/aquatic-life-benchmarks-and-ecological-risk (accessed Oct. 20, 2018).
57. Singhasemanon, N.; Nordmark, C.; Barry, T. *Diazinon and Chlorpyrifos in the Central Contra Costa Sanitary District Sewer System, Summer 1996*; California Department of Pesticide Regulation: 1998.
58. US EPA (United States Environmental Protection Agency). *Interim Reregistration Eligibility Decision for Diazinon, Case No. 0238*; Washington, DC, 2002.
59. US EPA (United States Environmental Protection Agency). *Interim Reregistration Eligibility Decision for Chlorpyrifos, Case No. 0100*; Washington, DC, 2006.
60. US EPA (United States Environmental Protection Agency). *Occurrence of Contaminants of Emerging Concern in Wastewater from Nine Publicly Operated Treatment Works*; EPA-821-R-09-009; Washington, DC, 2009.
61. McMahen, R. L.; Strynar, M. J.; Dagnino, S.; Herr, D. W.; Moser, V. C.; Garantziotis, S.; Andersen, E. M.; Freeborn, D. L.; McMillan, L.;

Lindstrom, A. B. Identification of Fipronil Metabolites by Time-of-Flight Mass Spectrometry for Application in a Human Exposure Study. *Environ. Int.* **2015**, *78*, 16–23.
62. Schreder, E. D.; La Guardia, M. J. Flame Retardant Transfers from U.S. Households (Dust and Laundry Wastewater) to the Aquatic Environment. *Environ. Sci. Technol.* **2014**, *48*, 11575–11583.
63. BACWA (Bay Area Clean Water Agencies). *Comment Letter: Imidacloprid - Preliminary Aquatic Risk Assessment (EPA-HQ-OPP-2008-0844)*; BACWA: Oakland, CA, 2017.
64. BACWA (Bay Area Clean Water Agencies). *Comment Letter: Dinotefuran - Preliminary Ecological Risk Assessment (EPA-HQ-OPP-2011-0920)*; BACWA: Oakland, CA, 2018.
65. Boix, C.; Ibáñez, M.; Bagnati, R.; Zuccato, E.; Sancho, J. V.; Hernández, F.; Castiglioni, S. High Resolution Mass Spectrometry to Investigate Omeprazole and Venlafaxine Metabolites in Wastewater. *J. Hazard. Mater.* **2016**, *302*, 332–340.
66. Margot, J.; Rossi, L.; Barry, D. A.; Holliger, C. A Review of the Fate of Micropollutants in Wastewater Treatment Plants. *Wiley Interdiscipl. Rev. Water* **2015**, *2*, 457–487.
67. Parry, E.; Young, T. M. Distribution of Pyrethroid Insecticides in Secondary Wastewater Effluent. *Environ. Toxicol. Chem.* **2013**, *32*, 2686–2694.
68. DPR (California Department of Pesticide Regulation). *Comment Letter: U.S. Environmental Protection Agency Ecological Risk Assessment and Registration Review Of Pyrethroids And Pyrethrins (Bifenthrin, Cyfluthrins (& Beta), Cypermethrin (Alpha & Zeta), Cyphenothrin, D-Phenothrin, Deltamethrin, Esfenvalerate, Etofenprox, Fenopropathrin, Flumethrin, Gamma-Cyhalothrin, Imiprothrin, Lambda-Cyhalothrin, Momfluorothrin, Permethrin, Prallethrin, Pyrethrins, Tau-Fluvalinate, Tefluthrin, Tetramethrin (Docket Identification Numbers: EPA-HQ-OPP-2010-0384, EPA-HQ-OPP-2010-0684, EPA-HQ-OPP-2012-0167, EPA-HQ-OPP-2009-0842, EPA-HQ-OPP-2011-0539, EPA-HQ-OPP-2009-0637, EPA-HQ-OPP-2009-0301, EPA-HQ-OPP-2007-0804, EPA-HQ-OPP2010-0422, EPA-HQ-OPP-2016-0031, EPA-HQ-OPP-2010-0479, EPA-HQ-OPP-2011-0692, EPA-HQ-OPP-2010-0480, EPA-HQ-OPP-2015-0752, EPA-HQ-OPP-2011-0039, EPA-HQOPP-2011-1009, EPA-HQ-2011-0885, EPA-HQ-OPP-2010-0915, EPA-HQ-OPP-2012-0501, EPA-HQ-OPP-2011-0907)*; DPR Environmental Monitoring Branch, 2017.

SETAC PRESS

Environmental Toxicology and Chemistry, Vol. 9999, No. 9999, pp. 1–10, 2016

Printed in the USA

Environmental Chemistry

PASSAGE OF FIPROLES AND IMIDACLOPRID FROM URBAN PEST CONTROL USES THROUGH WASTEWATER TREATMENT PLANTS IN NORTHERN CALIFORNIA, USA

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(Submitted 19 May 2016; Returned for Revision 22 July 2016; Accepted 1 November 2016)

Abstract: Urban pest control insecticides—specifically fipronil and its 4 major degradates (fipronil sulfone, sulfide, desulfinyl, and amide), as well as imidacloprid—were monitored during drought conditions in 8 San Francisco Bay (San Francisco, CA, USA) wastewater treatment plants (WWTPs). In influent and effluent, ubiquitous detections were obtained in units of ng/L for fipronil (13–88 ng/L), fipronil sulfone (1–28 ng/L), fipronil sulfide (1–5 ng/L), and imidacloprid (58–306 ng/L). Partitioning was also investigated; in influent, 100% of imidacloprid and $62 \pm 9\%$ of total fiproles (fipronil and degradates) were present in the dissolved state, with the balance being bound to filter-removable particulates. Targeted insecticides persisted during wastewater treatment, regardless of treatment technology utilized (imidacloprid: $93 \pm 17\%$; total fiproles: $65 \pm 11\%$ remaining), with partitioning into sludge (3.7–151.1 μg/kg dry wt as fipronil) accounting for minor losses of total fiproles entering WWTPs. The load of total fiproles was fairly consistent across the facilities but fiprole speciation varied. This first regional study on fiprole and imidacloprid occurrences in raw and treated California sewage revealed ubiquity and marked persistence to conventional treatment of both phenylpyrazole and neonicotinoid compounds. Flea and tick control agents for pets are identified as potential sources of pesticides in sewage meriting further investigation and inclusion in chemical-specific risk assessments. *Environ Toxicol Chem* 2016;9999:1–10. © 2016 SETAC

Keywords: Insecticide Water quality Persistant organic pollutants (POPs) Fate and transport Pesticides

INTRODUCTION

Over the last decade, 2 newer insecticides, fipronil and imidacloprid, have gradually replaced older active ingredients in common urban pest control applications, such as pet flea treatments and professional insect control products [1,2]. The phase-out of most organophosphate insecticides for urban uses in the early 2000s opened markets that soon were filled by fipronil and imidacloprid formulations. Continued growth of urban uses is likely in the present decade in large part because of the replacement of pyrethroids, an older class of insecticides that are widely detected in urban streams and have come under scrutiny for adverse impacts on the health of aquatic invertebrates [3–6], findings that triggered federal and state regulatory responses [7,8]. Fipronil, a phenylpyrazole insecticide, has multiple urban uses including sprays for the outdoor perimeter of buildings to control ants and other insects, underground injections to control termites, pet treatments for fleas and ticks, gels for crack and crevice treatment, insect control baits, and, except in California, landscape maintenance [1,9,10]. Imidacloprid, a neonicotinoid insecticide, has urban applications in lawn and landscape maintenance, outdoor structural pest control, indoor bedbug and nuisance insect control, underground injections to control termites, and pet treatments for fleas and ticks [1,11]. Imidacloprid is also used as an insecticidal component of manufactured materials such as polystyrene insulation, vinyl siding, adhesives, sealants, textiles for outdoor uses, and pressure-treated wood decking [11–13].

Both pesticides are toxic to sensitive aquatic invertebrates at low parts-per-trillion concentrations (<100 ng/L) [14,15]. In 2007, the US Environmental Protection Agency (USEPA) established aquatic life benchmarks for fipronil (11 ng/L), as well as its degradates fipronil sulfone (37 ng/L), fipronil sulfide (110 ng/L), and fipronil desulfinyl (590 ng/L) based on chronic exposure studies of multiple freshwater invertebrates [16]. Recently published invertebrate toxicity data [15] show chronic effects to aquatic invertebrates at concentrations of 7 ng/L to 8 ng/L for fipronil sulfone and 9 ng/L to 11 ng/L for fipronil sulfide, lower than the USEPA's 2007 benchmarks. Fish appear to be less sensitive to fipronil and its degradates; USEPA chronic aquatic life benchmarks for freshwater fish range from 6600 ng/L for fipronil to 590 ng/L for fipronil desulfinyl [16]. In 2008, the USEPA established an aquatic life benchmark of 1050 ng/L for imidacloprid based on chronic exposure studies of *Daphnia magna* [11]. However, a recent summary of chronic toxicity data indicates that mayflies can experience effects such as immobilization after long-term exposure at concentrations of less than 100 ng/L and that the majority of other invertebrates studied are 100 to 1000 times more sensitive to imidacloprid than *D. magna* [14]. A more recent evaluation by the European Union of imidacloprid toxicity data [17] has established a predicted no-effect concentration (PNEC) of 4.8 ng/L; this was based on species sensitivity distribution information incorporating recent toxicity data, such as the mayfly nymph immobilization effective concentration, 10% (EC10) value of approximately 30 ng/L [18]. Fish are less sensitive to

This article includes online-only Supplemental Data.

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Published online 3 November 2016 in Wiley Online Library (wileyonlinelibrary.com).
DOI: 10.1002/etc.3673

imidacloprid, as evidenced by the USEPA fish chronic benchmark of 1.2 mg/L [11].

Both fipronil and imidacloprid are commonly detected in urban streams [6,19,20]. For example, a survey of storm drains in California found median levels of fipronil to be 33 ng/L in northern California and 76 ng/L in southern California; fipronil sulfone (medians of 26 ng/L and 77 ng/L for northern and southern California, respectively) and fipronil desulfinyl (medians of 15 ng/L and 41 ng/L for northern and southern California, respectively) were also frequently detected [6,19]. Another California survey of urban surface waters measured maximum imidacloprid levels of 160 ng/L during the dry season and 670 ng/L during the wet season [6].

For both of these pesticides, relatively few data are available concerning levels in urban wastewater before and after treatment. This data gap also exists for treated and untreated wastewater sludge, despite ubiquitous urban application of these pesticides, as well as the demonstrated presence of another group of popular urban insecticides, the pyrethroids, in treated wastewater and biosolids [21]. Fipronil has been detected in treated wastewater discharged by 9 of 25 US wastewater treatment plants (WWTPs; <10–70 ng/L) [22]; 6 Florida WWTPs (16–110 ng/L) [23]; 7 of 9 Oregon and Washington municipal WWTPs (27–130 ng/L) [24]; 2 California WWTPs (<1–57 ng/L) [15]; and 1 southwestern US WWTP (13–21 ng/L) [25]. Some of the facilities studied thus far treat a mixture of wastewater and urban runoff (California, 1; Florida, 6). Past measurements of influent and effluent suggested little if any removal of fipronil during typical wastewater treatment [15,22,23,25]. However, prior studies were sometimes limited by featuring approximately 2- to 50-fold higher method detection limits, failing to monitor all major fipronil transformation products, or omitting analysis of suspended particulates that were removed by filtration or other treatment prior to analysis [15,22,23,25]. Presently available and still limited data on fipronil degradates suggest sporadic, low-level occurrence of fipronil desulfinyl [15,23,24], as well as fipronil sulfone, sulfide, and amide [25], in wastewater treatment flows. Fipronil and its degradates were also detected in 2 effluent-dominated rivers in southern California during low flow conditions [26]. Available data suggest that concentrations of fipronil in treated effluent frequently approach or exceed USEPA chronic invertebrate aquatic life benchmark [25,26].

Fipronil and its degradates, jointly referred to as total fiproles, feature logarithmic octanol–water partitioning coefficient ($\log K_{OW}$) values > 4. This characteristic enables them to sorb to particles in wastewater that settle during treatment, ultimately leading to a sequestration of fipronil-related compounds in sewage sludge and treated sludge deemed fit for application on land (biosolids). Two studies have reported measurable concentrations of fipronil and degradates in this matrix [22,25].

Likewise, few studies have examined imidacloprid in municipal wastewater. Imidacloprid was detected in <10% of treated effluent samples from 52 Oregon municipal WWTPs (202–387 ng/L), using a higher method detection limit of 200 ng/L; influent and biosolids were not sampled [27]. To date, there are no published studies reporting on measured imidacloprid levels in biosolids, possibly because the low log K_{OW} value of imidacloprid (<1) does not suggest partitioning into sludge as an important process. Studies of imidacloprid in wastewater in China and Spain (where allowable uses may differ from those in the United States) suggest that typical treatment technologies may result in low removal of imidacloprid from the liquid phase prior to discharge into receiving waters [28,29]. A study of an effluent-dominated waterway in Iowa indicated that treated wastewater can introduce imidacloprid to receiving waters [20].

In the present study, we explored the presence of fipronil, its 4 major degradates, and imidacloprid in urban wastewater before and after treatment, providing the first regional set of data for WWTPs across varying treatment technologies. Furthermore, to add to still limited literature data, we also analyzed sludges from the sampled plants for insecticide occurrence. Finally, we assessed sources related to urban uses of these pesticides.

MATERIALS AND METHODS

Standards and reagents

High-performance liquid chromatography (HPLC)–grade organic solvents (methanol, acetone, methylene chloride, and hexane) and water were purchased from Sigma-Aldrich and Thermo Fisher Scientific, respectively. Analytical standards of imidacloprid, fipronil, fipronil desulfinyl, and deuterated labeled standard [d_4] imidacloprid were obtained from Sigma-Aldrich. Analytical standards of fipronil sulfide, sulfone, and amide were obtained from Bayer and BASF. Labeled [$^{13}C_2{}^{15}N_2$] fipronil and [$^{13}C_4{}^{15}N_2$] fipronil sulfone were bought from Toronto Research Chemicals and Cambridge Isotope Laboratories, respectively. Stock solutions of analytical standards were prepared in acetonitrile and stored at –20 °C.

Sample collection

Single 24-h composite samples of influent and effluent were collected from each of 8 facilities that discharge to San Francisco Bay (San Francisco, CA, USA). Facilities that provided samples were selected based on multiple factors, including higher discharge levels, geographic diversity, and range of treatment technologies (secondary only vs tertiary filtration; Table 1). As a consequence of drought-related water use restrictions, facilities were operating well below capacities (Table 1). One facility sampled serves only a large airport and the associated operations. The remaining 7 locations, representative of more typical municipal WWTPs, had per capita daily influent flows of 235 L/person/d to 302 L/person/d. Autosamplers at all facilities provided flow-weighted composite samples, with the exception being the San José–Santa Clara influent compositer, which provides a flow-weighted composite of 6 subsamples collected regularly throughout the 24-h period. Wastewater recycling, including reverse osmosis treatment of <10% of the San José–Santa Clara facility secondary effluent, reduces effluent flow. Reverse osmosis recycling returns a concentrate that is mixed with effluent prior to discharge. The sampling location includes the returned concentrate volume and represents roughly 2% of the total effluent volume.

Influent, effluent, and dewatered/treated sludge samples were collected simultaneously during mid-week of September 2015. The San Francisco Bay region is subject to a mild, Mediterranean climate; September is within the dry season and was selected specifically as an appropriate period of study to avoid rainfall-related inflow and infiltration. Inflow of urban runoff would include fiproles and imidacloprid; by excluding runoff as a potential source, the study design allows specific insight regarding indoor sources. Of note, none of the facilities typically treat storm water. The mild climate in this coastal region also allows fleas to flourish year-round [30], motivating continued residential use of flea control pesticides. Wastewater

Table 1. Characteristics of wastewater treatment plants and processes monitored in the present study

WWTP	Population served (thousands)	Plant capacity (MGD)	Wastewater treatment				Sludge treatment	Influent flow (MGD)	HRT (h)	TSS (mg/L)	
			Primary	Secondary	Disinfection	Advanced				Inf	Eff
SFTP	[a]	2.2	PS	SBR	Cl2	—	AD	0.45	5.75	1004	20
PARP	220	39	PS	FFR, AS	UV	F	NT	16.86	22	322	<1
SJSC	1400	167	PS	AS	Cl2	F	AD	92.76	9	315	1
SLWP	55	7.6	PS	FFR, AS	Cl2	—	AD	4.15	10	517	9
SMWP	140	15	PS	AS	Cl2	F	AD	9.02	14.6	414	9
EBMUD	650	120	PS	AS	Cl2	—	AD	45.00	15	340	11
FSSD	139	23.7	PS	AS	UV	F	AD	11.21	24	237	<1
CCSD	471	53.8	PA, PS	AS	UV	—	NT	29.27	6.5	312	8

[a]Annually, 56 million people pass through airport facilities.
WWTP = wastewater treatment plant; MGD = million gallons per day; HRT = hydraulic retention time; TSS = total suspended solids; Inf = influent; Eff = effluent; SFTP = San Francisco International Airport Commission Mel Leong Treatment Plant; PARP = City of Palo Alto Regional Water Quality Control Plant; SJSC = San Jose-Santa Clara Regional Wastewater Facility; SLWP = San Leandro Water Pollution Control Plant; SMWP = City of San Mateo Waste Water Treatment Plant; EBMUD = East Bay Municipal Utility District Wastewater Treatment Plant; FSSD = Fairfield-Suisun Sewer District Wastewater Treatment Plant; CCSD = Central Contra Costa County Sanitary District Treatment Plant; PS = primary sedimentation; PA = pre-aeration; SBR = sequential batch reactor; FFR = fixed film reactor; AS = activated sludge; Cl2 = chlorine disinfection; UV = ultraviolet disinfection; F = filtration; AD = anaerobic digestion; NT = no treatment;

samples were collected in 2-L amber glass jars to which the biocide Kathon CG/ICP (for more information see the Supplemental Data) and sodium thiosulfate were added for disinfection and preservation. Sludge samples were collected in 0.5-L amber glass jars. Wastewater samples were refrigerated at 4 °C and analyzed within 10 d of collection, and sludge samples were stored at –20 °C until extraction.

Extraction of influent solid and biosolids samples.

Wastewater influent was separated into aqueous phase and particulates and analyzed separately to determine the distribution and total mass loading of pesticides entering the WWTPs. For this purpose, influent samples were centrifuged at 3000 *g* for 5 min, and settled particulates were dried under a gentle stream of nitrogen. Analyte extraction of solids from influent and of biosolids was performed using established protocols [25,31]. One gram of nitrogen-dried solid sample was spiked with 20 ng of labeled [$^{13}C_2{}^{15}N_2$] fipronil, [$^{13}C_4{}^{15}N_2$] fipronil sulfone, and 200 ng of labeled [d_4] imidacloprid, extracted with 10 mL acetone, twice, by 24 h of shaking, followed by 1 h of sonication. Later, extracts were centrifuged, supernatants were nitrogen-dried and reconstituted to 2 mL hexane, and Florisil cleanup (solid-phase extraction with a sorbent bed containing mixture of magnesium oxide and silica gel) was performed. Analytes were eluted successively from a Florisil cartridge (Sep-Pak Vac Florisil Cartridge 6 cc containing 1 g of sorbent; Waters) with 4 mL methylene chloride and 4 mL acetone. Later, 1 mL of each extract was mixed, evaporated with nitrogen, and reconstituted to 1 mL of water and methanol solution (50:50, v/v) for fipronil and its degradates (sulfone, sulfide, and amide). Similarly, extracts were mixed, dried, and reconstituted to 1 mL of hexane for fipronil desulfinyl, and 1 mL of water, methanol, and formic acid solution (80:20:0.1, v/v/v) for imidacloprid analysis.

Extraction of wastewater samples

The wastewater extraction protocol was similar to that described in previous studies [25,31]. First, 20 ng of labeled [$^{13}C_2{}^{15}N_2$] fipronil and [$^{13}C_4{}^{15}N_2$] fipronil sulfone, and 200 ng of labeled [d_4] imidacloprid were spiked to a 500-mL wastewater sample. Later, samples were loaded on a cartridge having reverse-phase functionalized polymeric styrene divinylbenzene sorbent (Strata X & XL, 500 mg/3 mL; Phenomenex) using an automatic solid-phase extraction instrument (Dionex AutoTrace 280; Thermo Scientific) at a constant flow rate of 2 mL/min. Cartridges were eluted with 8 mL of methanol and formic acid mixture (95:5, v/v). Extracts were dried and reconstituted similarly to solid samples and prepared for analysis by chromatography separation and tandem mass spectrometry (MS/MS).

Chromatography separation and MS/MS

Imidacloprid, fipronil, and degradates, except for fipronil desulfinyl, were separated by liquid chromatography (LC) and detected and quantified by electrospray ionization−MS/MS. Liquid chromatography mass spectrometric analyses were performed using a Shimadzu Prominence HPLC (Shimadzu Scientific) coupled to an ABSciex API-4000 MS/MS (Applied Biosystems). Liquid chromatographic separation was achieved by an XBridge C8-column (3.5-μm particle size, 2.1 mm × 100 mm; Waters). The injection volume was 50 μL. For fipronil and its degradates, the mobile phase consisted of water and methanol at a total flow rate of 0.2 mL/min with a total runtime of 10 min. The binary gradient consisted of 40% methanol with a 5-min ramp of 10% solvent content increase per minute to 95% methanol, where it was held for 3.5 min. For imidacloprid, the mobile phase consisted of 0.1% formic acid in water and methanol at a total flow rate of 0.2 mL/min with a total run time of 12 min. The binary gradient consisted of 20% methanol with a 6-min ramp of 16.7% solvent content increase per minute to 95% methanol, where it was held for 3.5 min. The electrospray ionization probe was operated in negative mode for fipronil and its degradates, and in positive mode for imidacloprid. Multiple reaction monitoring was used for qualitative analysis. Fipronil desulfinyl was analyzed using gas chromatography–electron impact–MS/MS because it exhibited a considerably lower detection limit than LC−MS/MS (see the Supplemental Data).

Quality assurance and quality control

For every 5 samples analyzed, 1 method blank was included in the analytical batch. Matrix spike and matrix spike duplicates were performed at a frequency of 1-in-4 and 1-in-6 for wastewater and solids, respectively. Replicate analyses were

performed at a frequency of 1-in-3 and 1-in-5 for wastewater and solids, respectively, to determine relative percentage deviation. Field duplicates (blind samples) were also collected and analyzed for all analytes for quality assurance. Every shipment of samples included 1 field/trip blank to judge the integrity of sample handling and shipping.

Method performance

The MS/MS method targeted analytes by monitoring 2 ion transitions. Mass spectrometry parameters optimized for multiple reaction monitoring are provided in Supplemental Data, Table S1. Method detection limits of analytes in wastewater ranged from 0.1 ng/L to 0.8 ng/L and in sewage particulates from 0.1 μg/kg to 1.1 μg/kg dry weight (Supplemental Data, Table S2) [25,31]. Relative percentage difference values determined for the studied analytes in samples and in the corresponding duplicates (laboratory and field duplicates) averaged 11 ± 12%. Absolute recoveries (average ± standard deviation) of analytes in all matrix spike and matrix spike duplicate samples were 58 ± 30%, and relative recoveries (isotope-corrected) were 98 ± 10%. Field blanks and method blanks (included to monitor for postsample collection contamination) showed no detectable levels of analytes.

RESULTS AND DISCUSSION

Detection of fipronil and its degradates in wastewater treatment streams

Fipronil, fipronil sulfone, and fipronil sulfide were detected with 100% detection frequency in all influent and effluent samples of 8 WWTPs analyzed (Figure 1; Supplemental Data, Tables S3 and S4). Fipronil amide, a product of fipronil hydrolysis, was absent in all influent samples (<0.3 ng/L), but was detected in effluent samples of 7 of 8 WWTPs, suggesting that hydrolysis took place primarily during biological treatment. The photolysis degradate, fipronil desulfinyl, was detected only in a single WWTP, in both influent and effluent. In this and 2 additional WWTPs, ultraviolet disinfection was performed but it did not lead to increase in the photolysis degradate. In all WWTPs examined, fipronil and fipronil sulfone were the most prevalent fiproles by concentration. In the aqueous phase of

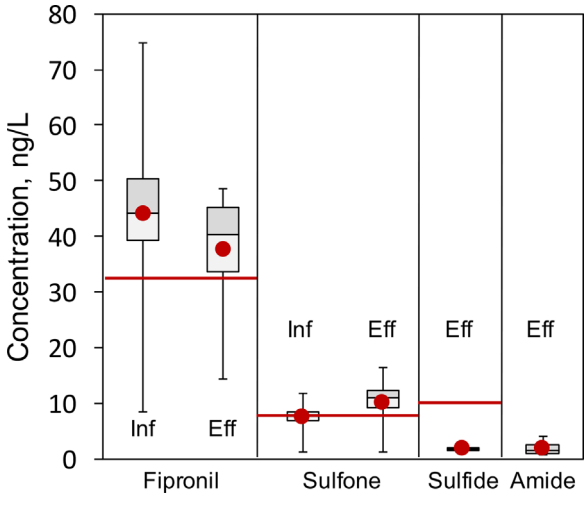

Figure 1. Detected concentrations of fipronil and its degradates (ng/L) in the dissolved phase from 8 wastewater treatment plants in northern California. Red horizontal lines indicate published chronic toxicity values for *Chironomus dilutus*, a freshwater invertebrate [15]. Inf = influent; Eff = effluent.

influent and effluent samples, fipronil concentrations ranged between 8.6 ng/L and 74.9 ng/L and between 14.3 ng/L and 48.6 ng/L, respectively, and fipronil sulfone concentrations ranged between 1.1 ng/L and 11.9 ng/L and between 1.1 ng/L and 16.3 ng/L, respectively. For 6 of the 8 WWTPs studied, sulfone concentration in the effluent was greater than the aqueous phase influent concentration (Figure 1). Fipronil sulfide, amide, and desulfinyl concentrations were less than 5 ng/L. Although the WWTPs studied performed a variety of treatment processes (Table 1), fipronil persistence was roughly comparable across all treatment regimes. Paired *t* test revealed that the total molar concentration of all fipronil-related compounds in aqueous phase influent and effluent at all 8 WWTPs was statistically indistinguishable ($p = 0.95$); however, it should be noted that the sampling strategy was not designed to account for hydraulic retention time (HRT) of treatment trains and instead was meant to yield an average concentration over a 24-h time period.

Distribution of fipronil and its degradates in wastewater

Previous studies have analyzed wastewater samples by filtering [15,23] or by analyzing supernatants [22,25]. As fipronil and its degradates have log K_{OW} values >4 (Supplemental Data, Table S2), there may be a considerable mass bound to the particulate fraction, unassessed by previous studies of influent. Among all 8 WWTPs studied, the majority of fipronil (76 ± 8% by mass) was present in the aqueous phase (Supplemental Data, Figure S1). For fipronil sulfone, however, 66 ± 7% of the mass was particulate bound. Fipronil sulfide, the anaerobic degradate, was present in the particulate fractions of all influent samples but was not detected in the aqueous phase (method detection limit = 0.2 ng/L). Of note, the molar distribution of fiproles in the influent phases likely reflects biotransformation in the sewer as well as physical partitioning and potential other, nonhydrophobic interactions. Individual mass distributions of fipronil and its degradates in all influent samples is provided in the Supplemental Data, Table S5. Of the total molar mass of fiproles, 62 ± 9% was present in the dissolved phase, and a considerable fraction (38 ± 9%) was particulate bound, which reflects the intermediate log K_{OW} values of fipronil and its degradates. Measured concentrations in different phases of analytes are provided in Supplemental Data, Table S3 and S4. As effluent samples featured low total suspended solids values between <1 mg/L and 20 mg/L, extraction and analysis of particulates from effluent was not feasible; however, considering the low amounts of particulates in treated effluent, calculations suggest that the sorbed mass of fipronil-related compound on effluent particulates was less than 0.75% of the total.

Among all 8 treatment facilities studied, the molar distribution of fipronil and its degradates differed by treatment stream and matrix, but some general trends were consistently seen across all WWTPs investigated (Figure 2). In influent, significant differences in the molar distribution of fipronil and its degradates were evident within the aqueous versus particulate phases. Aqueous phase influent was composed of 86 ± 3% fipronil and 14 ± 3% sulfone. In particulates, the molar distributions of fipronil, sulfone, and sulfide were 44 ± 4%, 46 ± 8%, and 9 ± 8%, respectively. Total influent was comprised of 70 ± 3% fipronil, 26 ± 4% sulfone, and 4 ± 4% sulfide. Individual molar distributions for each influent sample are provided in Supplemental Data, Table S5. Discharged effluent, on average, carried fiproles distributed in the following way: 74 ± 6% fipronil, 18 ± 6% sulfone, 4 ± 1% sulfide, 3 ± 2%

Total fiprole loading at 8 wastewater treatment plants in pico-mol/L

	Fipronil	Sulfone	Sulfide	Amide	Desulfinyl	Total fiproles
Influent - aq phase	806	131	0	0	3	940
Influent - particulates	234	251	44	0	0	528
Total influent	1040	382	44	0	3	1468
Effluent	690	180	34	28	6	938

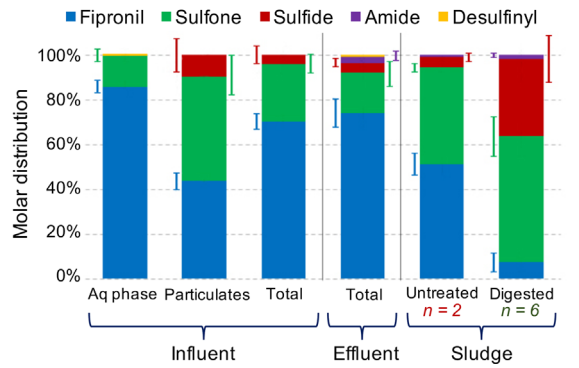

Figure 2. Molar distribution of fipronil and its degradates in treatment streams of 8 wastewater treatment plants. Error bars indicate standard deviation or min/max values when only 2 measurements were available (i.e., for untreated sludge).

amide, and $1 \pm 1\%$ desulfinyl. The small variability observed in the molar distribution in effluent from different treatment plants also suggests that the proportion of the fipronil and its degradates is not strongly influenced by factors such as unit operations, HRT, and sludge age.

Fate of fipronil and its degradates in wastewater and comparison with previous studies

On a molar concentration basis, $65 \pm 11\%$ of the sum of fipronil and its degradates entering each facility (considering both aqueous and particulate phases of influent) was measured in effluent. As mentioned earlier, aqueous phase influent contained $62 \pm 9\%$ of the total fiprole loading, also suggesting no significant removal from the aqueous phase during treatment, with reductions largely attributable to fiprole removal via partitioning to settleable particulates from the waste stream.

Detected total concentration (aqueous phase + sorbed phase) of the present study, termed "California 2015," are compared with previous studies in Figure 3. Influent and effluent of the same 8 WWTPs were analyzed by the California Department of Fish and Wildlife's Water Pollution Control Laboratory in fall 2014 at the behest of the Regional Monitoring Program for Water Quality in San Francisco Bay; however, the method of isotope dilution was not employed. Furthermore, neither sludge samples nor imidacloprid were analyzed, and samples were filtered prior to analysis. Therefore, data obtained in the 2014 study do not account for fipronil mass sorbed to wastewater particulates. The corresponding results are listed in Figure 3 as "California 2014," and concentrations detected are provided in Supplemental Data, Table S6. A comparison of concentrations and detection frequency of other studies shows the northern California data to be mostly consistent with those of prior work in different geographic regions (Figure 3). A study in the southwestern United States [25] is excluded from the comparison in Figure 3, as it studied fipronil and its degradates in only a single facility.

Accumulation of fipronil and its degradates in solids

Six of 8 treatment facilities performed anaerobic digestion of excess solids to produce treated sludge, whereas the remaining 2 facilities incinerated wastewater sludge after dewatering. The molar distribution of fipronil and its degradates in solids was consistent among WWTPs, but differed between anaerobically digested (biosolids) and untreated sludge (Figure 2). Raw excess sludge had $51 \pm 5\%$ fipronil, $43 \pm 2\%$ sulfone, $5 \pm 2\%$ sulfide, and $1 \pm 1\%$ amide, a molar distribution resembling that observed for influent-borne particulates (Figure 2). In anaerobically digested sludge, the molar distribution was different, with the anaerobic degradate fipronil sulfide accounting for $35 \pm 11\%$ and fipronil for only $8 \pm 4\%$ of all fiproles, indicating biotransformation of fipronil as a result of the treatment. The molar distribution of fipronil sulfone ($56 \pm 9\%$) and amide ($2 \pm 1\%$) was somewhat similar to that of untreated sludge. Individual molar distributions for solids from each WWTP are provided in Supplemental Data, Table S5.

Fipronil (0.2–44.1 μg/kg) and the sulfone (1.6–91 μg/kg) and sulfide (0.7–60.3 μg/kg) degradates were detected with 100% detection frequency, and fipronil amide was detected with 88% detection frequency (Figure 4). In the digested sludge produced by 6 of the 8 WWTPs, concentrations of the fipronil degradates sulfone and sulfide were considerably higher than those of the parent compound; this stands in sharp contrast to the composition of the (undigested) sludges produced in 2 facilities utilizing dewatering and incineration. Fipronil desulfinyl was not detected in any of the sludges. Only 2 prior studies have detected fipronil in sludge or biosolids. One of these studied fipronil only in sludge samples of 25 facilities nationwide [22], and another studied fipronil and its degradates in a single facility performing anaerobic digestion for solids treatment [25]. Detected total fipronil concentrations in these studies ranged between 3 μg/kg and 180 μg/kg, which is comparable to the levels observed in the present study (3.7–151.1 μg/kg as fipronil).

Detection of imidacloprid in wastewater treatment streams

Imidacloprid was detected with 100% detection frequency in all influent (58.1–306.1 ng/L) and effluent (83.8–305.2 ng/L) samples and was never detected in any of the sludge samples from the 8 WWTPs examined (Figure 5; Supplemental Data, Table S7). In influent, imidacloprid was only detected in the aqueous phase and was not detected on sewage particulates. Although the WWTPs studied employed different treatment processes (Table 1), the occurrence post-treatment of imidacloprid was a phenomenon extant at all facilities. Although sampling did not account for HRT, effluent concentrations accounted for $93 \pm 17\%$ of the loading arriving at the WWTPs on a concentration basis. Thus, none of the diverse treatment processes sampled was effective at imidacloprid removal.

At the San Francisco Airport WWTP, imidacloprid concentrations in effluent were approximately 3 times higher than influent levels, suggesting inconsistent loading into this facility that provides sanitary services to a major US airport. Alternate explanations could not be supported with available evidence [32]. Higher effluent than influent concentrations were not suggested to result from signal suppression because of matrix effects during the LC–MS/MS detection, as an isotope dilution method was used. Furthermore, proper sample preservation measures were taken, and no rainfall events occurred during the sampling event. Thus, the most likely reason for the observation was inconsistent loading at the treatment facility, particularly given that the sampling strategy was not designed to account for the HRT of the treatment train.

When this facility was excluded from the analysis, a 2-tailed paired *t* test for the remaining 7 plants revealed that influent and

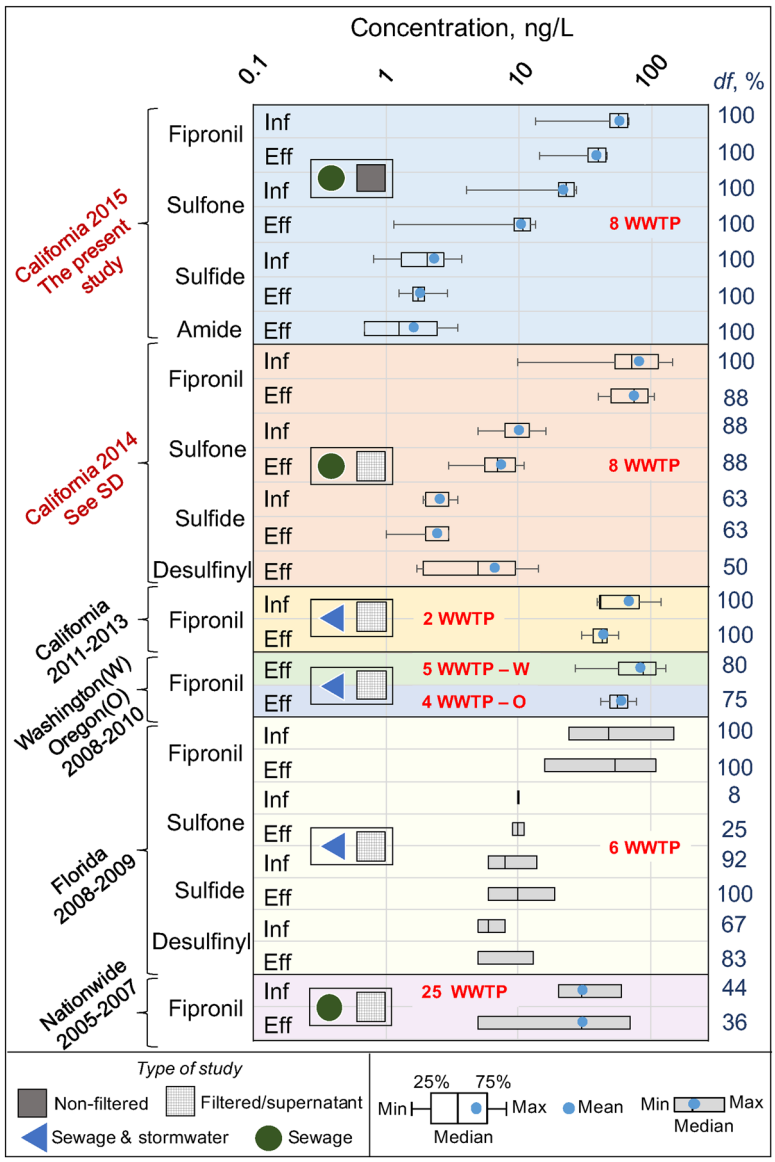

Figure 3. Concentrations of fipronil and its degradates in wastewater samples from 8 California wastewater treatment plants (present study) contrasted with data from past studies [15,22–24]. Years correspond to sampling period. df = detection frequency of compound in process flow; inf = influent; eff = effluent; SD = Supplemental Data.

effluent concentrations were statistically indistinguishable ($p = 0.49$; 95% confidence level), supporting the conclusion of pass-through of imidacloprid.

Levels of imidacloprid in effluent of northern California facilities determined in the present study are generally higher than those observed in a recent assessment of 12 WWTPs from across the United States, which reported a concentration range of 18.5 ng/L to 146.4 ng/L, a dataset included in Figure 5 [31]. An earlier study of effluent from 52 Oregon WWTPs found a relatively low level of detection (9.8% detection frequency);

WWTP	Fipronil	Sulfone	Sulfide	Amide
SFTP	0.2	1.6	1.8	0.1
PARP	*11.4*	*9.0*	*0.7*	*<0.1*
SJSC	0.5	9.1	4.3	0.4
SLWP	8.8	85.0	32.3	1.0
SMWP	17.7	91.0	43.0	1.4
EBMUD	5.6	71.0	60.3	1.4
FSSD	13.9	65.5	24.8	1.4
CCSD	*44.1*	*42.2*	*5.5*	*1.4*

Desulfinyl was not detected at detection limit of 0.3 µg/kg dry weight

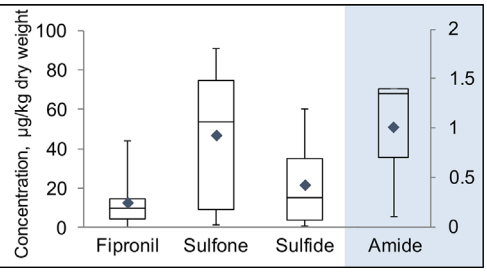

Figure 4. Concentrations of fipronil and its degradates detected in sludge samples obtained from 8 wastewater treatment plants in northern California in 2015. Highlighted in red italics are facilities not performing anaerobic treatment. In the plot, amide concentrations (highlighted blue) correspond to the secondary *y*-axis. See Table 1 for definition of site abbreviations.

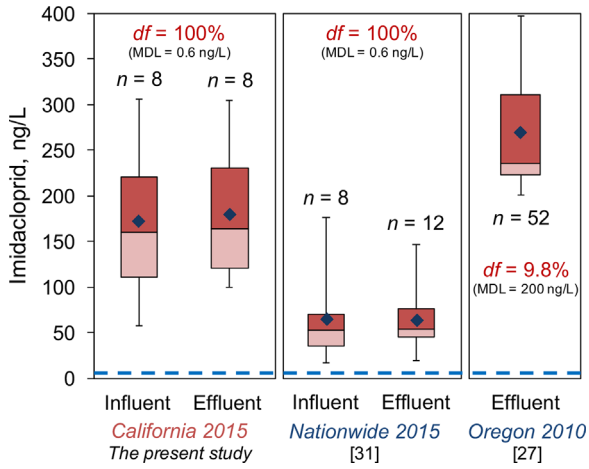

Figure 5. Detected concentrations of imidacloprid (ng/L) in 8 wastewater treatment plants in northern California and summary of data from previous studies [27,31]. Dashed blue horizontal line indicates European Union freshwater predicted no-effect concentration value [17]. df = detection frequency; MDL = method detection limit.

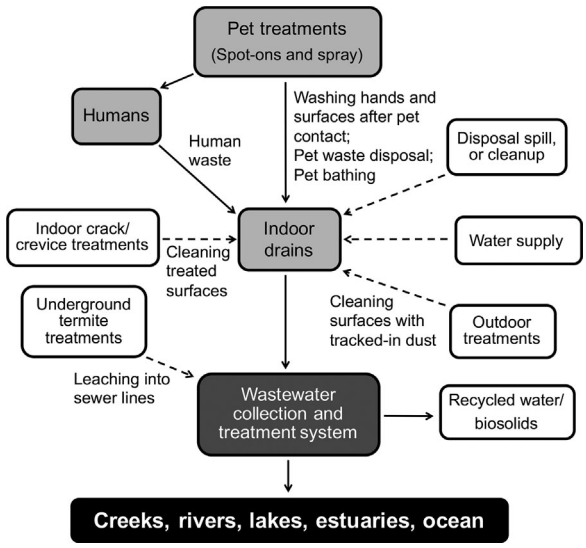

Figure 6. Conceptual model for sources of fipronil and imidacloprid in municipal wastewater. Dashed lines denote pathways believed to be relatively small in the present study. Uses without a clear pathway (e.g., containerized baits) and with unlikely pathways (e.g., air transport and deposition) [50] are excluded from the figure.

effluents with detectable imidacloprid had levels in the range of 202 ng/L to 387 ng/L (Figure 5) [27]. A limit of quantification of 200 ng/L [27], significantly higher than the method detection limit of the present study (0.6 ng/L), may account to some extent for the difference in results observed. Higher overall concentrations and detection frequencies in effluent from northern California may reflect regional, seasonal, and/or climate-related differences from other sampled facilities, such as lower dilution caused by drought-related water use reductions, presence of pests during all seasons because of the mild coastal climate, and pesticide use responding to regional pest pressures (e.g., high flea populations in California coastal areas) [30], suggesting the value of understanding regional and seasonal factors to inform estimates of the potential loading of imidacloprid in wastewater.

Fipronil and imidacloprid sources

Examination of the per capita influent load of wastewater pollutants can be instructive, as it eliminates effects of flow differences among WWTPs and provides a reference discharge quantity for comparison with various potential sources. For the 7 typical municipal WWTPs in the study, the measured per capita influent loads expressed in nanomoles per person per day, for fiproles (54 ± 9 nmol/person/d, mean $\pm$ standard deviation) and imidacloprid (190 ± 80 nmol/person/d) were relatively consistent. The concentration of contaminants in wastewater influent can vary by several orders of magnitude over the course of a single day for a single analyte, so a low variability in daily per capita load suggests a larger number of ubiquitous sources rather than episodic concentrated sources [33–35]. Although episodic discharges from spills, cleanup, or improper disposal of a pesticide are possible, such an event was not likely captured during this sampling event, as evidenced by similar per capita influent loads at all WWTPs.

As regulated pesticides, fipronil and imidacloprid have limited indoor uses in California: pet flea control, crack and crevice treatments intended for out of the way locations, and containerized bait stations [1,9]. All uses are considered unlikely to entail discharges to the sewer system [10,11].

A simple conceptual model (Figure 6) clarifies potential pathways between fipronil and imidacloprid use and the sewer system and facilitates examination of the potential importance of each discharge source. Although no fipronil and imidacloprid products, for either indoor or outdoor use, are designed to be directly discharged to indoor (sewer) drains, actions after use—such as bathing pets treated with flea control products, washing hands and other surfaces that come in contact with treated areas or pets, or wet-mopping treated indoor areas—provide indirect pathways for introduction of both pesticides to the sewer. Outdoor-use pesticides can enter sewer systems through cleaning of surfaces containing pesticides tracked indoors by pets and humans after outdoor applications. Leaching into sewer lines (which are not water tight) during underground building treatments is another possible pathway. However, leaking sewer laterals as a pathway would vary as a function of age of building sewer infrastructure. Drinking water supply may potentially be a source for contaminants. Although imidacloprid and fipronil concentrations have not been reported in any of the diverse water systems serving the 7 WWTPs, there is no or very limited agricultural and urban influence on drinking water sources for all but 2 of the WWTPs (Supplemental Data, Table S8). The low variability of per capita influent loads in the 7 municipal WWTPs, despite differing building sewer infrastructure ages and differing water sources, renders tap water an unlikely or minor source that nevertheless deserves future investigation. A third indirect source—human waste—has been verified for imidacloprid, which is known to be present in human urine [36], but is only suspected for fipronil based on rat oral exposure studies where most fiprole mass was excreted in feces [37]. As noted, episodic discharges from spills, cleanup, and improper disposal are likely small pathways, given the low data variability.

An examination of potential pathways suggests that pet flea treatments may be the primary source of both pesticides in WWTP influent. Pet flea treatments have typical concentrations of 9.8% fipronil and 9.1% imidacloprid; single pet applications involve 0.07 g to 0.4 g fipronil or 0.04 to 0.4 g imidacloprid. In contrast, the only other type of uncontainerized indoor treatments—crack and crevice applications—entails pesticide concentrations of 0.05% or less. Even the highest concentration (0.05%), professional-sized (33-g) fipronil crack and crevice

product on the market contains <0.02 g fipronil; 40 to 1200 of these crack and crevice products would need to be emptied directly into the sewer daily to achieve the influent fipronil load at the 7 typical municipal WWTPs sampled (see the Supplemental Data for calculations).

The transport of pesticides indoors from outdoor applications has been well documented [38], and fipronil is nearly omnipresent in indoor residential dust [39]. Reported concentrations were >20 times higher in households owning a dog treated with fipronil-containing spot-on products than those without treated pets [39], suggesting that residues associated with flea treatments for pets are more significant than residues tracked indoors from outdoor applications.

Dog and cat ownership in the United States is 0.24 and 0.27 per capita, respectively [40,41], and survey data indicate that 75% of dog and cat households use a flea/tick product [42]. The prevalent use of flea and tick treatment is consistent with ubiquitous rather than episodic source. Residues associated with pet products may be transferred to companions or indoor spaces [43] or may be transported directly down the drain through bathing. Washing surfaces and materials that have come in contact with and accumulated pesticides, such as companion hands, pet bedding, and companion clothing, represents indirect pathways of pesticides to wastewater.

A 2012 study [43] that quantified the mass of fipronil transferred to cotton gloves worn while owners petted their dogs for 2 min reported levels of 5600 μg 24 h postapplication, declining to 220 μg at 2 wk, and 76 μg at 4 wk, which coincides with recommended retreatment. To evaluate flea and tick treatments as a potential indirect source to wastewater, the daily influent loads measured at the WWTP are converted to mass per dog per day. Assuming fipronil has a 30% market share, each fipronil-treated dog would provide 300 μg/d, suggesting (by comparison with the hand transfer quantities) that hand washing and other indirect transfer could be a large source (see the Supplemental Data for calculations). Because flea treatments remain on pet fur for weeks after treatment [43], dog washing may result in an even greater proportion of applied pesticide discharging to the sewer system. Although comparable studies are not available for imidacloprid, the similarity of use patterns suggests comparable pathways. Imidacloprid's higher solubility may result in a larger portion washing off during bathing.

The results for the San Francisco airport WWTP, which has no on-site residential or animal populations, were the lowest reported influent concentrations for both analytes, with a midrange effluent concentration for imidacloprid compared with the other WWTPs evaluated. Airport facilities managers report no professional applicator use of imidacloprid, and fipronil is only applied via containerized baits and gels. This suggests that indirect pathways from off-site use are the major source, but does not eliminate the potential for discharges associated with nonprofessional use of retail products. Transport of pesticides through hand washing, introduction of human waste of the airport's transient population, and discharges associated with retail product use could contribute the relatively small influent loads (fiproles, 79 μmol/d; imidacloprid, 400 μmol/d) received at this unique WWTP. Available retail products contain similar mass as the total daily load (fiproles, 38 μmol/container; imidacloprid, 878 μmol/container).

Environmental implications

Several studies have demonstrated that organic micropollutants (such as pharmaceuticals, personal care products, and household pesticides) and their degradates persist through conventional wastewater treatment [32,44–46]. Wastewater effluents flow continuously into diverse freshwater and saltwater aquatic environments, creating continuous ecosystem exposure to entrained pollutants. The potential for pesticides in wastewater effluents to cause adverse effects on aquatic species depends not only on their concentrations, but also on site-specific factors at the discharge point such as dilution (if any), presence of substances that may alter bioavailability or toxicity (e.g., dissolved organic carbon), and presence of other toxicants with cumulative toxic effects. Water available to dilute effluents may already contain both fipronil-related compounds and imidacloprid from upstream sources [20]. Partitioning and fate in the receiving water can have long-term implications not revealed solely by effluent pesticide concentrations, a possibility for fipronil and its degradates, which are likely to partition into sediment based on log K_{OW} values > 4 (Supplemental Data, Table S2).

A direct comparison of fiprole and imidacloprid concentrations in these effluents with established chronic toxicity reference values [15,17] suggests a potential for harm to aquatic species, meriting further investigation. Prior work has shown that for the majority of freshwater macroinvertebrates, fipronil degradates are more toxic than fipronil [15]; these findings were not available when the USEPA established its aquatic life benchmarks in 2007 [16]. A comparison of detected concentrations with 96-h EC50 values for *Chironomus dilutus* is shown in Figure 1. It can be seen that degradate (fipronil sulfone, sulfide, and amide) concentrations in effluent were increased relative to influent as a result of the treatment. Therefore, change in fiprole distribution did not result in a marked decrease in toxicity and potentially may have increased toxicity for 7 of the 8 WWTPs (see Supplemental Data, Table S9, for calculation). A similar conclusion was reached in a prior study on a WWTP discharging into a freshwater environment [25]. However, these toxicity thresholds are derived from data for freshwater organisms in laboratory conditions, and thus may not accurately reflect potential risks in an estuarine environment such as San Francisco Bay. The present study did not include measurement of the toxicity or bioavailability of the effluent-borne insecticides to downstream biota. At present, there is a lack of toxicity data on susceptible receptor organisms in these saltwater settings. As a result, appropriately protective thresholds such as PNECs have not been established for saltwater environments, and thus further investigation is called for.

Other factors specific to San Francisco Bay may inform an evaluation of the potential impacts of effluent discharges containing these pesticides, particularly as findings from the present study suggest that existing treatment technology appears to be unable to significantly remove these pesticides. For example, effluents discharged in the southernmost regions of the Bay experience less dilution and oceanic exchange than effluents discharged in more central locations. Effluents are not the only pathway for these pesticides to enter San Francisco Bay; other studies have detected fipronil and imidacloprid in the region's urban creeks and storm water discharges [6,15,19,47]. As predicted, fipronil and its degradates have partitioned to Bay sediment (data publicly available via cd3.sfei.org), with levels of fipronil sulfone approaching a toxicity threshold for freshwater invertebrates [48]. As a result, the parent compound has been classified as an emerging contaminant of moderate concern for San Francisco Bay [49]. Imidacloprid has not yet been evaluated by local authorities relative to the region's tiered risk and management action framework for emerging

contaminants [49]. Results from the present study may inform ongoing regional monitoring and management efforts as well as broader state and federal actions to limit the potential for environmental contamination with these pesticides and to develop modeling approaches to better predict pesticide wastewater discharge and fate in municipal WWTPs and in receiving waters.

These findings must be considered in light of other important considerations. A one-time sampling event, as conducted in the present study and other similar studies [25,29,31,45], cannot assess the effects of temporal variations in pesticide use and discharge, particularly as it relates to seasonality. Although the San Francisco Bay region is less likely to display large shifts in urban flea control pesticide use, with its mild climate and relatively uniform flea pest pressures [30], seasonality is likely to be a major influence in other urban areas with marked seasonal temperature shifts. Another consideration is the potential for pesticide contamination of the water sources supplying tap water to urban residents. Although most of the source waters for San Francisco Bay urban water supplies related to the present study are essentially free of agricultural, urban, and treated wastewater influences (Supplemental Data, Table S8), the same cannot be said for the water supplies of many other regions. Source or tap water testing for relevant pesticides is likely to be an important element of studies conducted elsewhere. A third consideration concerns the wastewater treatment technology used. Although the treatment trains employed by WWTPs participating in the present study were diverse, they do not cover all available technologies. Alternate technologies, such as reverse osmosis, may have different impacts on pesticide levels, and could be explored in future studies.

CONCLUSIONS

The levels of fiproles and imidacloprid measured in wastewater influent and treated wastewater effluent suggest that conventional treatment has little promise for reducing the release of fiproles or imidacloprid into the environment once discharged to the sewer system. An investigation of potential sources suggests that pet flea and tick products are the primary source of fiprole and imidacloprid to WWTP influent. Additional work is needed to quantify the relative contribution of suggested sources and pathways (e.g., pet products, human waste, underground termite treatments). The findings of the present study, particularly identification of pet products as a likely primary source, can inform upcoming USEPA risk assessments for fipronil and imidacloprid, which for the first time will evaluate the aquatic risks associated with urban use of these pesticides [10,11]. Available toxicity thresholds have been established only for freshwater environments, highlighting the need for saltwater toxicity studies to evaluate the risks of these pesticides to the ecological health of estuarine and ocean environments in addition to freshwater systems.

Supplemental Data—The Supplemental Data are available on the Wiley Online Library at DOI: 10.1002/etc.3673.

Acknowledgment—The present study was funded by the Regional Monitoring Program for Water Quality in San Francisco Bay (Contribution 783) and in part by Award Numbers R01ES015445 and R01ES020889, and their supplements from the National Institute of Environmental Health Sciences (NIEHS). The authors acknowledge participants from the following wastewater treatment plants in our study: Palo Alto Regional Water Quality Control Plant, Fairfield Suisun Sewer District, Central Contra Costa Sanitary District, East Bay Municipal Utility District, East Bay Dischargers Authority, City of San Mateo Wastewater Treatment Plant, San Jose/Santa Clara Regional Wastewater Facility, and San Francisco International Airport Sanitary Waste Treatment Plant. The authors also thank E.F. Willis-Norton for assistance with the earlier 2014 sampling campaign and P.L. Tenbrook for assistance with development of the conceptual model. Reviews by D. Muir, W. Arnold, H. Stapleton, wastewater participants, and anonymous reviewers led to significant improvements.

Disclaimer—The views expressed herein are those of the authors and do not necessarily reflect those of the California Department of Pesticide Regulation, the NIEHS, or the National Institutes of Health.

Data Availability—Most of the data are available in the Supplemental Data. Additional data requests should be directed to the corresponding author (halden@asu.edu).

REFERENCES

1. California Department of Pesticide Regulation. 2016. *California Product/Label Database Queries & Lists*. Sacramento, CA, USA.
2. Simon-Delso N, Amaral-Rogers V, Belzunces LP, Bonmatin JM, Chagnon M, Downs C, Furlan L, Gibbons DW, Giorio C, Girolami V, Goulson D, Kreutzweiser DP, Krupke CH, Liess M, Long E, McField M, Mineau P, Mitchell EAD, Morrissey CA, Noome DA, Pisa L, Settele J, Stark JD, Tapparo A, Van Dyck H, Van Praagh J, Van der Sluijs JP, Whitehorn PR, Wiemers M. 2015. Systemic insecticides (neonicotinoids and fipronil): Trends, uses, mode of action and metabolites. *Environ Sci Pollut Res* 22:5–34.
3. Weston DP, Holmes RW, You J, Lydy MJ. 2005. Aquatic toxicity due to residential use of pyrethroid insecticides. *Environ Sci Technol* 39:9778–9784.
4. Holmes RW, Anderson BS, Phillips BM, Hunt JW, Crane DB, Mekebri A, Connor V. 2008. Statewide investigation of the role of pyrethroid pesticides in sediment toxicity in California's urban waterways. *Environ Sci Technol* 42:7003–7009.
5. Kuivila KM, Hladik ML, Ingersoll CG, Kemble NE, Moran PW, Calhoun DL, Nowell LH, Gilliom RJ. 2012. Occurrence and potential sources of pyrethroid insecticides in stream sediments from seven U.S. metropolitan areas. *Environ Sci Technol* 46:4297–4303.
6. Ensminger MP, Budd R, Kelley KC, Goh KS. 2013. Pesticide occurrence and aquatic benchmark exceedances in urban surface waters and sediments in three urban areas of California, USA, 2008–2011. *Environ Monit Assess* 185:3697–3710.
7. California Code of Regulations. 2012. *Pesticides and Pest Control Operations; 6000, 6970, 6972*. Title 3. Sacramento, CA, USA.
8. US Environmental Protection Agency. 2009. Environmental hazard and general labeling for pyrethroid non-agricultural outdoor products notification. Office of Pesticide Programs,. Washington, DC.
9. Ensminger M. 2014. Review of representative currently registered fipronil product labels in California. Department of Pesticide Regulation, Sacramento, CA.
10. US Environmental Protection Agency. 2011. Problem formulation for the environmental fate and ecological risk, endangered species, and drinking water assessments in support of the registration review of fipronil. Office of Pesticide Programs, Washington, DC.
11. US Environmental Protection Agency. 2008. EFED Problem formulation for the registration review of imidacloprid. Office of Pesticide Programs, Washington, DC.
12. US Environmental Protection Agency. 2001. Notice of pesticide registration: Preventol TM insecticide. Office of Pesticide Programs, Washington, DC.
13. US Environmental Protection Agency. 2014. Label amendment—Addition of use in adhesives and caulking; product name: Preventol TM preservative insecticide. Office of Pesticide Programs, Washington, DC.
14. Morrissey CA, Mineau P, Devries JH, Sanchez-Bayo F, Liess M, Cavallaro MC, Liber K. 2015. Neonicotinoid contamination of global surface waters and associated risk to aquatic invertebrates: A review. *Environ Int* 74:291–303.
15. Weston DP, Lydy MJ. 2014. Toxicity of the insecticide fipronil and its degradates to benthic macroinvertebrates of urban streams. *Environ Sci Technol* 48:1290–1297.
16. US Environmental Protection Agency. 2007. Ecological risk assessment for fipronil uses. Office of Pesticide Programs, Washington, DC.
17. European Commission. 2015. (Revised) Directive 98/8/EC concerning the placing of biocidal products on the market; imidacloprid; product-type 18 (insecticides, acaricides and products to control other arthropods). Brussels, Belgium.

18. Roessink I, Merga LB, Zweers HJ, Van den Brink PJ. 2013. The neonicotinoid imidacloprid shows high chronic toxicity to mayfly nymphs. *Environ Toxicol Chem* 32:1096–1100.
19. Budd R, Ensminger M, Wang D, Goh KS. 2015. Monitoring fipronil and degradates in California surface waters, 2008–2013. *J Environ Qual* 44:1233–1240.
20. Hladik ML, Kolpin DW. 2016. First national-scale reconnaissance of neonicotinoid insecticides in streams across the USA. *Environ Chem* 13:12–20.
21. Markle JC, van Buuren BH, Moran K, Barefoot AC. 2014. Pyrethroid pesticides in municipal wastewater: A baseline survey of publicly owned treatment works facilities. In *Describing the Behavior and Effects of Pesticides in Urban and Agricultural Settings*, Vol 1168. ACS Symposium Series. American Chemical Society, Washington, DC, pp 177–194.
22. Heidler J, Halden RU. 2009. Fate of organohalogens in US wastewater treatment plants and estimated chemical releases to soils nationwide from biosolids recycling. *J Environ Monit* 11:2207–2215.
23. Foster AL, Katz BG, Meyer MT. 2012. Occurrence and potential transport of selected pharmaceuticals and other organic wastewater compounds from wastewater-treatment plant influent and effluent to groundwater and canal systems in Miami-Dade County, Florida. US Geological Survey, Reston, VA, USA.
24. Morace JL. 2012. Reconnaissance of contaminants in selected wastewater-treatment-plant effluent and stormwater runoff entering the Columbia River, Columbia River Basin, Washington and Oregon, 2008–10. US Geological Survey, Reston, VA, USA.
25. Supowit SD, Sadaria AM, Reyes EJ, Halden RU. 2016. Mass balance of fipronil and total toxicity of fipronil-related compounds in process streams during conventional wastewater and wetland treatment. *Environ Sci Technol* 50:1519–1526.
26. Sengupta A, Lyons JM, Smith DJ, Drewes JE, Snyder SA, Heil A, Maruya KA. 2014. The occurrence and fate of chemicals of emerging concern in coastal urban rivers receiving discharge of treated municipal wastewater effluent. *Environ Toxicol Chem* 33:350–358.
27. Hope BK, Pillsbury L, Boling B. 2012. A state-wide survey in Oregon (USA) of trace metals and organic chemicals in municipal effluent. *Sci Total Environ* 417–418:263–272.
28. Campo J, Masia A, Blasco C, Pico Y. 2013. Occurrence and removal efficiency of pesticides in sewage treatment plants of four Mediterranean River Basins. *J Hazard Mater* 263:146–157.
29. Qi W, Singer H, Berg M, Muller B, Pernet-Coudrier B, Liu H, Qu J. 2015. Elimination of polar micropollutants and anthropogenic markers by wastewater treatment in Beijing, China. *Chemosphere* 119:1054–1061.
30. Rust M. 2010. Fleas—Integrated pest management in and around the home. Pest notes publication 7419. University of California Statewide Integrated Pest Management Program, Sacramento, CA, USA.
31. Sadaria AM, Supowit SD, Halden RU. 2016. Mass balance assessment for six neonicotinoid insecticides during conventional wastewater and wetland treatment: Nationwide reconnaissance in United States wastewater. *Environ Sci Technol* 50:6199–6206.
32. Köck-Schulmeyer M, Villagrasa M, López de Alda M, Céspedes-Sánchez R, Ventura F, Barceló D. 2013. Occurrence and behavior of pesticides in wastewater treatment plants and their environmental impact, *Sci Total Environ* 458–460:466–476.
33. Teerlink J, Hering AS, Higgins CP, Drewes JE. 2012. Variability of trace organic chemical concentrations in raw wastewater at three distinct sewershed scales. *Water Res* 46:3261–3271.
34. Ort C, Lawrence MG, Rieckermann J, Joss A. 2010b. Sampling for pharmaceuticals and personal care products (PPCPs) and illicit drugs in wastewater systems: Are your conclusions valid? A critical review. *Environ Sci Technol* 44:6024–6035.
35. Ort C, Schaffner C, Giger W, Gujer W. 2005. Modeling stochastic load variations in sewer systems. *Water Sci Technol* 52:113–122.
36. Ueyama J, Harada KH, Koizumi A, Sugiura Y, Kondo T, Saito I, Kamijima M. 2015. Temporal levels of urinary neonicotinoid and dialkylphosphate concentrations in Japanese women between 1994 and 2011. *Environ Sci Technol* 49:14522–14528.
37. Tingle CCD, Rother JA, Dewhurst CF, Lauer S, King WJ. 2003. Fipronil: Environmental fate, ecotoxicology, and human health concerns. *Rev Environ Contam Toxicol* 176:1–66.
38. Simcox NJ, Fenske RA, Wolz SA, Lee IC, Kalman DA. 1995. Pesticides in household dust and soil: Exposure pathways for children of agricultural families. *Environ Health Perspect* 103:1126–1134.
39. Mahler BJ, Van Metre PC, Wilson JT, Musgrove M, Zaugg SD, Burkhardt MR. 2009. Fipronil and its degradates in indoor and outdoor dust. *Environ Sci Technol* 43:5665–5670.
40. American Pet Products Association. 2015. 2015-2016 APPA national pet owners survey. Greenwich, CT, USA.
41. US Census Bureau. 2016. American Fact Finder—Monthly population estimates for the United States: April 1, 2010 to December 1, 2016. July 1 2015 population estimate, US resident population. Washington, DC.
42. Puro G. 2015. *Pet Medications in the US*, 4th ed. Packaged Facts, Rockville, MD, USA.
43. Bigelow Dyk M, Liu Y, Chen Z, Vega H, Krieger RI. 2012. Fate and distribution of fipronil on companion animals and in their indoor residences following spot-on flea treatments. *J Environ Sci Health B* 47:913–924.
44. Gerecke AC, Schärer M, Singer HP, Müller SR, Schwarzenbach RP, Sägesser M, Ochsenbein U, Popow G. 2002. Sources of pesticides in surface waters in Switzerland: Pesticide load through waste water treatment plants—Current situation and reduction potential, *Chemosphere* 48:307–315.
45. Heidler J, Sapkota A, Halden RU. 2006. Partitioning, persistence, and accumulation in digested sludge of the topical antiseptic triclocarban during wastewater treatment. *Environ Sci Technol* 40:3634–3639.
46. Heidler J, Halden RU. 2007. Mass balance assessment of triclosan removal during conventional sewage treatment. *Chemosphere* 66: 362–369.
47. Weston DP, Chen D, Lydy MJ. 2015. Stormwater-related transport of the insecticides bifenthrin, fipronil, imidacloprid, and chlorpyrifos into a tidal wetland, San Francisco Bay, California. *Sci Total Environ* 527–528:18–25.
48. Maul JD, Brennan AA, Harwood AD, Lydy MJ. 2008. Effect of sediment-associated pyrethroids, fipronil, and metabolites on *Chironomus tentans* growth rate, body mass, condition index, immobilization, and survival. *Environ Toxicol Chem* 27:2582–2590.
49. Sutton R, Sedlak M. 2015. Contaminants of emerging concern in San Francisco Bay: A strategy for future investigations. 2015 Update. SFEI Contribution 761. Regional Monitoring Program for Water Quality in San Francisco Bay, San Francisco Estuary Institute, Richmond, CA.
50. Starr JM, Gemma AA, Graham SE, Stout DM 2nd. 2014. A test house study of pesticides and pesticide degradation products following an indoor application. *Indoor Air* 24:390–402.

Science of the Total Environment 599–600 (2017) 960–966

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Fipronil washoff to municipal wastewater from dogs treated with spot-on products

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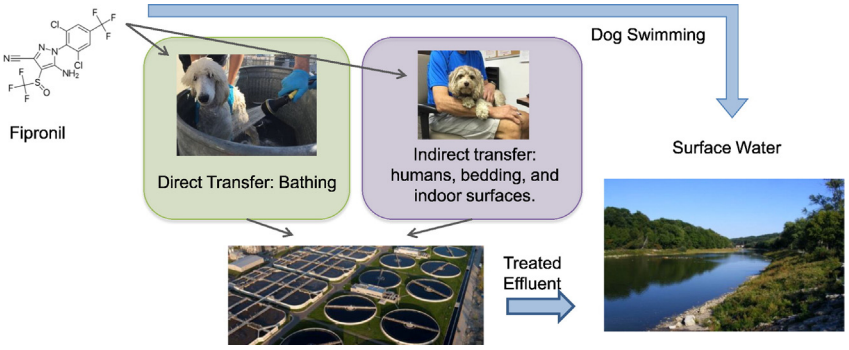
HIGHLIGHTS

- Pathway for pesticide spot-on products to wastewater catchment confirmed.
- Total mass of fiproles measured in rinsate ranged from 3.6–230.6 mg per dog.
- Fipronil spot-on products a source to wastewater influent.
- Fipronil measurable to at least 28 days post application.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 1 April 2017
Received in revised form 28 April 2017
Accepted 28 April 2017
Available online xxxx

Editor: Jay Gan

Keywords:
Fipronil
Wastewater
Pesticides
Pet flea and tick products

ABSTRACT

Fipronil and fipronil degradates have been reported in treated wastewater effluent at concentrations that exceed USEPA Aquatic Life Benchmarks, posing a potential risk to the surface waters to which they discharge. Fipronil is a common insecticide found in spot-on flea and tick treatment products that have the potential for down-the-drain transport and direct washoff into surface water. Volunteers currently treating their dogs with a fipronil-containing spot-on product were recruited. Dogs were washed either 2, 7, or 28 days after product application, and rinsate from 34 discrete bathing events were analyzed by LC-MS/MS for fipronil and fipronil degradates (collectively known as fiproles). Total fipronil application dosage ranged from 67.1–410.0 mg per dog following manufacturers' recommendation based on dog body weight. Total mass of fiproles measured in rinsate ranged from 3.6–230.6 mg per dog (0.2– 86.0% of mass applied). Average percentage of fiproles detected in rinsate generally decreased with increasing time from initial application: 21 ± 22, 16 ± 13, and 4 ± 5% respectively for 2, 7, and 28 days post application. Fipronil was the dominant fiprole, >63% of total fiproles for all samples and >92% of total fiproles in 2 and 7 day samples. Results confirm a direct pathway of pesticides to municipal wastewater through the use of spot-on products on dogs and subsequent bathing by either professional groomers or by pet owners in the home. Comparisons of mass loading calculated using California sales data and recent wastewater monitoring results suggest fipronil-containing spot-on products are a potentially important source of fipronil to wastewater treatment systems in California. This study highlights the potential for other active ingredients (i.e., bifenthrin, permethrin, etofenprox, imidacloprid) contained in spot-on and other pet products (i.e., shampoos, sprays) to enter wastewater catchments through bathing activities, posing a potential risk to the aquatic organisms downstream of wastewater discharge.

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http://dx.doi.org/10.1016/j.scitotenv.2017.04.219
0048-9697/

1. Introduction

Wastewater treatment plants continuously discharge to rivers, streams, estuaries, and the ocean, carrying contaminants that are not removed during treatment. Arid and semi-arid municipalities struggle to meet demands of urban water use resulting from climate change, population growth and development, leading to increased reliance on wastewater effluent to maintain base flow in urban streams (Luthy et al., 2015). The discharge of treated wastewater effluent to surface water is a major pathway for the introduction of contaminants, including pesticides, to the environment (Luo et al., 2014). Contaminants not removed during treatment, pose a potential risk to aquatic organisms living near or downstream of wastewater outfalls, particularly in water bodies dominated by wastewater effluent. Studies reporting pesticide occurrence in wastewater treatment systems are largely limited to influent and effluent data without information on relative source contribution within a sewershed (Markle et al., 2014; Parry et al., 2015; Sadaria et al., 2016a; 2016b; Supowit et al., 2016; Weston and Lydy, 2010; Weston et al., 2013).

The use of pesticides in outdoor urban areas and subsequent off-site transport to surface water has been documented during storm events (Budd et al., 2015; Ensminger et al., 2013; Thuyet et al., 2012; Weston et al., 2015) and during dry weather conditions as a result of urban irrigation of lawns (Budd et al., 2015; Ensminger et al., 2013; Luo et al., 2013). Resultant surface water pesticide concentrations have frequently exceeded toxicity thresholds resulting in regulatory action by the state of California by both pesticide and water agencies (CDPR, 2012; CVRWQCB, 2017). The majority of U.S. cities rely on separate collection and treatment of stormwater and sanitary discharges; however, some older systems rely on a combined collection system. A 2013 study in Sacramento sampled sub-catchments in the same larger sewershed representing both sole sanitary discharge and combined collection system. Pyrethroid concentrations were comparable in both sub-catchments (Weston et al., 2013), indicating down-the-drain transport of pesticides to sanitary discharge is an important component of total urban mass flux to surface water. Insecticide concentrations (i.e., bifenthrin, permethrin, fipronil, and fipronil sulfone) have been reported at concentrations that exceed USEPA Aquatic Life Benchmarks in treated wastewater effluent (Markle et al., 2014; Sadaria et al., 2016b; USEPA, 2014b). Although the current USEPA Aquatic Life Benchmark for imidacloprid of 1050 ng/L is higher than reported wastewater effluent concentrations (58–306 ng/L) (Sadaria et al., 2016b; USEPA, 2014b), chronic toxicity testing has shown mayfly species are more sensitive to imidacloprid exposures with a reported 28-d EC10 value of approximately 30 ng/L(Roessink et al., 2013; Sadaria et al., 2016b; USEPA, 2014b).

Pesticides used in flea and tick treatments from pet products enter wastewater treatment systems during routine bathing of dogs. Sadaria et al. (2016b) proposed a conceptual model that indicates flea and tick spot-on pet products are the primary source of fipronil and imidacloprid to a wastewater catchment. However, direct measurements of washoff or relative mass flux contribution from sources within a sewershed have not yet been reported. The USEPA is in the process of publishing draft environmental risk assessments for pyrethroids, imidacloprid, and fipronil (December 2016, January 2017, and anticipated summer of 2017 respectively), including the relative contribution from wastewater systems (USEPA, 2017). E-FAST (Exposure and Fate Assessment Screening Tool) is used to predict wastewater effluent concentrations; however, pet spot-on products are not currently included as a source (USEPA, 2014a). At the state level, acting in accordance with the federal Clean Water Act, the Central Valley Regional Water Quality Control Board is in the process of adopting numeric limits for pyrethroids in treated wastewater effluent in response to pyrethroid 303d (impaired water bodies) listings (CVRWQCB, 2017). Developing an understanding of pesticide sources and transport pathways to wastewater treatment catchments is a crucial first step to inform mitigation scenarios and regulatory solutions.

Flea and tick treatments are available with a wide range of pesticide active ingredients (a.i.'s) through several application methods (i.e., spot-on, shampoo, collars, ingestible) for domestic dogs and cats. Dogs are frequently bathed in residential bathtubs, self-serve grooming facilities, or through professional grooming services, where rinsate and dislodged pesticides directly enter a sewer system. Cats are not typically bathed in the same fashion, and thus indirect transfer is a more likely pathway for pesticide residues associated with cat flea and tick treatments to enter the sewershed. The aim of this study is to measure the fraction of fipronil and fipronil degradates, collectively known as fiproles, washed off during routine bathing. However, residues will also be introduced into wastewater treatment catchment through cleaning of indoor surfaces, human showering and washing hands, laundering of materials that have come in contact with pet (i.e., pet bedding, human companion clothes). Studies designed to measure direct human exposure resulting from fipronil spot-on treatments report dislodgeable fiprole residues from a single encounter with a treated pet in the microgram range up to four weeks post application (Cochran et al., 2015; Dyk et al., 2012). Dyk et al. (2012)also quantified pesticide residues on interior surfaces and animal bedding. For the purpose of this study, it was necessary to select a single a.i. and application method to provide a meaningful set of results. Fipronil spot-on products were selected based on parts-per-trillion toxicity of both the parent and degradates and the availability of fipronil containing products (average 8391 kg of dog products per year sold from 2011 to 2015 in California) (CDPR, 2016b).

Fipronil is a phenylpyrazole insecticide registered for uses including structural pest control, bait and gel products, agriculture, and topical flea and tick treatment for pets. In California, fipronil is not registered for agricultural uses. Fiproles are toxic to aquatic invertebrates in the low parts-per-trillion concentration range (Table 1). Fiproles are ubiquitous in San Francisco Bay Area treated wastewater effluent at concentrations that exceed toxicity thresholds posing a risk to aquatic organisms in surface waters receiving discharge (Sadaria et al., 2016b). Detailed studies addressing the removal efficiency of fiproles as a function of specific treatment technology are not available; however, the plants in the above study are all tertiary treatment plants indicating source control, not engineered treatment solutions, may be necessary to reduce effluent concentrations.

The goal of this study is to directly quantify the mass of fiproles washed off volunteer dogs during routine bathing. We compare the measured values to reported wastewater influent monitoring results to investigate the relative contributions from spot-on products to overall sewershed loading. Using available California sales data and commercial shelf survey, we investigate the potential mass transfer of fipronil compared to other a.i,'s. Results will direct future California Department of Pesticide Regulation (CDPR) monitoring efforts.

2. Materials and methods

We solicited volunteer pet owners that were currently using a fipronil containing spot-on product on their dog. Volunteers washed their pet 1–7 days prior to pesticide application, and then applied the product of choice according to the manufacturers' label directions. Pet owners applied the pesticide by squeezing the product from a small applicator onto their pet's neck according to label instructions. Some fraction of the product dose is likely left inside the applicator introducing variability to the total mass applied. Label instructions for the four product brands used by volunteers varied only slightly. All product labels recommend reapplication after 30 days, and indicate products are effective for three months. Frontline Plus™, Petlock Plus™, and Sentry Fiproguard™ labels state the product is waterproof after it has dried and pets can swim and bathe post application. The Pet Armor Plus™ label does not claim to be waterproof. Volunteers reported using one of four fipronil-containing spot-on products. Each manufacturer offers a dose appropriate for pet size (according to body mass), all containing

Table 1
Summary of toxicity and wastewater effluent concentrations reported for pesticides commonly found in pet products.

Compound	Aquatic invertebrates[a]		Wastewater effluent (ng/L)
	Acute (ng/L)	Chronic (ng/L)	
Fipronil	110	11	14–49[b]
Fipronil sulfide	1065	110	1.3–2[b]
Fipronil desulfinyl	100,000	10,300	<0.39–1.2[b]
Fipronil sulfone	360	37	1.1–16.3[b]
Fipronil amide	—	—	<0.2–4.1[b]
Permethrin	10.6	1.4	ND–170[c]
Etofenprox	400	170	NA
S-methoprene	16,500	51,000	NA
Phenothrin	2200	470	NA
Imidacloprid	34,500	1050	83–305[b]

[a] USEPA Aquatic Life Benchmarks (USEPA, 2014b).
[b] (Sadaria et al., 2016b).
[c] (Markle et al., 2014).

8.8–9.1% fipronil. Products come in individually-sized doses with between 67 and 405 mg fipronil per application. Thirty-four dogs were washed in total, with 11, 13, and 10 at 2, 7, and 28 days respectively post application. A complete summary of product types and sizes used on volunteer dogs is found in the supporting information (SI), Table A.1. Several dogs were volunteered for multiple discrete washoff events.

All dogs were weighed (Cardinal Detecto digital scale) and the breed and fur coarseness recorded. Small dogs, roughly <10 kg, were washed in a plastic tub. All larger dogs were washed in a galvanized-metal tub retrofitted with a PVC spout to drain wash-water. Photos are included in SI Figs. A.1–A.3. Between discrete bathing events, the equipment was rinsed with tap water, rinsed with methanol, and finally rinsed with deionized water. Five equipment blanks were collected from the sampling equipment throughout the study.

On the designated day post application, each dog was thoroughly wetted with tap water. Shampoo (WAHL Home Products™ Oatmeal Formula product used throughout study) was then applied to provide lather over the entire animal (volume of shampoo recorded). Following lather, each animal was thoroughly rinsed with tap water. The entire rinsate, including the water added to initially wet the animal, was considered a single sample. The volume of rinsate for small dogs was determined using the mass of the plastic container before and after water collection. After washing large dogs, the rinsate volume was discharged to a plastic basin using a 1-L volumetric beaker to record the volume. The sample volume, soap volume, and dog mass are reported in the SI. First, a 500 mL sub-sample was collected from the entire composite washoff for analysis of fiproles in a glass amber bottle. A 1-L sample was also collected for analysis of total suspended solids (TSS) (Ensminger, 2016). Water quality parameters of rinsate were measured using a YSI Sonde (YSI EXO1).

Chemical analysis of fipronil and degradates was conducted at the California Department of Food and Agriculture's Environmental Safety Lab. A 10-mL aqueous sample is diluted with deionized water to volume of 100 mL before liquid-liquid extraction. Each sample was placed into a 250-mL separatory funnel with 50 mL of methylene chloride and shaken for two minutes. The methylene chloride phase was poured over 70 g of anhydrous sodium sulfate to remove residual water. Extraction steps were repeated two subsequent rounds. The anhydrous sodium sulfate was rinsed with an additional 40 mL of methylene chloride. The resultant extract was evaporated to dryness on a rotary evaporator with a water bath at 30 ± 1 °C and a vacuum maintained at 0.44 bars of mercury. Samples were reconstituted with acetone to a final volume of 1.0 mL. A 5-μL aliquot of extracts was analyzed by liquid chromatography with tandem mass spectrometry (LC-MS/MS) (on an ABSciex QTRAP 5500 Negative Electrospray Ionization (ESI-)).

An untreated dog was washed according to stated protocol to provide a representative shampoo containing matrix for method development and matrix spikes. Triplicate analysis of shampoo containing matrix water spiked at 2, 3, and 5 μg/L with recoveries between 81 and 121%. Method detection limit was developed by analyzing seven matrix spike replicates at 0.5 μg/L. Adopted reporting limits of 1.0 μg/L for fipronil, fipronil sulfide, fipronil sulfone, and fipronil desulfinyl and 1.5 μg/L for fipronil amide and fipronil desulfinyl amide were >10 times the respective method detection limit. Study samples were extracted within three days of sample collection based on acceptable matrix recoveries (80–120%) in spiked samples refrigerated up to three days. Dilutions were made as needed to fit within the calibration range (5–500 μg/L). Further details on instrument and quantification parameters are found in the SI, Tables A.2 and A.3.

3. Calculations

Total mass of fipronil and degradates measured in this study are reported as mass washoff per dog and % washoff per dog (Eqs (1) and (2)). We assume the 500-mL sample is a representative concentration of total rinsate volume. We also assume pet owners applied the entire pesticide dose with negligible residue remaining in the product applicator.

$$mass\ washoff\ per\ dog\ (\mu g) = fiprole\ concentration\left[\frac{\mu g}{L}\right] \times rinsate[L] \quad (1)$$

$$\%washoff = \frac{mass\ washoff\ per\ dog\ (\mu g)}{mass\ applied\ per\ dog\ (\mu g)} * 100 \quad (2)$$

One objective of the study is to understand the relative contribution of fiproles from pet spot-on treatments to total wastewater fiprole loading to wastewater treatment plants. To compare sources, wastewater monitoring data and spot-on sales data are converted to monthly per capita fiprole loading.

Sadaria et al. (2016b) report service area population and influent fiprole concentrations for seven bay area wastewater treatment plants using 24-h composite samples. Using Eq. (3), a total monthly per capita fiprole load is calculated. We assume fiprole concentrations are representative of a month (30 days). The results are not normalized for pet ownership, but instead we assume an even per capita distribution.

$$total\ monthly, per\ capita\ fiprole\ load = \left(\frac{influent\ \left[\frac{\mu g}{L}\right] * monthly\ flow[L]}{service\ area\ population}\right) \quad (3)$$

An estimate of total monthly spot-on monthly per capita fiprole load is calculated using California statewide sales data from 2011 to 2015 and California population information (Bureau USC, 2016; CDPR, 2016c). The fraction of total fiprole dislodged during bathing is estimated using analytical results from this study and represented by $f_{dislodged}$. Eq. (4) also assumes some fraction (f_{washed}) of treated animals is washed within 28 days of treatment in a location directly plumbed to the sewer.

$$monthly\ per\ capita\ fiproles\ load\ from\ spot-on\ products = \frac{sales\ of\ spot-on\ \left[\frac{\mu g}{month}\right]}{population} * f_{dislodged} * f_{washed} \quad (4)$$

A ratio of Eqs (4) and (3) represents the relative contribution of spot-on fiproles to total wastewater loading.

4. Results and discussion

Fiproles were detected in 100% of the samples. Results from 34 discrete bathing events are reported as total mass of fiproles (Eq. (1)). Generally, there was a decrease in washable fiprole fraction and a decrease in variability with increasing time post application (Fig. 1). A paired *t*-test revealed no significant difference between percent washoff of 2 and 7 day samples ($p = 0.246$), but there was a significant difference

between both 2 and 28 day samples and 7 and 28 day samples ($p = 0.003$ and 0.0009, respectively). Total fiprole mass recovered ranged from 0.2% to 86% of total mass available (Eqs (1) and (2)). The mass dosage of fipronil in each package ranged from 67 to 405 mg based on the mass of the dog. Total recovered mass of fiproles was between 3.6 and 230.6 mg per dog (using Eq. (1)).

Fipronil and fipronil sulfone were detected in 100% of the samples. Fipronil desulfinyl, fipronil sulfide, and fipronil amide had detection frequencies of 88%, 76%, and 52%, respectively. Desulfinyl fipronil amide was not detected in any of the samples. Fipronil was the dominant form of fiprole and accounted for >63% of total fiproles in all samples and >92% of total fiproles when considering only 2 and 7 days post-application sampling events (Fig. 2). The highest percentage of degradates were found in two discrete 28-day samples collected from the same dog that was reported as having spent all time outdoors. Measured degradates were fipronil sulfone and fipronil desulfinyl, both of which are reported photolysis products (Simon-Delso et al., 2015).There were no trends or relationships observed as a function of dog size. Finally, the measured TSS did not correlate with percent washoff ($r^2 = 0.0131$).

Equipment blank samples contained measurable fipronil in all but one of the samples; however, with mass recovered ranging from 13 to 56 μg fipronil compared to sample recoveries from 113 to 224,900 μg, the potential for carry over is considered insignificant and blank correction calculations were not made. Fipronil amide, fipronil sulfone, and fipronil desulfinyl were measured in some equipment blanks near detection limits. Some fipronil carry-over between samples likely occurred and would be most important for the 28-day samples, which exhibited relatively low overall recoveries.

Fiproles dislodged during routine bathing can enter a wastewater catchment through residential bathtubs, self-serve grooming facilities, and professional grooming facilities. In order to provide some perspective on reported washoff percentage, a comparison between per capita fiprole concentrations based on (1) wastewater monitoring concentrations and an (2) product sales data are provided using Eqs (3) and (4). A recent study by Sadaria et al., (2016b) and others measured fipronil and fipronil degradates entering seven wastewater treatment plants, six serving residential municipalities in the San Francisco Bay Area. Using Eq. (3), the reported total influent fiprole concentrations for six plants are transformed to mass contributed per month per person (with an average of 0.71 ± 0.11 mg fiproles/person/month).

Rather than calculate a single per capita contribution from sales data we present a range of values to characterize the range of possibilities using Eq. (4). California sales data report an average of 8390 kg per year of fipronil sold in the form of spot-on dog treatment from 2011 to 2015 (CDPR, 2016c). The California 2015 State Census reported a population of 39,144,818 (Bureau USC, 2016). For $f_{dislodged}$ we use 0.21, 0.16, and 0.04 to represent average observed wash-off during 2-day, 7-day, and 28-day time points respectively measured during this study. There is no reliable data to inform f_{washed}, or the estimate of for the fraction of fipronil treated dogs washed within 28 days of treatment in locations (i.e., residential bathtubs, self-serve grooming facilities, and professional grooming facilities) that discharge to wastewater catchments (Fig. 3). The authors present this range of values to demonstrate the importance of spot-on pesticide products to overall sewershed loading.

Using this approach, we can see that washing 25% of treated dogs within 7 days of treatment would account for the entire fiprole load in the sewershed. Results suggest spot-on products are an important source of fiproles to wastewater treatment plants. Treated wastewater effluent in the same Northern California study reported fipronil concentrations between 14 and 45 ng/L, which are above the USEPA chronic aquatic benchmark for fipronil (11 ng/L) (Table 1).

Additional mass from both cats and dogs treated with flea and tick treatments can enter wastewater treatment plants from cleaning activities. Fipronil concentrations have been reported on indoor residential dust, and homes with a dog treated with a fipronil-containing spot-on products resulted in 2 to 3 orders of magnitude higher concentration in dust than comparable households that did not have treated pets (Mahler et al., 2009). The transport pathway of organic chemicals bound to household dust to wastewater treatment plants has been confirmed using flame retardant concentrations in household dust and laundry rinsate (Schreder and La Guardia, 2014). Further, human contact with treated pets can lead to down-the-drain transport of fiproles through showering, washing hands, and human excrement.

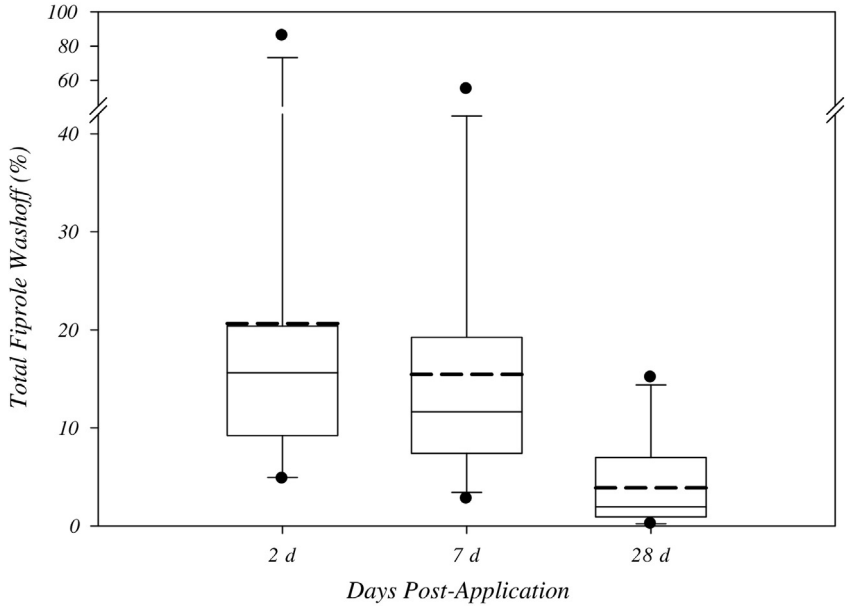

Fig. 1. Percent wash-off of total fiproles as a function of time. Number of discrete samples is 11, 13 and 10. The box encloses the 25th to 75th percentile, whiskers note 5th and 95th percentile, median black solid line dissecting box, blue dashed line the mean, and black circle minimum and maximum.

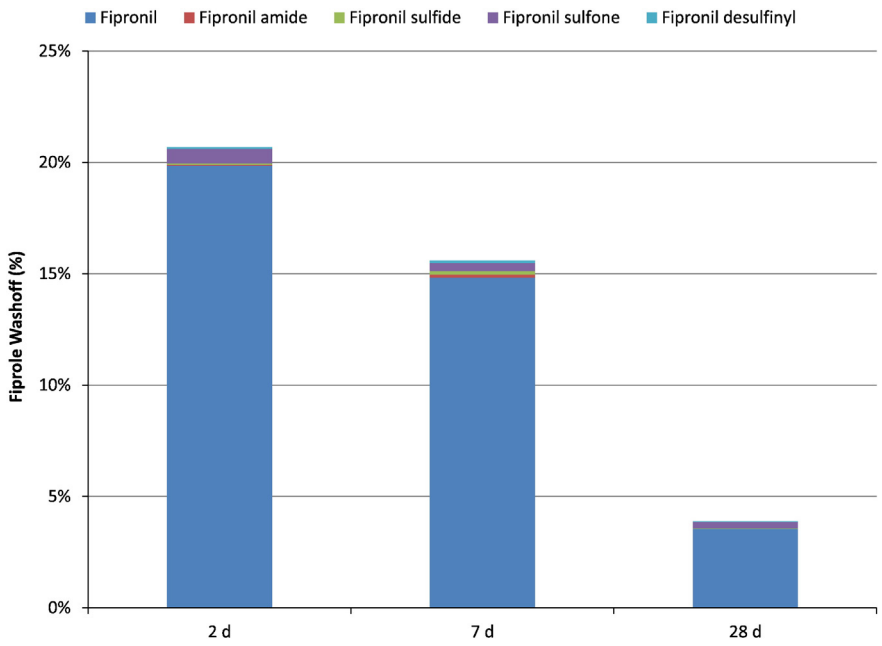

Fig. 2. Average percent fipronil and degradate washoff at two, seven, and twenty-eight days post-application. Values expressed as percent total mass applied.

4.1. Other active ingredients

Direct quantification of washoff potentials for the many spot-on products containing other a.i.'s is beyond the scope of this study. However, California pesticide sales data for 2011–2015 identify fipronil, permethrin, imidacloprid, etofenprox, phenothrin, and s-methoprene as the most common a.i.'s used in spot-on products by mass (Fig. 4) (CDPR, 2016b). A 2014 shelf-survey conducted in the Sacramento region identified 99 pesticide products for pets available to the consumer (34 spot-on products, 14 collars, 28 grooming products, and 23 sprays) (Vander Werf et al., 2015). In addition to the a.i.'s listed above, pet products contain piperonyl butoxide, propoxur, cyphenothrin, esfenvalerate, tetramethrin, novaluron, prallethrin, tetrachlorvinphos, cyhalothrin, and cypermethrin, many of which have not been measured in municipal wastewater. Monitoring data available for fipronil and permethrin in wastewater effluent suggest treatment processes in place do not reduce pesticide concentrations below toxicity thresholds; therefore, these pesticides pose a potential risk to the surface waters to which they discharge (Table 1), particularly in effluent dominated streams in arid regions and estuaries with limited mixing. As noted in the introduction, the current USEPA Aquatic Life Benchmark for imidacloprid does not consider more recent chronic toxicity testing for

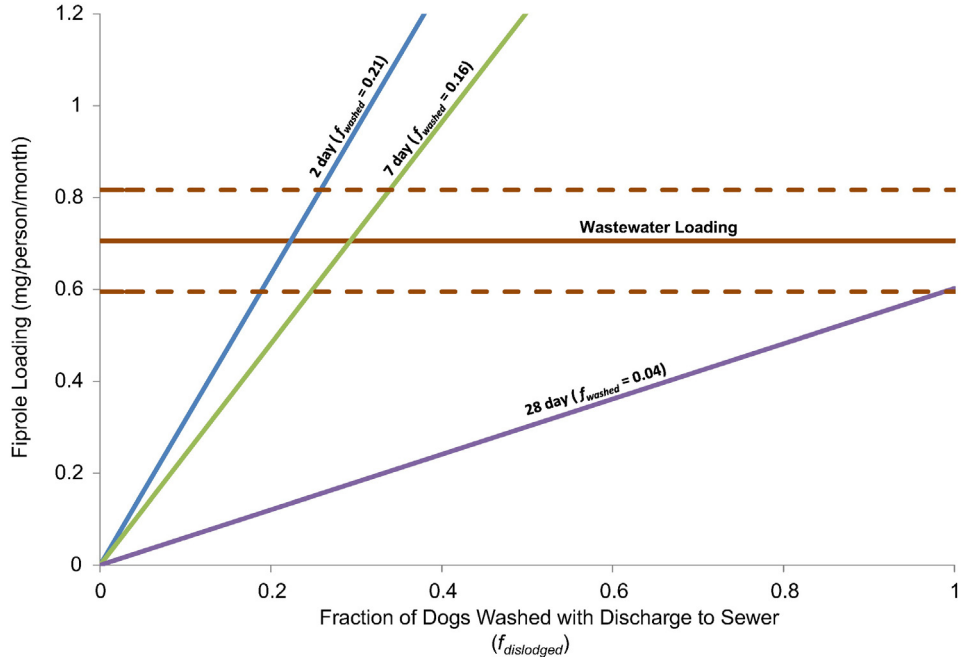

Fig. 3. Comparison between per capita loading using wastewater monitoring data in solid brown (Eq. (3)) and sales data as a function of $f_{dislodged}$ and f_{washed} (Eq. (4)). Dotted wastewater lines represent one standard deviation of Sadaria et al., 2016b dataset (n = 6). The value of $f_{dislodged}$ represents average washoff values measured for 2, 7, and 28 days of 0.21, 0.16, and 0.04, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

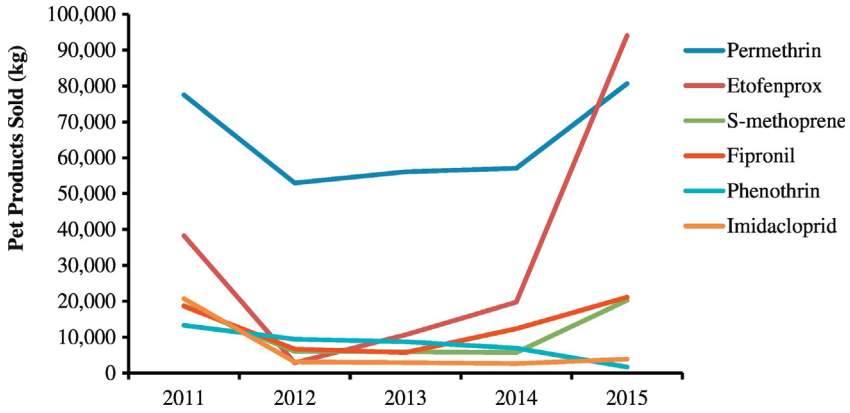

Fig. 4. Kg sold per year of top six pesticides found in pet products from 2011 to 2015. The synergist piperonyl butoxide, and disinfectants dodecyl dimethyl ammonium chloride and alkyl dimethylbenzyl ammonium were excluded from the ranking (CDPR, 2016c).

mayflies. The lack of wastewater effluent data for etofenprox, s-methoprene, and phenothrin represents a data gap that is necessary to fully evaluate the impact of pesticides found in pet products to wastewater effluent.

A.i.'s found in pet products have a wide range of physical and chemical properties that impact initial washoff; however, the pathway has been established. The removal efficiency of specific pesticides during wastewater treatment is still largely unknown. Additional studies are needed to characterize the occurrence and fate of pesticides entering wastewater treatment systems.

5. Conclusion

Fiproles were detected in 100% of the samples up to the 28–day pretreatment interval. Results confirm the down-the-drain transport of pesticides contained in spot-on treatments. Fipronil persisted with little break down to fipronil degradates during the entire 28-day treatment period. At 28 days post application, fiproles can be dislodged and transported down the drain at the magnitude of mg per pet. Measurements of dislodgeable pesticide residues during routine bathing confirm spot-on fipronil treatments contribute a substantial mass fraction of total fipronil loading to the wastewater catchment. The calculated estimates are relatively conservative and do not consider indirect transfer of pesticide residues associated with spot-on residues transported through the cleaning of indoor surfaces, human showering, laundering of materials that have come in contact with pet (i.e., pet bedding, human clothes), and human excrement. Other potential sources of indirect transfer include additional registered uses for fipronil (e.g., indoor crack and crevice, subterranean termite treatments, agriculture (excluding California), urban applications). It is beyond the scope of this study to quantify all potential sources; however, based on our measurements and calculations, spot-on flea and tick treatments have the potential to contribute up to the entire reported wastewater load and thus should be considered as an important source.

Spot-on flea and tick treatments may also be directly transferred to surface water in locations where treated pets swim. The total recovered mass of fiproles was between 3.6 and 230.6 mg per dog. The mass available may pose a risk to small water bodies.

It is beyond the scope of this paper to investigate the human health implications of coming in contact with treated pets; however, it is worth noting that fipronil is the focus of a human health risk assessment initiated by CDPR (CDPR, 2016a). Groomers, children, and adult pet owners may come in contact with fipronil regularly since current product labels do not require personal protective gear during application.

Acknowledgements

We would like to thank the many volunteers for taking the time to coordinate pesticide application on their dogs and allowing us to wash them; Terri and Sean Barry, Kyle and Angie Blaikie, Ryan Cheperka, April DaSilva, Mike Ensminger, Kean Goh, Desiree Haight, Dave Kim, Tara and Derek Lindahl, Kevin Richardson, Nan Singhasemanon, Rae Vander Werf, and Susan Wilson. We would like to thank Jesse Ybarra for constructing wash basins, Kaylynn Newhart and Sue Peoples for coordinating details of sample collection and analysis, and Leah Judson, Rae Vander Werf, April DaSilva, Mariah Thomas, Korena Goodell for help washing dogs. Finally, we thank Xuyang Zhang, Kean Goh, and Nan Singhasemanon for providing critical review of the manuscript.

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2017.04.219.

References

Budd, R., Ensminger, M., Wang, D., Goh, K.S., 2015. Monitoring fipronil and degradates in California surface waters, 2008–2013. J. Environ. Qual. 44, 1233–1240.
Bureau USC, 2016. American fact finder - Montly population estimates for the United States: April 1, 2010 to December 1, 2016. U.S. Census Bureau, Washington, DC.
CDPR, 2012. DPR 11–004 Prevention of Surface Water Contamination by Pesticides, 6970 and 6972 of Title 3 California Code of Regulations (3 CCR).
CDPR, 2016a. Notice of Initiation of Human Health Risk Assessment for the Active Ingredient Fipronil, California Notice 2016–02.
CDPR, 2016b. Pesticide Information Portal, Pesticide Use Reporting (PUR) data.
CDPR, 2016c. Pesticide Sales in California [Agency Internal Database].
Cochran, R.C., Yu, L., Krieger, R.I., Ross, J.H., 2015. Postapplication Fipronil exposure following use on pets. J. Toxic. Environ. Health A 78, 1217–1226.
CVRWQCB, 2017. Central Valley Pyrethroid Pesticides TMDL and Basin Plan Ammendment. Central Valley Regional Water Quality Control Board.
Dyk, M.B., Liu, Y., Chen, Z., Vega, H., Krieger, R.I., 2012. Fate and distribution of fipronil on companion animals and in their indoor residences following spot-on flea treatments. J. Environ. Sci. Health B 47, 913–924.
Ensminger, M., 2016. Analysis of whole sample suspended sediments in water. In: Branch, E.M. (Ed.), Standard Operating Procedure. California Department of Pesticide Regulation.
Ensminger, M., Budd, R., Kelley, K., Goh, K., 2013. Pesticide occurrence and aquatic benchmark exceedances in urban surface waters and sediments in three urban areas of California, USA, 2008–2011. Environ. Monit. Assess. 1–14.
Luo, Y.Z., Spurlock, F., Jiang, W.Y., Jorgenson, B.C., Young, T.M., Gan, J., et al., 2013. Pesticide washoff from concrete surfaces: literature review and a new modeling approach. Water Res. 47, 3163–3172.
Luo, Y., Guo, W., Ngo, H.H., Nghiem, L.D., Hai, F.I., Zhang, J., et al., 2014. A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment. Sci. Total Environ. 473–474, 619–641.

Luthy, R.G., Sedlak, D.L., Plumlee, M.H., Austin, D., Resh, V.H., 2015. Wastewater-effluent-dominated streams as ecosystem-management tools in a drier climate. Front. Ecol. Environ. 13, 477–485.
Mahler, B.J., Van Metre, P.C., Wilson, J.T., Musgrove, M., Zaugg, S.D., Burkhardt, M.R., 2009. Fipronil and its degradates in indoor and outdoor dust. Environ. Sci. Technol. 43, 5665–5670.
Markle, J.C., van Buuren, B.H., Moran, K.D., Barefoot, A.C., 2014. Pyrethroid pesticides in municipal wastewater: A baseline survey of publicly owned treatment works facilities in California in 2013. Pyrethroid Working Group.
Parry, E., Lesmeister, S., Teh, S., Young, T.M., 2015. Characteristics of suspended solids affect bifenthrin toxicity to the calanoid copepods *Eurytemora affinis* and *Pseudodiaptomus forbesi*. Environ. Toxicol. Chem. 34, 2302–2309.
Roessink, I., Merga, L.B., Zweers, H.J., Van den Brink, P.J., 2013. The neonicotinoid imidacloprid shows high chronic toxicity to mayfly nymphs. Environ. Toxicol. Chem. 32, 1096–1100.
Sadaria, A.M., Supowit, S.D., et al., 2016a. Mass balance assessment for six neonicotinoid insecticides during conventional wastewater and wetland treatment: nationwide reconnaissance in United States wastewater. Environ. Sci. Technol. 50 (12), 6199–6206.
Sadaria, A.M., Sutton, R., Moran, K.D., Teerlink, J., Brown, J.V., Halden, R.U., 2016b. Passage of fiproles and imidacloprid from urban pest control uses through wastewater treatment plants in northern California, USA. Environ. Toxicol. Chem. (n/a-n/a).
Schreder, E.D., La Guardia, M.J., 2014. Flame Retardant Transfers from U.S. Households (Dust and Laundry Wastewater) to the Aquatic Environment. Environ. Sci. Technol. 48, 11575–11583.
Simon-Delso, N., Amaral-Rogers, V., Belzunces, L.P., Bonmatin, J.M., Chagnon, M., Downs, C., et al., 2015. Systemic insecticides (neonicotinoids and fipronil): trends, uses, mode of action and metabolites. Environ. Sci. Pollut. Res. Int. 22, 5–34.
Supowit, S.D., Sadaria, A.M., Reyes, E.J., Halden, R.U., 2016. Mass balance of fipronil and total toxicity of fipronil-related compounds in process streams during conventional wastewater and wetland treatment. Environ. Sci. Technol. 50, 1519–1526.
Thuyet, D.Q., Jorgenson, B.C., Wissel-Tyson, C., Watanabe, H., Young, T.M., 2012. Wash off of imidacloprid and fipronil from turf and concrete surfaces using simulated rainfall. Sci. Total Environ. 414, 515–524.
USEPA, 2014a. E-FAST- Exposure and Fate Assessment Screening Tool Version 2014.
USEPA, 2014b. Office of Pesticide Program's Aquatic Life Benchmarks.
USEPA, 2017. Registration Review Process.
Vander Werf, R., Aldana, A., Teerlink, J., Budd, R., 2015. Budd R., Retail Store Survey of Consumer-Use Indoor Pesticide Products, 2014. Department of Pesticide Regulation, California.
Weston, D.P., Lydy, M.J., 2010. Urban and agricultural sources of pyrethroid insecticides to the Sacramento-San Joaquin Delta of California. Environ. Sci. Technol. 44, 1833–1840.
Weston, D.P., Ramil, H.L., Lydy, M.J., 2013. Pyrethroid insecticides in municipal wastewater. Environ. Toxicol. Chem. 32, 2460–2468.
Weston, D.P., Chen, D., Lydy, M.J., 2015. Stormwater-related transport of the insecticides bifenthrin, fipronil, imidacloprid, and chlorpyrifos into a tidal wetland, San Francisco Bay, California. Sci. Total Environ. 527–528, 18–25.

Chapter 8

Pyrethroid Pesticides in Municipal Wastewater: A Baseline Survey of Publicly Owned Treatment Works Facilities in California in 2013

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Publicly Owned Treatment Works (POTWs), also known as wastewater or sewage treatment plants, are typically owned by local city and county agencies. Approximately 564 California POTWs collectively treat approximately 3.47 billion gallons per day. This study was a survey of a diverse group of 32 California POTWs that together treat more than 40% of California's wastewater and was designed to show which of eight Group III pyrethroids (bifenthrin cyfluthrin, cypermethrin, deltamethrin, esfenvalerate, fenpropathrin, lambda-cyhalothrin, and permethrin) might potentially be found in the influent, effluent and biosolids of California's POTWs. Consistent with the intent of this study as a survey, the samples were grab samples (influent, effluent and biosolids) taken at a single point in time.

In Describing the Behavior and Effects of Pesticides in Urban and Agricultural Settings; Jones, et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2014.

Introduction

Synthetic pyrethroid insecticides are potential contaminants of wastewater. As a class, these insecticides are widely used in both urban and rural environments. In the urban environment, pyrethroids are used for lawn and garden care, pet care (shampoos, spot-on products and collars to prevent fleas), controlling insects around and inside buildings (flies, ants and spiders), head lice and scabies treatments, mosquito abatement, sewer manhole treatments, termite control and some clothing treatment. A number of researchers (*1–3*) have detected these products in aquatic surface waters and sediment samples at levels potentially harmful to aquatic invertebrates. In addition, Rogers (*4*) , Gomez (*5*) and Turner (*6*) have identified pyrethroids in influent, effluent and sludge from sewage treatment plants in Europe and the USA. Weston and Lydy (*7*) have shown that pyrethroids are present in secondary-treated municipal wastewater in California at concentration levels above the LC_{50} for the test system organism, *Hyalella azteca*.

In August 2006, the California Department of Pesticide Regulation initiated a data reevaluation of pesticides containing pyrethroid active ingredients. The data requirements included "monitoring in areas appropriate to the use" and applied to products likely to enter wastewater treatment plants. Shortly thereafter, the Pyrethroid Working Group (PWG), an industry-based group that was formed in 1990 to collectively address questions raised by the United States Environmental Protection Agency on aquatic ecotoxicity of cotton-use pyrethroids, committed to work with the California Department of Pesticide Regulation (DPR) to develop a program that will meet the requirements of the pyrethroid re-evaluation for monitoring in effluents of Publicly Owned Treatment Works. The member companies of the PWG are: Amvac Corporation, Bayer CropScience, BASF Corporation, DuPont Crop Protection, FMC Corporation, Pytech/Cheminova, Syngenta Crop Protection, and Valent USA Corporation.

In order to meet the requirements of the study, the PWG joined in a partnership with Tri-TAC. Tri-TAC's name reflects its membership and role: "Tri" from its three sponsoring organizations (the League of California Cities, the California Association of Sanitation Agencies, and the California Water Environment Association); and "TAC" from its role as a Technical Advisory Committee. Tri-TAC works with State and Federal Regulatory Agencies and interest groups on matters related to Publicly Owned Treatment Works (POTWs), with the goal of improving the overall effectiveness and accountability of environmental projects that impact POTWs in California. The PWG would be responsible for conducting the study, while Tri-TAC would be a key advisor in the development of the study protocol, obtain volunteers for the study, review of the analytical data and peer review the final report.

Materials and Methods

Study Design

This project was designed to meet the requirements from the Department of Pesticide Regulation as well as being comparable to California's Surface Water

In Describing the Behavior and Effects of Pesticides in Urban and Agricultural Settings; Jones, et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2014.

Ambient Monitoring Program (SWAMP) guidelines. These requirements called for eight (Group III) pyrethroids in at least 20 POTWs to be monitored in effluent, influent, and biosolids matrices. The eight pyrethroids to be monitored were bifenthrin, cyfluthrin, cypermethrin, deltamethrin, esfenvalerate, fenpropathrin, lambda-cyhalothrin, and permethrin. Analyses for total organic carbon, total suspended solids, and total solids were added. Prior to the initiation of the study, a Quality Assurance Project Plan (QAPP) was prepared by the Study Director and the study design was reviewed by the SWAMP Quality Assurance Help Desk and found to be SWAMP-comparable.

A total of 32 POTW facilities volunteered for this program. A total of 31 sites collected effluent (one of the sites served as a dechlorination facility for other POTWs), 31 sites collected influent and 24 sites collected biosolids (not all of the sites either collect or treat the biosolids at their facility). Facilities varied in volume of wastewater treated, location, treatment processes used (primary, secondary, tertiary), customer base (industrial, commercial and residential) and population served. The facilities participating in this study are regulated by seven of the nine California Regional Water Quality Boards and represent more than 40% of the total wastewater treatment volume in California (see Tables 1 and 2). Each of the sites was pre-assigned a letter code (A through GG). The only individuals who knew the identity of the sites were the Study Director, the Quality Assurance Manager, the Engineering Consultant and the individual responsible for shipping and receiving at the distribution laboratory.

Table 1. All California POTWs and POTW Survey Volunteers by Flow (Totals may not add up due to rounding.). Source: EPA 2008 Needs Survey data (*8*) and Tri-TAC survey of volunteers.

All California POTWs			*POTW Study Volunteers*		
Flow (MGD)	***#POTWs***	***Total Discharge Flow (MGD)***	***Flow (MGD)***	***#POTWs***	***Total Discharge Flow (MGD)***
<1	337	81	<1	3	1
1-9.9	174	617	1-9.9	11	58.3
10-19.9	30	400	10-19.9	7	102.6
20-100	22	944	20-100	6	249.5
>100	6	1,427	>100	5	1,079.4
Total	**569**	**3,469**	**Total**	**32**	**1,490.8**

Total Discharge Flow is the sum of the daily average flow for every POTW in the size category. Note: None of the study volunteers had "combined" systems (i.e., they do not deliberately collect and treat urban runoff).

Each of the POTWs was asked to collect consecutive grab samples of influent, effluent and, where available, biosolids. In addition, samples of influent and effluent were collected for total suspended solids (TSS) and total organic

carbon (TOC). The facilities were asked to deliver the samples to the analytical laboratory no later than the afternoon following sampling using either a courier or overnight shipment service to ensure analytical hold times for influent and effluent (72 hours) were met. A total of 724 samples were collected for the study.

Table 2. California POTWs with Discharge Permits and POTW Pyrethroid Survey Volunteers by Region (Totals may not add up due to rounding.). Source: EPA 2008 Needs Survey data (*8*)and Tri-TAC survey of volunteers.

All California POTWs			*POTW Pyrethroid Study Volunteers*		
Water Board Region	***#POTWs with NPDES Permits***	***Total Discharge Flow (MGD)***	***Water Board Region***	***#POTWs with NPDES Permits***	***Total Discharge Flow (MGD)***
1-North Coast	232	20	1-North Coast	2	18.4
2-SF Bay	43	674	2-SF Bay	7	178.9
3-Central Coast	22	81	3-Central Coast	4	13.5
4-Los Angeles	27	1.152	4-Los Angeles	7	645.1
5-Central Valley	60	388	5-Central Valley	3*	97.5
6-Lahontan	4	4	6-Lahontan	0	0
7-Colorado River	12	18	7-Colorado River	0	0
8-Santa Ana	19	389	8-Santa Ana	2	332
9-San Diego	12	286	9-San Diego	7	205.4
Total	**222**	**3,011**	**Total**	**32**	**1,490.8**

Total Dischage Flow is the sum of the daily average flow for every POTW in the region. Note: Two volunteers are not dischargers so table does not represent total volume treated.

Two laboratories, Caltest Analytical Laboratory located in Napa, California and Morse Laboratories, Incorporated (a wholly-owned subsidiary of Analytical Bio-Chemistry Laboratories, Inc.) located in Sacramento, California were selected for the analytical work. The laboratories were chosen based on their ability to work at trace (parts per trillion) levels, the availability of proven pyrethroid analytical methods and the ability to confirm pyrethroids using secondary ion mass spectrometry. Both laboratories were asked to prepare and analyze the samples using their routine methods, instrumentation, and quality control samples. The Study Director provided each laboratory with a set of eight stable isotope-enriched (d6) standards of each of the eight pyrethroids in the study

to be used as internal standards and surrogates as well as a standardized reporting format.

Caltest was selected as the Study Distribution Laboratory. This laboratory was responsible for securing the sample containers, sending the containers to the 32 POTWs, receiving the samples from the POTWs and preparing and distributing the test materials to Morse Laboratories. In addition, Caltest was responsible for pyrethroid analysis of influent, effluent and biosolids, the analysis of total suspended solids (TSS) and total organic content (TOC) on influent and effluent and total solids (TS) on the biosolids.

Laboratory Analysis

The analytical methods and detectors used for the project are listed in Table 3.

Pyrethroids Analysis in Influent and Effluent Samples by GC-MSD/NCI (Morse)

The method described herein is capable of determining bifenthrin, cypermethrin, cyfluthrin, deltamethrin, esfenvalerate, fenpropathrin, lambda-cyhalothrin and permethrin in influent and effluent wastewater. Esfenvalerate-d6 and fenpropathrin-d6 are used as surrogate standards in this method. The surrogates are added to the sample prior to the initial extraction step to demonstrate extraction efficiency. Pyrethoid residues are extracted from wastewater by first adding methanol and sodium chloride to the aqueous sample, then partitioning the mixture two times with hexane. The upper hexane layer is passed through sodium sulfate, evaporated to dryness and re-dissolved in a small volume of hexane. The hexane extract is then subjected to a Bond Elut® LRC Silica solid phase extraction (SPE) procedure prior to residue determination. analysis is performed using an Agilent GC-MS (A6890/5973N) in negative chemical ionization (NCI) mode, using selective ion monitoring mode of detection and quantification. The instrument is initially calibrated using a minimum of five standards (of increasing concentrations) that meets a RSD or Grand Mean of < 15%. Quantitation for all samples is performed using mid-calibration level standards, bracketing every four samples. The limit of quantitation of the method for effluent wastewater and water is 0.50 ng/L for esfenvalerate, fenpropathrin, lambda-cyhalothrin, bifenthrin, cypermethrin and cyfluthrin, 1.0 ng/L for deltamethrin and 5.0 ng/L for permethrin. The limit of quantitation of the method for influent wastewater is 5.0 ng/L for esfenvalerate, fenpropathrin, lambda-cyhalothrin, bifenthrin, cypermethrin and cyfluthrin, 10 ng/L for deltamethrin and 50 ng/L for permethrin.

The method provides for an optional Bond Elut® Florisil SPE cleanup for the influent wastewater if further extract cleanup is deemed necessary (as determined by unacceptable chromatography resulting from co-elution of interfering compounds or analyte GC response enhancement/suppression). For samples where additional cleanup is necessary, the fortified (spike) samples were treated the same way and re-analyzed to verify recovery. The limit of quantitation (LOQ) remains as stated.

Table 3. List of Analytical Methods and Detectors

Analyte or Group	*Matrix*	*Method*	*Detector Type*	*Prep/ Extraction/ Digestion*	*Lab*
TOC	Influent/ Effluent	SM 5310B	NDIR	SM 5310B	Caltest
TSS	Influent/ Effluent	SM 2540D	Analytical Balance (0.0001g)	None	Caltest
TS	Biosolids	SM 2540G	Analytical Balance (0.0001g)	None	Caltest
Pyrethroids	Influent/ Effluent	8270(M)	GCMS-NCI	SW846 3510C	Caltest
Pyrethroids	Biosolids	8270(M)	GCMS-NCI	SW846 3540C	Caltest
Pyrethroids	Influent/ Effluent	Morse Method 201, Rev. 1	GCMS-NCI	Ref. (*12*)	Morse
Pyrethroids	Biosolids	Morse Method 213 original	GCMS-NCI	Ref. (*12*)	Morse

Pyrethroids Analysis in Biosolids by GC-MSD/NCI (Morse)

The method described herein is capable of determining bifenthrin, cypermethrin, cyfluthrin, deltamethrin, esfenvalerate, fenpropathrin, lambda-cyhalothrin and permethrin in wastewater treatment dewatered cake. Esfenvalerate-d6 and fenpropathrin-d6 are used as surrogate standards in this method. The surrogates are added to the sample prior to the initial extraction to demonstrate extraction efficiency. Pyrethroid residues are extracted from wastewater dewatered cake by first homogenizing with methanol, followed by multiple extractions with methanol:methylene chloride (50:50, v/v) using a platform shaker (2 extractions). Following extraction, the crude extract (supernatant) from each shaking is decanted through sodium sulfate into the same 250-mL mixing cylinder and the combined extract is brought to a known volume. An aliquot of the combined sample extract is evaporated to dryness, reconstituted in hexane, then purified by subjecting to a Bond Elut® LRC Silica solid phase extraction (SPE) followed by a Bond Elut® Florisil SPE procedure. The purified extract is evaporated to dryness, re-dissolved in 1.0 mL of internal standard solution with ultrasonication and submitted for residue determination. The analysis is performed using an Agilent GC-MS (A6890/5973N) in negative chemical ionization (NCI) mode, using selective ion monitoring mode of detection and quantification. The instrument is initially calibrated using a minimum of

five standards (of increasing concentrations) that meets a RSD or Grand Mean of < 15%. Quantitation for all samples is performed using mid-calibration level standards, bracketing every four samples. The limit of quantitation of the method is 2.5 ng/g for bifenthrin, cypermethrin, cyfluthrin, esfenvalerate, fenpropathrin, lambda-cyhalothrin, 5.0 ng/g for deltamethrin, and 25 ng/g for permethrin.

Pyrethroids Analysis in Influent, Effluent, and Biosolids by GC-MS/NCI SIM (Caltest)

Sample preparation for influent and effluent employs EPA SW846 (*9*) -3510C (*10*) extraction method, which calls for 500 ml of influent, or 1,000 ml of effluent to be extracted. A surrogate (Esfenvalerate-d6) is added to the sample prior to the addition of extraction solvents to demonstrate extraction efficiency and the original container is solvent rinsed with dichloromethane (DCM) to start the liquid-liquid extraction process, using 60 mL of DCM followed by vigorous shaking, settled & drained (repeated twice more). Biosolids are extracted by SW846 (*9*)-3540C (*11*) method employing the soxhlet extraction process with 1200 mL of DCM. The sample extract (influent, effluent or biosolids) is solvent exchanged into hexane then passed through a three-phase clean-up step (GCB-graphitized carbon; PSA-Primary & Secondary Amine; alumina), then is concentrated and brought to final volume of 1 mL. The sample analysis for all matrices (influent, effluent and biosolids) is performed using SW846-8270, as modified in the Pyrethroid Working Group method for sediments (*12*). The analysis is performed using an Agilent GC-MS (A7890/5975) in negative chemical ionization (NCI) mode, using selective ion monitoring mode of detection and quantification. The instrument is initially calibrated using a minimum of five standards (of increasing concentrations) that meets a RSD or Grand Mean of < 15%, which then is confirmed by a second-source calibration verification standard to +/- 30%. Quantitation for all samples is performed using mid-calibration level standards, bracketing every four samples.

Total Suspended Solids (TSS) by Gravimetric Analysis (Caltest)

This analysis is performed using Standard Methods 2540 D where a well-mixed sample is filtered through a weighed glass fiber filter and the residue retained on the filter is dried to a constant weight at 103-105 °C. The filter is weighed repeatedly (maximum 5 weightings) until a constant, dried weight is achieved, and the final weight is factored to the sample volume used to determine value of the residue as mg/L. The practical range of the determination is 3 mg/L to 20,000 mg/L.

Total Organic Carbon (TOC) Analysis by NDIR (Caltest)

This analysis is performed using Standard Methods 5310 B for the determination of total organic carbon in waters which contain carbonaceous matter that is soluble. The applicable range for the instrument is 0.5 mg/L to 200 mg/L. A preserved sample (pH <2) contained in a 40 mL VOA vial is placed into the auto-sampler of the TOC analyzer, a Shimadzu TOC CSH. The sample is sparged in acid and injected onto a furnace containing a platinum catalyst. The sample is combusted in an oxygen rich environment to form carbon dioxide which is carried to the non-dispersive infra-red, (NDIR), detector.

Total Solids as Percentage Solids by Gravimetric Analysis (Caltest)

This analysis is performed using Standard Methods 2540 G / EPA 160.4 for the determination of total solids as a percentage of sample weight. Place 25-50 grams of a well-mixed aliquot of the sample in a pre-weighed evaporating dish and evaporated to constant dryness at 103-105 °C. The vessel containing the dried sample is weighted repeatedly (maximum 5 weightings) until a constant, dried weight is achieved. The final weight is divided by the initial weight of the sample aliquot, multiplied by 100, to calculate the solids-only portion of the sample expressed as percentage of the original, semi-solids sample weight.

Results and Discussion

This study was a survey designed to show which of the Group III pyrethroids might be found in influent, effluent and biosolids of California POTWs and to gain an understanding of the range and magnitude of these residues. Consistent with the intent of the study as a survey, the samples were grab samples taken at a single point in time. The samples were not flow or time weighted nor was there an attempt to account for the hydrologic travel time from influent to effluent or an investigation of the pyrethroid concentrations that might occur at different times of the year. For these reasons, care must be taken to avoid over-interpreting the data.

The project developed a comprehensive QA Project Plan with detailed quality control criteria including holding times. All sites were sampled in duplicate and each site's samples were analyzed by two, distinct laboratories. A full suite of QC samples (MS, MSD, LCS) were analyzed with each batch of samples. Analytical data was third-party validated by a team including analytical chemists, QA personnel, and project management. All data was required to meet control limits and quality objectives outline in the QA project plan.

Figure 1 is a graph of the residue profile for effluent (31 sites). To construct this graph the pyrethroid residues from each of the samples were plotted on the x-axis. The graph shows that, typically, the major residue in terms of concentration is permethrin (approximately 85% of the total pyrethroid residue). Cypermethrin is next at approximately 10% of the total residue followed by

cyfluthrin, bifenthrin and lambda-cyhalothrin, Esfenvalerate, deltamethrin and fenproprathrin were minor constituents in the profile. Similar profiles were observed in influent and biosolids.

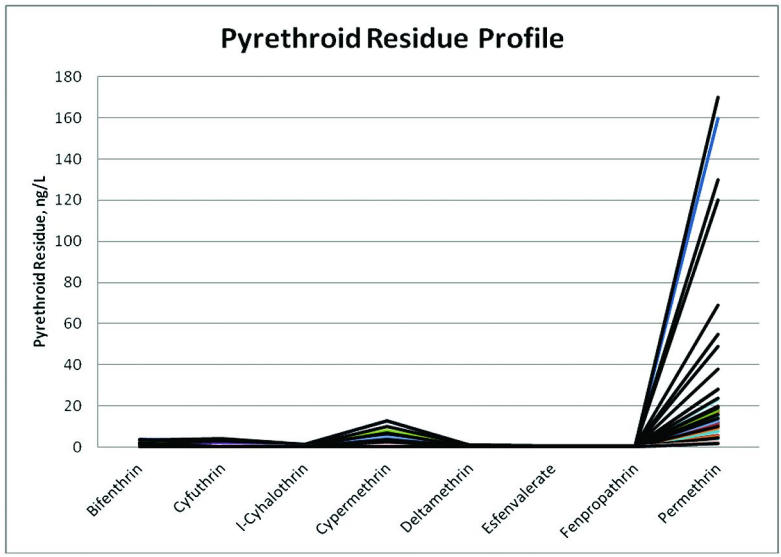


Figure 1. Pyrethroid Residue Profile (ng/L) in Effluent-All Sites.

For effluent, a total of 62 samples were analyzed for pyrethroid residues (Analysis of samples from 31 sites by both laboratories). Total pyrethroid residues ranged from non-detectable to a maximum residue of 190 ng/L. The most frequently detected pyrethroids in effluent were bifenthrin (82%), followed by cypermethrin (81%) and then permethrin (65%). Fenpropathrin has the lowest frequency of detection (3.3%). The range of residues and the median residues for each of the 8 pyrethroids can be found in Table 4. Three sites contained no detectable residues of the 8 monitored pyrethroids. Six sites contain trace residues at or near the level of detection.

For influent, a total of 67 samples (62 samples plus 5 repeats) were analyzed for pyrethroid residues. Total pyrethroid residues ranged from 42 ng/L to a maximum of 3800 ng/L. Permethrin was the predominant pyrethroid found both in terms of frequency of detection (100%) and maximum residue (3800 ng/L) found. Bifenthrin (96%), cyfluthrin (88%), lambda-cyhalothrin, (81%) and cypermethrin (81%) were also detected in most samples. Fenpropathrin was rarely detected (4.5%) although at one site it was the predominant residue found. Fenpropathrin was found in the effluent and biosolids sample from this site and was confirmed by both labs as the dominant pyrethroid. In a query of the State of California's Surface Water Ambient Monitoring Program's database, fenpropathrin was rarely detected, but had been found in sediment samples from agricultural areas. The range of residues and the median residues found for each of the 8 pyrethroids can be found in Table 5.

Table 4. Comparison of Pyrethroid Residues in Effluent from 31 California POTWs

	Bifenthrin ng/L	*Cyfluthrin ng/L*	*Lambda-Cyhalothrin ng/L*	*Cypermethrin ng/L*	*Deltamethrin ng/L*	*Esfenvalerate ng/L*	*Fenpropathrin ng/L*	*Permethrin ng/L*	*Total Pyrethroid[1] ng/L*
# of Samples	62	62	62	62	62	62	62	62	62
# of Detects	51	37	30	50	10	20	2	40	56
% Detected	82	60	48	81	16	32	3.2	65	90
Maximum	3.9	4	1.6	13	1.2	0.6	0.8	170	190
Minimum	ND[2]	ND	ND	ND	ND	ND	ND	ND	ND
Average[3]	0.89	0.60	0.30	2.11	0.31	0.25	0.22	20	25
Median[3]	0.6	0.3	0.2	1.3	0.3	0.2	0.2	9.4	13

[1] Total pyrethroids=sum of the Group III pyrethroids. [2] ND=Non-detected (<LOD or MDL). [3] For average and median calculations, ND values are assumed to be at the LOD or MDL value.

Table 5. Comparison of Pyrethroid Residues in Influent from 31 California POTWs

	Bifenthrin ng/L	*Cyfluthrin ng/L*	*Lambda-Cyhalothrin ng/L*	*Cypermethrin ng/L*	*Deltamethrin ng/L*	*Esfenvalerate ng/L*	*Fenpropathrin ng/L*	*Permethrin ng/L*	*Total Pyrethroid[1] ng/L*
# of Samples	67	62	67	67	67	67	67	67	67
# of Detects	64	59	54	54	29	31	3	67	67
% Detected	96	88	81	81	43	46	4.5	100	100
Maximum	74	55	72	200	210	360	130	3800	3800
Minimum	ND[2]	ND	ND	ND	ND	ND	ND	30	42
Average[3]	15	11	5.6	35	8.0	8.1	4.6	330	420
Median[3]	9.7	7.4	2.8	21	3.3	1.7	1.7	230	300

[1] Total pyrethroids=sum of the Group III pyrethroids [2] ND=Non-detected (<LOD or MDL) [3] For average and median calculations, ND values are assumed to be at the LOD or MDL value.

For biosolids, a total of 52 samples (48 samples plus 4 repeats) from 24 sites were analyzed for pyrethroid residues. Total pyrethroid residues ranged from a low of 130 ng/g to a maximum of 13000 ng/g on a dry weight basis. Bifenthrin was in 96% of the samples. Permethrin (92%), followed by cypermethrin (90%), cyfluthrin (87%) and lambda-cyhalothrin (52%) were the next most frequently detected. Median residues for total pyrethroid in biosolids were 1500 ng/g on a dry weight basis. The range of residues and the median residues for each of the 8 pyrethroids can be found in Table 6.

Box and whisker plots were used to compare the range of residues found in influent and effluent from all sites. Figure 2 shows distribution of pyrethroid residues found in influent and effluent for bifenthrin, cypermethrin and cyfluthrin. For all pyrethroids, the average effluent concentration is less than 10% of the influent concentration.. Similar profiles are obseved for the other pyrethroids.

To examine differences in treatment type (primary, secondary and tertiary), scatter plots of the effluent concentrations for each of the pyrethroids were prepared. The sites were separated by treatment type and then the residues plotted against each site. Figure 3 shows the plots for permethrin and Figure 4 shows the plots for cypermethrin. All of the pyrethroids show a similar profile. Clearly there is a pattern of a reduction in residues as the wastewater receives further treatment, but this correlation is imperfect. There are secondary treatment sites that have lower residues than some of the tertiary sites and there are tertiary sites that have higher residues than the median secondary treatment sites.

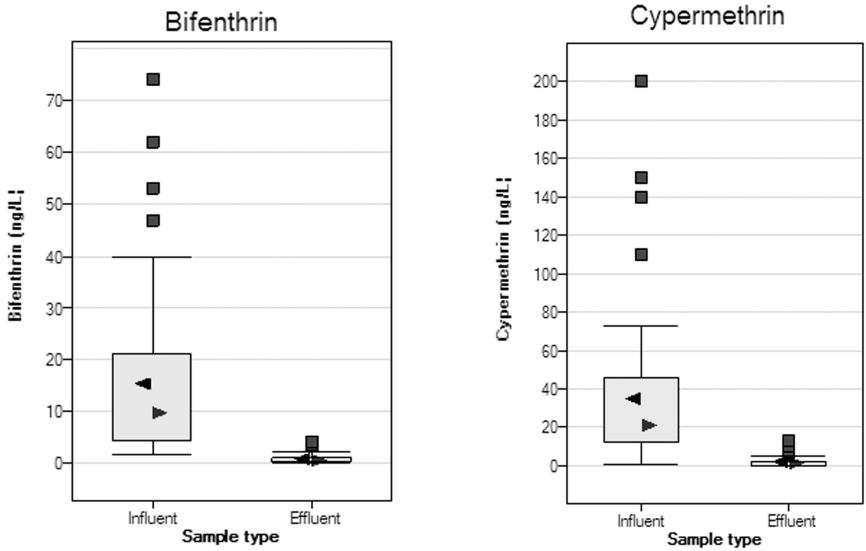
Hydrophobic compounds, such as pyrethroid pesticides, tend to sorb to solids (biosolids) and organic matter. Plots of the pyrethroid residues in effluent versus total suspended solids (TSS) were made for each of the individual pyrethroids. In all instances, there is a trend toward higher residues with increasing TSS, however, the pattern is not definitive and the correlation is strongly influenced by the data from the primary treatment site. Plots of the correlation using the cypermethrin data are shown both with the primary site included (Figure 5) and taking this data out (Figure 6). Including the primary site data, the correlation is poor (r^2=31.4%) and several data points fall just outside of the 95% confidence limits. Excluding the primary site, there is no correlation between the pyrethroid concentration and TSS (r^2=6.8%).

Similarly, plots of pyrethroid residues in effluent versus total organic content (TOC) were made to examine potential relationships. Again, there is a trend toward higher pyrethroid residues with increasing TOC in effluent, but the pattern is not definitive.

Table 6. Comparison of Pyrethroid Residues in Biosolids from 24 California POTWs

	Bifenthrin ng/L	*Cyfluthrin ng/L*	*Lambda-Cyhalothrin ng/L*	*Cypermethrin ng/L*	*Deltamethrin ng/L*	*Esfenvalerate ng/L*	*Fenpropathrin ng/L*	*Permethrin ng/L*	*Total Pyrethroid[1] ng/L*
# of Samples	52	52	52	52	52	52	52	52	52
# of Detects	50	45	27	47	16	16	3	48	52
% Detected	96	87	52	90	31	31	5.8	92	100
Maximum	1100	190	200	1000	78	42	71	11000	13000
Minimum	ND[2]	ND	ND	ND	ND	ND	ND	ND	130
Average[3]	150	34	29	110	28	15	12	1500	1900
Median[3]	120	29	28	79	24	14	6.8	1200	1500

[1] Total pyrethroids=sum of the Group III pyrethroids. [2] ND=Non-detected (<LOD or MDL). [3] For average and median calculations, ND values are assumed to be at the LOD or MDL value.



Left Arrow-Average Concentration
Right arrow-Median Concentration

Left Arrow-Average Concentration
Right arrow-Median Concentration

Figure 2. Distribution of Bifenthrin and Cypermethrin in Influent and Effluent.

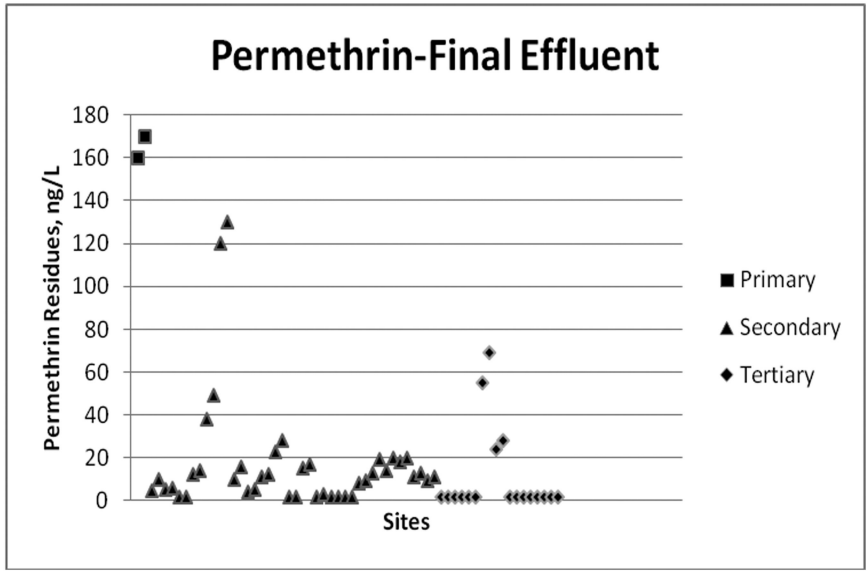


Figure 3. Comparison of Treatment Effects-Permethrin Concentrations in Final Effluent.

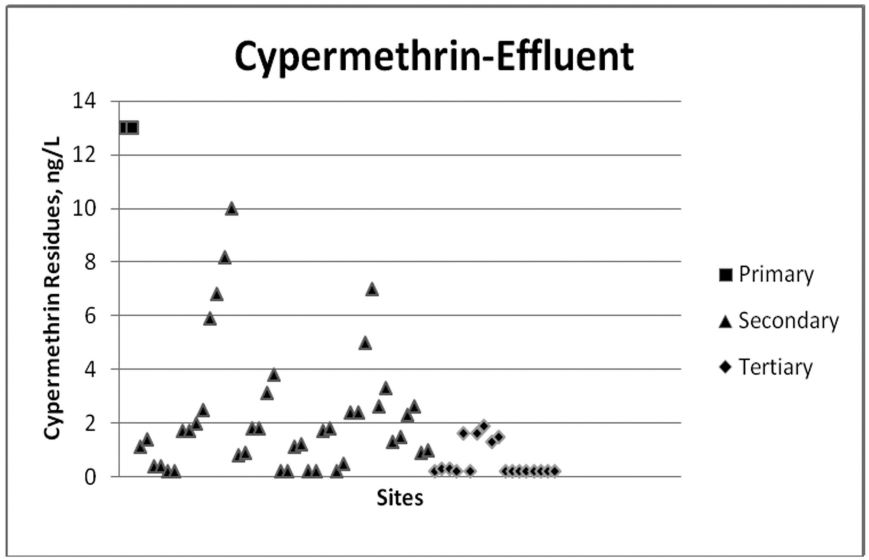


Figure 4. Comparison of Treatment Effects-Cypermethrin Concentrations in Final Effluent

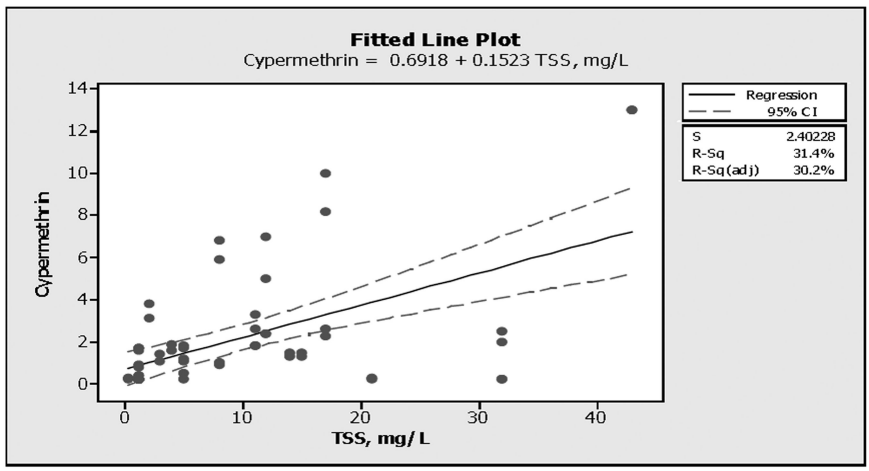


Figure 5. Cypermethrin(ng/L) vs. Total Suspended Solids (TSS, mg/L) in Effluent-With Primary Site.

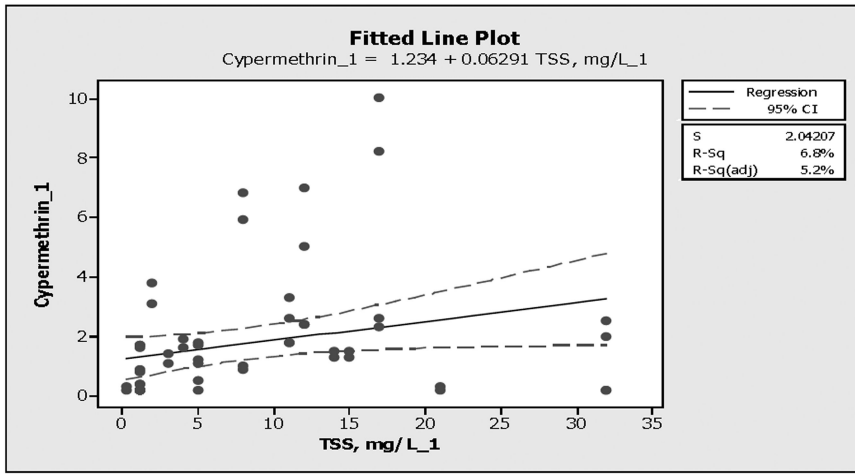


Figure 6. Cypermethrin(ng/L) vs. Total Suspended Solids (TSS, mg/L) in Effluent-Without Primary Site

Conclusions

This project was established to achieve a baseline understanding of the range and frequency of detections of eight Group III pyrethroid insecticides in California publicly-owned treatment works. Only one grab sample was collected for each matrix at a given site. The samples were not timed between influent, effluent, and biosolids collection. This was a targeted study design and was not intended to support a statistically nor comprehensive approach to site characterization or to characterize the type of facilities. However, with these caveats, the following observations can be made.

- In effluent, pyrethroids were detected in 28 of the 31 sites examined. Bifenthrin (82%) was the most frequently detected pyrethroid in effluent followed by cypermethrin (81%) and permethrin (65%).Total pyrethroid residues in effluent ranged from non-detectable to a maximum of 190 ng/L. The median residue was 13 ng/L.
- In influent, permethrin was the predominant residue both in terms of the frequency of detection (100%) and the maximum residues found (3800 ng/L). Bifenthrin (96%), cyfluthrin (88%), l-cyhalothrin (81%) and cypermethrin (81%) were also frequently detected. Total residues of pyrethroid in influent ranged from 42 ng/L to a maximum of 3800 ng/L. The median residue was 300 ng/L.
- As expected for hydrophobic compounds, the highest residue concentrations were found in the biosolids. Bifenthrin was the most frequently detected (96%) in the 24 facilities examined followed by permethrin (92%) and cyfluthrin (87%). Total pyrethroids found ranged from 130 ng/g to 13,000 ng/g on a dry weight basis. Median residue was 1500 ng/g dry weight.

- Pyrethroid residues suggest a trend towards greater reduction as treatment increases from primary to tertiary. The percentage of tertiary plants with pyrethroids near the reporting limit is greater than for secondary plants. However, the trend is not definitive.
- For secondary and tertiary plants with measurable residues, effluent residues are less than 10 % of influent residues with four exceptions-3 secondary and 1 tertiary.
- The correlation between total suspended solids and pyrethroid residues is suggestive, but not compelling. Regression analysis does not show statistically significant correlation.

References

1. Weston, D. P.; You, J. C.; Lydy, M. J. Distribution and toxicity of sediment associated pesticides in agriculture-dominated water bodies of California's Central Valley. *Environ. Sci. Technol.* **2004**, *38* (10), 2752–2759.
2. Kelley, K., K. Starner Monitoring Surface Waters and Sediments of the Salinas and San Joaquin River Basins for Organophosphate and Pyrethroid Pesticides, 2004. http://www.cdpr.ca.gov/docs/emon/pubs/ehapreps.htm?filter=surfwater (accessed October 1, 2013).
3. Bacey, J.; Spurlock, F.; Starner, K.; Feng, H.; Hsu, J.; White, J.; Tran, D. M. Residues and toxicity of esfenvalerate and permethrin in water and sediment, in tributaries of the Sacramento and San Joaquin Rivers, California, USA. *Bull. Environ. Contam. Toxicol.* **2005**, *74* (5), 864–871.
4. Rogers, H. R.; Campbell, J. A.; Crathorne, B.; Dobbs, A. J. The occurrence of chlorobenzenes and permethrins in twelve U.K. sewage sludges. *Water Res.* **1989**, *23* (7), 913–921.
5. Gómez, M. J.; Martínez-Bueno, M. J.; Lacorte, S.; Fernandez-Alba, A. R.; Aguera, A. Pilot survey monitoring pharmaceuticals and related compounds in a sewage treatment plant located on the Mediterranean coast. *Chemosphere* **2007**, *66* (2007), 993–1002.
6. Turner, T.; Cartmell, E.; Lester, J. N.; Casse, F.; Comber, S. D.; Scrimshaw, M. D. The pharmaceutical use of permethrin: sources and behavior during municipal sewage treatment. *Arch. Environ. Contam. Toxicol.* **2011**, *61* (2), 193–201.
7. Weston Donald, P.; Lydy Michael, J. Urban and agricultural sources of pyrethroid insecticides to the Sacramento-San Joaquin Delta of California. *Environ. Sci. Technol.* **2010**, *44* (5), 1833–1840.
8. *Clean Watersheds Needs Survey*; EPA-832-R-10-002; U.S. Environmental Protection Agency, 2010. http://water.epa.gov/scitech/datait/databases/cwns/2008reportdata.cfm.
9. *Method 3540C – Soxhlet Extraction (SW-846) (Revision 3)*; U.S. Environmental Protection Agency: Washington, DC, 1996.
10. *Method 3510C – Separatory Funnel Liquid-Liquid Extraction (Revision 3)*; U.S. Environmental Protection Agency: Washington, DC, 1996.

11. *Method 8270D - Semivolatile Organic Compounds by Gas Chromatography /Mass Spectrometry (GC/MS) (Revision 4)*; U.S. Environmental Protection Agency: Washington, DC, 2007.
12. Robinson, N. J.*Draft Method: Residue Analytical Method for the Determination of Residues of Bifenthrin, Cypermethrin, Cyfluthrin, Deltamethrin, Esfenvalerate, Fenpropathrin, Lambda-Cyhalothrin and Permethrin in Sediment*; Report for the Pyrethroid Working Group; Syngenta Crop Protection, Greensboro, NC, 2005.

Chapter 10

Conducting Ecological Risk Assessments of Urban Pesticide Uses

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Recent studies have reported pesticides in toxicologically significant concentrations in surface water, sediments, stormwater, and publicly owned treatment works (POTW) influent/effluent wastewater from residential uses at locations across the United States. The USEPA faces many challenges in assessing the ecological risks from indoor and outdoor residential pesticide uses, many of which stem from limitations in quantifying exposure from the wide array of application scenarios available for residential pesticide use. Data on the timing, frequency and location of residential pesticide application at a national scale has been collected and submitted to the USEPA. These data will be useful for constructing representative residential exposure scenarios. In the absence of these data and tools, the USEPA has relied on urban monitoring data for conducting the ecological risk assessments. The use of certain chemicals as mosquito adulticides has resulted in exposure and risk to non-target aquatic organisms. Various methods and approaches to assess exposure are presented to conduct ecological risk assessments of these insecticides. Pesticides released to domestic wastewater from indoor residential uses are being assessed with the Exposure and Fate Assessment Screening Tool (E-FAST). Bench-scale treatability studies and POTW monitoring data will be used to refine exposure estimates of pesticides in wastewater, surface water and biosolids resulting from indoor uses.

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Introduction

Urban uses of pesticides are widespread and their use patterns present many challenges in conducting a national scale ecological risk assessment (ERA). Pesticides are used outdoor and indoor in residential, public, commercial, industrial and military areas. In California alone, nearly ten million pounds of pesticides active ingredients were used in the year 2009 (California Department of Pesticide Regulations Pesticides Use Reporting or CDPR PUR database (*1*)). Use in urban areas includes nearly thirty PUR categories with the top five being structural pest control, rights-of-ways, public health, landscaping, and indoor homeowner use.

Ecological risks associated with urban uses of pesticides is a critical emerging issue. As highlighted by the 2007 USGS report "*The Quality of our Nation's Waters* (*2*)," urban streams have the highest frequency of U.S. stream sites with pesticide concentrations that exceed aquatic life benchmarks (83%). Agriculturally dominated streams had the next highest frequency of aquatic life benchmark exceedance (57%), followed by mixed use streams (42%) and undeveloped sites (13%). This chapter describes major risk assessment challenges and approaches being considered by USEPA for assessing ecological risks from urban/residential pesticide uses. Specifically, three residential/urban assessment scenarios are described: (1) stormwater discharges resulting from outdoor uses; (2) exposure from adulticide uses; and (3) releases to POTWs (waste water discharges) from indoor uses. Within each of these assessment scenarios, the available methods and data being considered for modeling pesticide exposure and risk are summarized. In addition, the results from selected model-based assessments are compared to available information from targeted pesticide monitoring studies.

Assessing Stormwater Discharges from Outdoor Urban Uses

Outdoor urban uses of pesticides can result in significant exposure to water bodies through drift and runoff. These uses include structural pest control, rights of ways, and landscaping. Many pesticides are labeled for outdoor uses to control insect pests such as ants, cockroaches, fleas, occasional invaders, spiders, and wasps, in addition to others used for lawn care. Control is accomplished by professional pest control operators (PCOs) and homeowners through different pesticide formulations, application methods, and timing.

Many types of documentation, information and data are used by USEPA in conducting the ecological risk assessment for all pesticides including those used outdoors in urban settings. In a regulatory setting, labels are considered first in determining pesticide exposure in various compartments of the environment, as the label is the legal document governing the permitted pesticide use patterns. Labels specify pesticide contents of active(s)/inert material(s), formulation type, target pests/areas, and detailed use instructions (application rate, number of applications permitted, frequency, timing and type of applications. In addition to label use information, pesticide usage data are also important as it indicates quantity, seasonality, historical and geographic usage extent of currently registered

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pesticides. Monitoring data are also important and could be the only reliable exposure data available for use in a risk assessment due to limitations associated with the current modeling approaches. Important aspects of exposure modeling uncertainties for outdoors uses include establishing a conceptual model for varied types of outdoor uses along with percent/type of areas treated, percent of pesticide available for washoff, and other possible sources of pesticide contamination (*i.e.*, drift, contaminated airborne particles and others). As discussed in more detail later, recent studies have concentrated in obtaining such important modeling parameters in addition to many other data such as frequency/seasonality of applications, and most frequently used application rate, frequency, equipment and formulations. This data could be used as inputs for the exposure models to characterize and refine the exposure estimates.

Use Characterization

Early CDPR Surveys (2001-2005)

The California Department of Pesticide Regulation (CDPR) funded a number of use and usage surveys between 2001 and 2005 to get a better understanding of the pesticide use pattern in urban environments. The 2001 survey (*3*), involved the San Diego Creek and East Costa Mesa/Newport Beach watershed areas of Orange County, CA. A majority of the surveyed people that apply pesticide products (58.3%) reported applications one to three times, or four to six times per year. Another survey was conducted in 2002, of residents of the Chollas Creek area of San Diego County and the Delhi Channel area in Orange County (*4*). Ants and other insects were the primary target pests. The most frequent use pattern of pesticide application was once every few months (43.1%). Of the responses, 47.2% indicated that they had purchased or used a weed control product, 77.1% indicated that they purchased or used an insecticide, and 32.5% indicated they had purchased or used a product to control plant diseases. The 2003 survey covered the areas of the Arcade Creek watershed in Sacramento, Five Mile Slough watershed in Stockton and San Francisco Bay (*5*). From 20-41% indicated they did not apply pesticides in their homes and 37-65% of respondents identified insects as their primary pest of concern. Other pests included snails/slugs (24.4-29.2%) and vertebrates (15-27%). The majority (58-64%) indicated they applied pesticides on hard surfaces such as perimeters of buildings, driveways, sidewalks, or walls; further 44-47% responded that they applied pesticides 1-3 times per year.

The previous surveys examined residential users of pesticides; in contrast, a 2005 survey (*6*) evaluated pesticide use by pesticide managers and applicators in three urban watersheds: Arcade Creek (Sacramento County), Chollas Creek (San Diego County), and Upper Newport Bay/San Diego Creek (Orange County), CA. The CDPR PUR Report database indicated that in 2003 structural PCO use comprised 40% of the total reported non-agricultural use, rights-of-ways (32%), landscape maintenance (15%), public health (12%), and regulatory pest control (1%) in Sacramento, Orange and San Diego Counties. Structural pest control comprised 93-98% of the total insecticide usage. An analysis of usage indicated that organophosphates had been declining and pyrethroids increasing. Rights-of-

ways accounted for 47-60% of the total herbicide use. The top herbicides used were glyphosate and diuron. Landscape maintenance reported 38-53% of the total herbicide use. The most commonly applied herbicide was glyphosate. San Diego County was the major urban pesticide user (48%), followed by Orange County and Sacramento County.

Pyrethroid Working Group Use Surveys (2009-2013)

In response to concerns over increasing pyrethroid use and detections in California, a survey was conducted by Pyrethroid Working Group (PWG) for CDPR in 2009 (MRID 48762913 (*7*)), which assessed pesticide usage by professional pest management companies. Outdoor usage represented 83% of the total pounds of pesticides applied in urban environment, with indoor usage constituting the balance. Application frequency was monthly or every other month for residential customers (80% of responses) and monthly for commercial customers (83% of responses) (Table 1). For outdoor use, the dominant type of formulations used were liquid sprays (liquids 95% and wettable powder 2%); granules represented 3%, with very small amounts of baits. The most common equipment used in applying liquid sprays included power sprayers, followed by handheld or back pack sprayers. Granular products were most often used in broadcast application. Treatment types included home or fence perimeter treatments (1-2 feet up and 1-5 feet out with 1x1 ft being the most common) and/or spot treatment while treatment of the entire yard was less common. Hard surfaces such as patios, outdoor congregation areas and driveways were almost always treated. Less commonly treated areas include vertical walls and uncovered storage. Pest management professionals were asked to name the "Top 5" pesticide products they used, based on volume. The product most commonly named was Termidor (fipronil, named by 73% of respondents). The named products were related to their corresponding active ingredients, which included bifenthrin, fipronil, and deltamethrin (named among the "Top 5" by 60-75% of the pest management professionals surveyed); followed by indoxacarb, *beta*-cyfluthrin, permethrin, cyfluthrin, cypermethrin, *lambda*-cyhalothrin and chlorfenapyr (named among the "Top 5" used by 22-33% of the pest management professionals surveyed); and thiamethoxam, abamectin, and pyriproxyfen (named among the "Top 5" by 2-10% of the pest operators surveyed). Timing of application for most compounds was found to be throughout the year although few compounds were applied more often either in spring and winter or in the summer.

Another survey of PCOs and LCOs was sponsored by PWG (Winchell and Cyr, MRID 49292101 (*8*)). The survey covered six national regions, excluding California and included both pest control operators (PCOs) and lawn care operators (LCOs). Pyrethroids were associated with 58% of the outdoor insecticide applications overall for all regions. Overall, for all regions the percentage uses were bifenthrin (40%), cyfluthrin/*beta*-cyfluthrin (17%), *lambda*-cyhalothrin (12%), deltamethrin (11%), permethrin (9%), cypermethrin (8%), and other pyrethroids (2%). The percent of LCOs and PCOs that applied

each pyrethroid active ingredient, by use site, is depicted in Figure 1. Seven types of surfaces were investigated of which only a selection is presented in the figure.

Table 1. Service Interval for Residential and Commercial Pesticide Accounts

Service Interval	*Residential (%)*	*Commercial (%)*
Weekly	4	6
Monthly	39	83
Every other month	41	7
Quarterly	12	0
Other	0	4

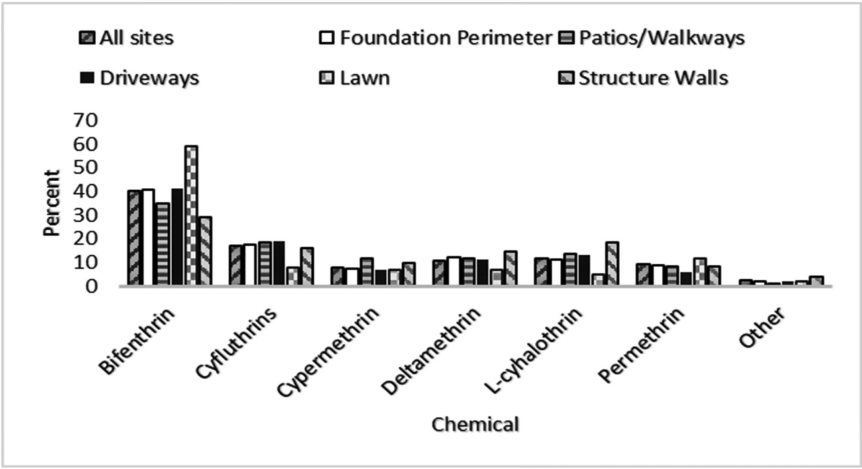

Figure 1. Percent of Respondents' Pyrethroid Active Ingredient Use in Outdoor Applications by Selected Use Sites, Excluding California.

The percent applying pyrethroids to different types of surfaces in an urban environment, including California, is depicted in Figure 2. By far, the foundation perimeter treatments are the most commonly applied by PCOs. Note that all regions but California receive approximately the same number of building foundation perimeter treatments. Meanwhile, lawn treatments are lower. The methodology to estimate California use was different since the questions asked to PCOs and LCOs were different. The foundation perimeters treatment represented an estimated value since this specific question was not asked in California.

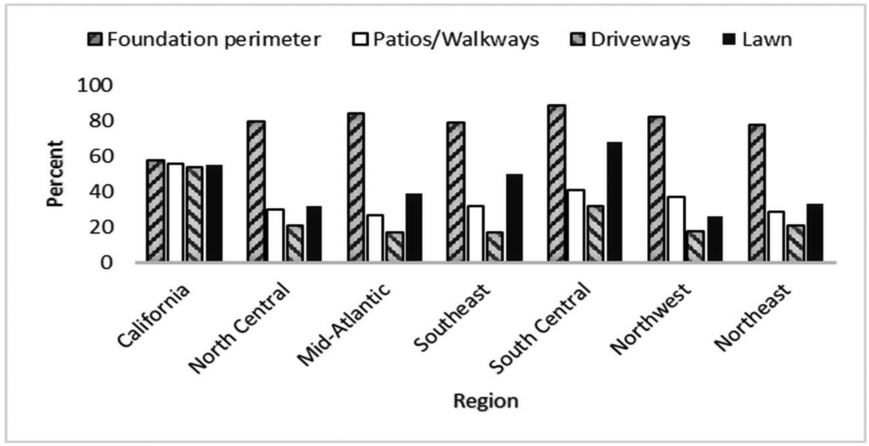

Figure 2. Percent of PCOs and LCOs Applying Pyrethroids to Selected Sites by Region.

The number of applications per year, average area treated, and the active ingredient most commonly used on each of the use sites for all regions, except CA, is summarized in Table 2. Each use site receives on average close to 4 applications per year although the foundation perimeters are treated more often than other use sites, and the fraction of the use site ranges from 36% (driveways away from the garage door or wall) to 77% for lawns. The active ingredient most commonly applied is bifenthrin, irrespective of the use site.

Figure 3 summarized for each active ingredient, the frequency by which PCOs and LCOs responded that they used each active ingredient for each region. This figure confirms that bifenthrin is the active ingredient most commonly used. Note the high use of cypermethrin in the south central region, compared to the other regions. Approximately a two-fold increase of cypermethrin applied as compared to other regions, is unexplained at this time.

These surveys were supplemented by work by Fugate and Hall (*9*), which includes frequency of consumer use of specific insecticides, in and around homes, outdoor non-plant, and lawn and garden in 2011. (This report was not provided to the USEPA. Rather, certain data were extracted and provided in MRIDs 49292101 (*8*) and 49292102 (*10*)). Nationally, the likelihood of consumer use of LCO services to apply fertilizer and chemicals is 14% and consumer use of PCO services is 26%. The likelihood of a consumer to purchase lawn and garden insecticides is 31% and outdoor non-plant insecticides is 15%. The likelihood of a consumer applying lawn and garden insecticide is 47% and outdoor non-plant insecticides is 28%. Bifenthrin is the insecticide most likely to be purchased, followed by *lambda*-cyhalothrin.

Table 2. Averages of Treatments per Year, Fraction of Use Site Surface Area Treated and Pyrethroid Active Ingredient Most Commonly Used by Use Site in Six National Regions, Excluding California

Use Site Type of Surface	*Average Number of Treatments Per Year*	*Fraction of Use Site Surface Area Treated*	*Most Commonly Used Active Ingredient*
Building foundation perimeters	4.25	2.4 ft up; 2.9 ft out	Bifenthrin
Patios and walkways away from building	3.73	44%	Bifenthrin
Driveways away from the garage door and wall	3.66	36%	Bifenthrin
Lawn	3.62	77%	Bifenthrin
Landscape and ornamental areas	3.82	63%	Bifenthrin
Structure walls	3.71	42%	Bifenthrin
Eaves	3.38	44%	Bifenthrin

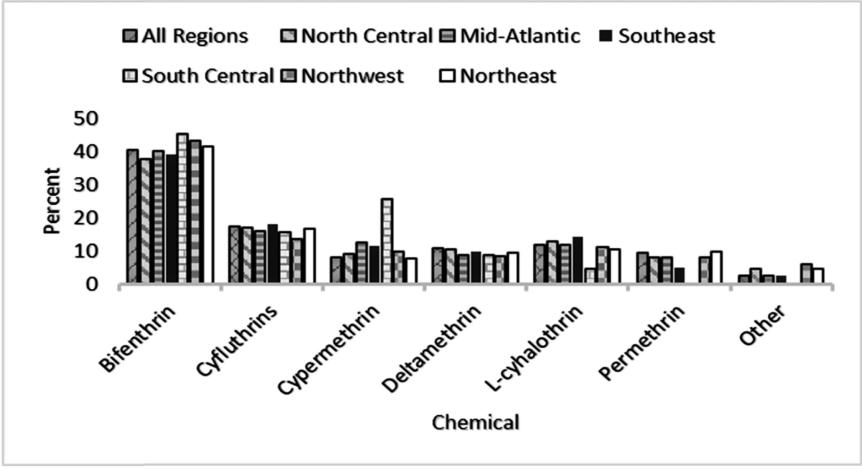

Figure 3. Percent of Respondents' Pyrethroid Active Ingredient Use in Outdoor Applications by Region, Excluding California.

Winchell (*10*) (MRID 49292102 (*10*)) provided an interpretation of the following studies: MRIDs 48762913 (*7*), 49292101 (*8*), Wilen (*3*), and the work by Fugate and Hall (*9*). Winchell used certain data manipulations to derive suitable variables, with the potential to be useful in modeling for aquatic exposure in an urban environment. These manipulations were different for CA and other regions of the U.S. due to differences in survey design. These variables for aquatic modeling include 1) the fraction of the use site treated with each active ingredient; 2) the seasonal application frequency made to each use site; and, 3) the percentage of the use site's surface area that is treated. The work by

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Fugate and Hall (*9*) helped to establish the extent of pyrethroid use in different geographical regions of the U.S. (compared to other insecticides), and the fraction of the households receiving pyrethroid applications outdoors (including LCOs, PCOs, and resident's applications), and to compare against the 2010 and 2013 results. Regarding the frequency of applications, it was estimated that in CA, it ranged from 4-8 per year, while in other regions of the U.S., it ranged from 4-5 per year. The percentage of the use site surface area, treated with pyrethroids was not asked in the CA surveys and data for other regions of the U.S. would be used to cover CA.

Value of Surveys

These reports include data on the frequency of homeowners using lawn care or pest control services, the frequency of consumers using outdoor non-plant and lawn & garden insecticides, and data on the frequency of a consumer using specific insecticide active ingredients. The datasets provided the starting point to determine the overall likelihood of an individual homeowner using an applicator service, and then from the survey responses, determine the likelihood by region and use site of the top six pyrethroids being used by both professional applicators and/or homeowners themselves.

Of all the above surveys, it is apparent that the most recent ones, conducted in 2009 and 2013 (MRIDs 48762913 (*7*), 49292101 (*8*), and 49292102 (*10*)), with supplemental data from Wilen (*3*), and Fugate and Hall (*9*), may be used to estimate the needed usage and the amount of pesticide applied on each use site per region. The studies have the potential to establish the conceptual model for outdoor pesticide exposure for a variety of outdoor use sites, along with percent/type of areas treated, and, with the help of the washoff studies, the percent of pesticide available for wash-off, and other possible sources of pesticide contamination (*i.e.*, drift, contaminated airborne particles and others). But more than that, they could be used in characterizing and refining exposure and in finding mitigation measures to reduce exposure, such as frequency/seasonality of applications, and most frequently used application rate, frequency, equipment, and formulations (typical application pattern), percent area treated by each use site, *etc*. Winchell (*10*) (MRID 49292102 (*10*)) synthetizes previous useful studies in tables that are suitable to do the above tasks for the pyrethroid insecticides.

Modeling Approach for Stormwater Discharges

The Environmental Fate and Effects Division (EFED) currently obtains estimated exposure concentrations (EECs) by modeling the residential and impervious scenarios in the Pesticide Root Zone Model coupled with the Exposure Analysis Modeling System (PRZM/EXAMS). Two PRZM/EXAMS runs are executed for each application type/weather combination. The application types are dependent on the label and may include three types of applications: (1) application to pervious areas alone with drift to adjacent impervious surfaces such as application to a lawn and/or garden adjacent to impervious driveway and/or

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porch; (2) application to impervious surfaces alone with drift to adjacent pervious surfaces such as application to driveway and/or porch adjacent to a lawn and/or garden; or (3) a combined application to pervious and impervious surfaces such as application to both impervious driveway and/or porch and to the lawn and/or garden).

At the present time, the CA impervious PRZM scenario is considered as the most suitable available modeling approach for impervious runoff. The PRZM CA impervious scenario may be used in the Tier 2 coupled aquatic models PRZM/EXAMS along with the CA residential or other appropriate scenario such as CA rights-of-ways (ROW) to obtain EECs. The "residential" and various other "urban" use patterns require the PRZM CA residential and CA impervious scenarios for modeling. Both scenarios are run separately. This approach assumes that no watershed is completely covered by either the ¼ acre lot (the basis for the residential scenario) or undeveloped land (the basis for the ROW scenario), for residential and ROW use patterns, respectively. By modeling a separate scenario for impervious surfaces, it is also possible to estimate the amount of exposure that could occur when the pesticide is over-sprayed onto this surface. Using two scenarios in tandem requires post-processing of the modeled output in order to derive a weighted EEC that represents the contribution of both the pervious (*i.e.*, residential and ROW scenarios) and the impervious surfaces. Exposure from both scenarios can also be weighted and aggregated. The second critical assumption is that 50% of a ¼ acre lot will be pervious and 50% impervious. In addition to the footprint of the typical house, it is assumed that a typical house would have a driveway of approximately 25 by 30 feet or 750 square feet and roughly 250 square feet of sidewalk. A typical suburban home could also be assumed to have roughly 300 square feet of deck space and 900 square feet of garage. Finally, it is assumed that a substantial portion of the typical home would be planted in landscaping (*e.g.*, residential lawn and/or ornamentals) with an estimate of 2,000 square feet. The sum of all these areas is 5,200 square feet. Taking a total ¼-acre lot size of 10,890 square feet and subtracting the house square footage yields a total remaining area of 5,690, or roughly 50% of the total lot untreated area. The residential and impervious scenarios are parameterized to represent a California urban site. For modeling uses in other metropolitan regions (not located in California), the residential and impervious scenarios can be run with meteorological files from other locations of the U.S.

Pathway Identification Study

The main objective of this study (Davidson *et al.*, MRID 49137401 (*11*); and Davidson *et al.* (*12*)) was to identify the major transport mechanisms of pyrethroids from a range of outdoor residential applications and determine the effects of mitigation measures put in place by the USEPA to control off-site transport. The study was conducted at a test facility which represented typical California residential developments. It consisted of six replicate house lots which included front lawns, stucco walls, garage doors, driveways and residential lawns. The off-site movement of different pyrethroids applied to these surfaces

(representing pervious and impervious surfaces) was assessed using irrigation and simulated artificial rainfall to complement the natural rainfall events. The results showed that natural and simulated rainfall events contributed to the majority of mass loss compared to the mass loss due to lawn irrigation. Runoff losses expressed as a percentage of chemical applied were highest for the driveway and garage door surfaces compared to grass lawn, grass perimeter and house wall surfaces. Also, a comparison of historic applications with revised application due to label changes showed that the amount of losses from garage and driveway were dramatically reduced (40 times lower) using the revised application practices.

Washoff/Runoff Study from Impervious Surfaces

The main objective of the study was to examine the potential for simulated rain to washoff of a pyrethroid (cypermethrin) that had been applied to different external building materials using two different representative formulations (Trask *et al.* (*13*); MRID 48072902 (*14*)). The building materials selected were those typically used for construction of residential/urban structures in California that may receive applications of pyrethroids. These included: clean painted/unpainted concrete, clean painted/unpainted stucco, clean painted/unpainted wood with a dusty surface, clean vinyl/aluminum siding and clean asphalt. Washoff quantified as percent of applied mass of cypermethrin ranged from <0.01/0.07 to 16.8/11.3% for the two representative formulations. Clean vinyl siding had the highest percent of applied cypermethrin in runoff whereas clean unpainted stucco had the least amount of cypermethrin in washoff. All building materials had similar runoff volumes except for the clean asphalt which was lower in comparison.

Runoff Losses from Treated Turfgrass

In a study conducted in 2008, the authors examined the potential of pyrethroid insecticides uses on turf to contribute to residue detections in Sacramento, CA urban sediments, particularly due to over irrigation (*i.e.*, irrigation producing excess runoff) (Hanzas *et al.* (*15*); and MRID 47647801 (*16*)). Model pyrethroids included bifenthrin and *beta*-cyfluthrin in both granular and liquid formulations. Four treated turf plots were prepared, using normal irrigation or three over irrigation events. Runoff flow was measured during the irrigation events and runoff samples taken and analyzed for bifenthrin and *beta*-cyfluthrin. For the bifenthrin over irrigated plots, during the first irrigation event, 0.052-0.081% of the applied chemical was found in runoff, while no reported bifenthrin was found in the non-over irrigated plots. Meanwhile, for *beta*-cyfluthrin, 0.23-0.58% of the applied was found in runoff of the first over irrigation, with no runoff in the non-over irrigated plots. During the normal simulated rainfall event, simulating a winter storm, the amount of chemical present in runoff was much smaller (≤0.011% of the applied for all chemicals and formulations). It was noted that for *beta*-cyfluthrin, the majority of the chemical loss occurred during the first over

irrigation event while for bifenthrin the loss was more evenly distributed across three over irrigation events, particularly for the granular formulation.

Monitoring of Urban Waters

Two recent extensive reviews are available on monitoring of urban pesticides in receiving water bodies in the United States, especially in California. The first review was submitted to US EPA by the PWG covering available data for synthetic pyrethroid in surface water and sediment in the United States (Giddings, *et al.*, MRID 49314703 (*17*)). The second review was conducted for the California Stormwater Quality Association (CASQA) and the County of Sacramento covering monitoring data from California urban watersheds on pyrethroids and fipronil toxicity (Ruby, MRID 49354001 (*18*)). This section deals with only few examples of targeted surface water/sediment monitoring data for pesticides used outdoors. Therefore, selected chemistry data are included herein with emphasis on pesticides used in urban areas and reaching surface waters mainly by urban runoff into surface waters (urban creeks and lakes and rivers passing through urban areas). Urban runoff water, contaminated with urban pesticides, is usually pumped, drained and/or naturally flow into these water bodies. Many factors will affect detected concentrations in these water bodies such as the pesticide physical/chemical and fate properties; labeled use patterns; pattern of timing of the application; application procedure; usage intensity (depends mainly on pest pressure which is associated with many factors such as climate); hydrological setting, urban drainage (sources/quantities); and characteristics of urban areas/receiving waters, climatic conditions. Effects of these factors, will be included when reported.

Monitoring of Stormwater Discharges and Affected Water Bodies

Urban areas stormwater discharges and affected water bodies were extensively monitored in California. Targeted monitoring data in these studies were for stormwater discharges and affected water bodies (water and underlying sediment). In the first study, monitoring data were for eight pyrethroids and the organophosphate insecticide chlorpyrifos (*19*). In the second study, monitoring data were for 63 insecticides/herbicides/degradates in the water column plus nine pyrethroids and chlorpyrifos in water and underlying sediment (*20*). For northern California, the first study included the city of Vacaville and urban areas along the American River, Sacramento River and San Joaquin River (the cities of Folsom, Cordova, Sacramento and Stockton) while the second study included the cities of Roseville, Martinez/Pleasant Hill, Stockton and Dublin. For southern California, the second study included urban areas of Laguna Nigel, AlisoViejo, San Diego, and Lakeside (Figure 4). Sampling events took place during or shortly after rain events (Rain) and during the dry season (Dry). Sources of pesticides contamination were verified to be stormwater run-off from treated residential areas during the rainy season and landscape water run-off from treated landscaped areas during the dry season.

In Describing the Behavior and Effects of Pesticides in Urban and Agricultural Settings; Jones, et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2014.

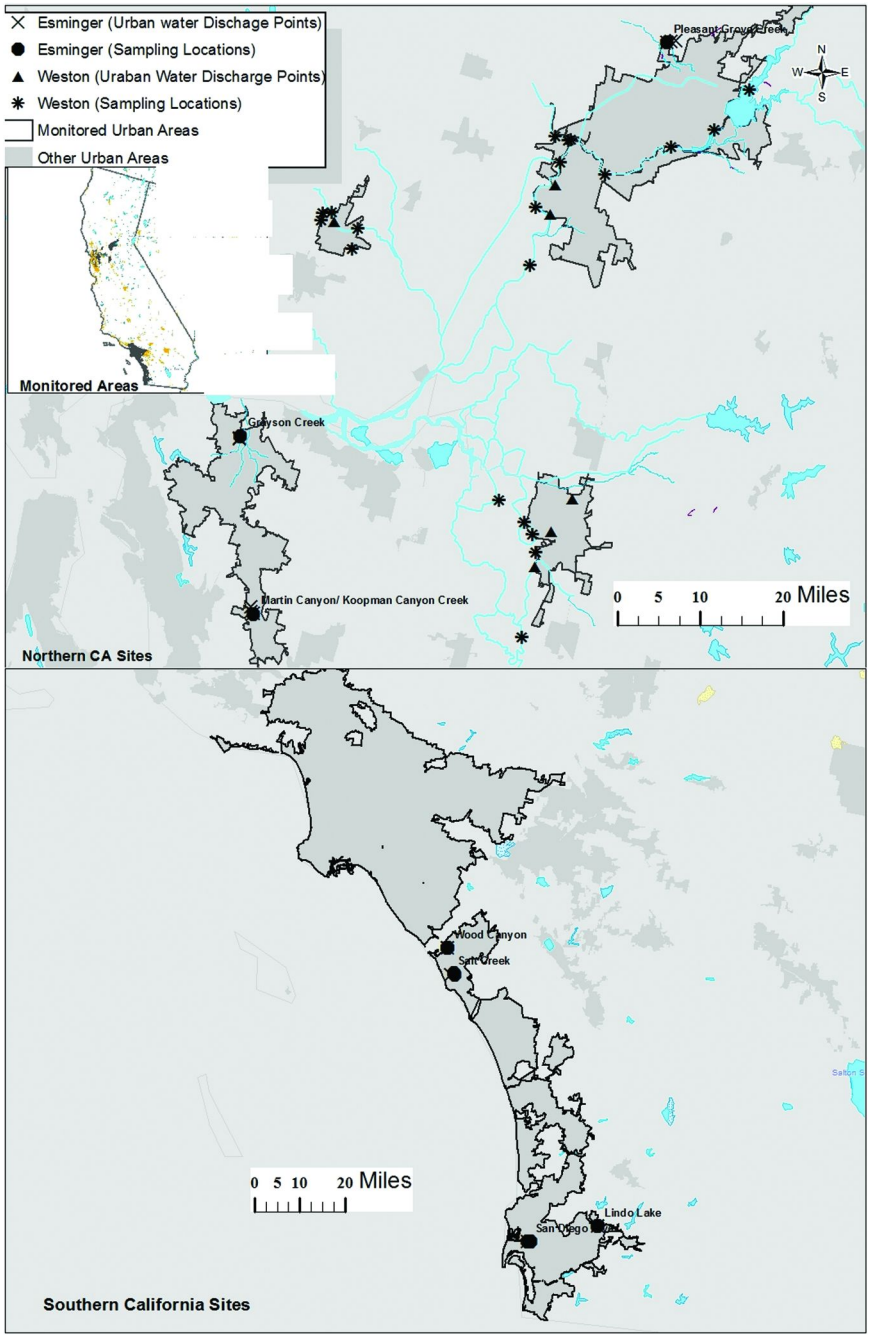

Figure 4. Monitored urban areas in Northern and Southern California (Weston and Lydy (19); and Ensminger and Kelley (20)).

In the Weston and Lydy study (*19*), concentrations detected in sump waters were high enough to be of toxic concern and were found to be related to either the pyrethroids or chlorpyrifos based on the toxicity identification evaluation (TIE) data. This was also confirmed by chemical analyses and comparison to known toxicity thresholds. Chemical analyses of 33 sump water samples show that the overall percentage of samples containing concentrations exceeding 1 ng/L ranged from 3 to 79% for eight pyrethroids and chlorpyrifos. The majority of the samples contained bifenthrin (79%) and chlorpyrifos (77%) with lesser percentages containing: permethrin (61%), cyfluthrin (55%), λ-cyhalothrin (*lambda*-cyhalothrin, 45%), cypermethrin (33%), deltamethrin (12%), esfenvalerate (6%) and fenpropathrin (3%). As expected, pesticides in sump waters that were discharged (by pumping) into receiving creeks and rivers were diluted to lower levels. Varied levels of pesticides and toxicity were found in receiving creeks and rivers as it passed through the urban areas of Sacramento (the Sacramento River), Stockton (the American River) and Vacaville (two urban creeks). Water column toxicity, related to the pyrethroid bifenthrin, was not observed in the Sacramento River but was evident along the urban creeks, the American river, and at only one site in the San Joaquin River. For example, no evidence of contamination with pyrethroids and toxicity was observed upstream in the water as the creeks enter the city of Vacaville while a high level of toxicity was observed in waters leaving the city downstream. In these water samples, pyrethroid concentrations were 4-10 times the toxicity with, bifenthrin and cyfluthrin providing most of the toxic units (TU). The level of pesticide contamination in receiving waters appeared to be related to the intensity of rain events. For example, no toxicity was observed in water samples taken from the San Joaquin River near Stockton just after the first rain event, but toxicity was evident, in one location at the edge of the city, following a more intense second rain event. Again, water toxicity was established to be related to pyrethroids as it contained 0.7 TU of bifenthrin and 0.3 TU of permethrin.

Monitoring data from the Ensminger and Kelley (*20*) study may be considered as an example of concentrations and detection frequencies (DFs) for registered and extensively used pesticides in urban areas. Therefore, data from this study are summarized herein for reported DFs and concentrations of insecticides, herbicides and pyrethroids detected in urban drain waters (DRNs) and receiving water bodies (RWBs) during dry (Dry) and rainy (Rain) seasons. Table 3 contains reported sampling information and abbreviations used in this summary and associated graphs. In the summary, statewide data reported for all locations in the study are used to obtain maximum and minimum concentrations and DFs for each pesticide. DFs are calculated for each pesticide as percent (%) from the number of samples containing that pesticide over the detection limit (number of detects) divided by the total number of samples (number of detects plus non-detects; trace detections were considered, in this summary, as non-detects). The summary includes data on pesticides that were most frequently detected in the samples of DRNs and RWBs during Dry and Rain events. The number of samples for each urban area are included in the summary table as it is an important indicator for intensity of sampling (Table 3).

Table 3. Reported Sampling Information and Abbreviations Used in the Summary of Ensminger and Kelley (*20*) Statewide Monitoring Data

Urban Area	*City (Source Of Urban Runoff Water "Drn")*	*Receiving Water Body "Rwb"*	*Sampling Season*	*Number Of Samples (N)* [1]					
				Insect[2]		*Herb*[3]		*Pyreth*[4]	
				Drn	*Rwb*	*Drn*	*Rwb*	*Drn*	*Rwb*
Sacramento **"Sac"**	Roseville	Pleasant Grove Creek	Dry	14	5	12	4	8	3
			Rain	12	4	12	4	9	3
San Francisco Bay **"Sfb"**	Martinez/Pleasant Hill; And Dublin	Grayson Creek; And Martin Canyon/Koopman Canyon Creek	Dry	20	8	20	8	10	4
			Rain	17	7	17	7	12	5
Greater Los Angeles (Orange County) **"Orn"**	Laguna Nigel; And Aliso Viejo	Salt Creek; And Wood Canyon Creek	Dry	23	9	24	10	9	3
			Rain	4	2	4	2	None	None
San Diego **"Snd"**	San Diego; And Lakeside	San Diego River; And Lindo Lake	Dry	14	10	14	10	None	None
			Rain	5	2	5	2	None	None
Statewide			Dry/Rain	8	8	8	8	5	5

[1] ***Number of Samples (n)*** = The total number of samples for each sampling event. For example, in the Sacramento area (SAC), insecticides were monitored in 14 drain water samples (DRN) during the dry season (Dry) and in 12 drain water samples (DRN) during the rainy season (Rain). Additionally, insecticides were also monitored in 5 receiving water samples (RWB) during the dry season (Dry) and in 4 receiving water samples (RWB) during the rainy season (Rain). [2] ***Insect*=** Monitored Insecticides: carbaryl (carb), chlorpyrifos (Chl) diazinon (Diaz), fipronil (Fip), fipronil degradates (FipD= desulfinyl fipronil, desulfinyfepronil amide, fipronil amide, fipronil sulfide, and fipronil sulfone), malathion (Mal), and oxamyl (oxa). [3] ***Herb*=** Monitored Herbicides: 2,4-D (2,4-D), ACET, bromacil (Brom), dicamba (Dicam), diuron (Diur), MCPA, oryzalin (Oryzal), oxyfluorfen (Oxyfl), pendimethalin (Pendi), prodiamine (Prodi), prometon (Promet), simazine (Simaz), triclopyr (triclo) and trifluralin (Trifl). [4] ***Pyreth*=** Monitored Pyrethroids: bifenthrin (bif), cyfluthrin (Cyf), λ-cyhalothrin (λ-cyh), cypermethrin (cyp), fenvalerateesfenvalerate (FenEsV) and permethrin (Per= *cis* and *trans*).

In this summary, concentrations and DFs for each pesticide are examined in DRNs vs. RWBs, Dry vs. Rain, and in varied geographical locations. The objectives are to summarize reported data as DFs and concentrations for pesticides detected in urban surface waters and examine the effects of dry flow vs. rainstorm flow and geographic location on these parameters. Summaries are established for the top five insecticides, five herbicides and all of the monitored pyrethroids.

Insecticides Detection Frequencies/Concentrations

The top five insecticides that were frequently detected in source and receiving waters include carbaryl, fipronil, fipronil degradates (total of desulfinyl fipronil, desulfinyfipronil amide, fipronil amide, fipronil sulfide, and fipronil sulfone), malathion, and diazinon (Figure 5). The insecticides chlorpyrifos and oxamyl were not in the top 5 because they were both less frequently detected in DRNs (DF = 8-24% "N = 2" and 4% "N = 1", respectively) and oxamyl was not detected in RWBs although chlorpyrifos was at a DF of 29% (N=1).

A summary is calculated from reported monitoring data for each insecticide as follows:

(1) For each geographic location (SAC, SFB, ORN and SND), the Max/Min DFs and concentrations are calculated separately for DRN waters (Dry and Rain) and RWBs (Dry and Rain) from the Dry and Rain data;
(2) A statewide Max/Min DFs and concentrations are calculated for DRN waters and RWBs separately from the combined SAC, SFB, ORN and SND values arrived at from step 1;
(3) Each set of statewide values, such as Carb-DRN or Carb-RWB, was calculated from eight data entries (N = 8 = 2 x 4; two each for SAC, SFB, ORN and SND) and in case of no detection the value of N will be <8 and no detection at all the value of N will be zero.

Data in Figure 5 show that the most frequently detected insecticides in source and receiving waters were carbaryl, fipronil and fipronil degradates (75-100%; N= 4-6). The organophosphate insecticides malathion, and especially diazinon, were detected at lower range of frequencies (24-100%; N= 2-5). Data show no apparent differences in DFs between source waters (DRN) and receiving waters (RWB) possibly due to proximity of sampling in location and timing. Except for fipronil, the maximum detected concentrations for the top 5 insecticides ranged from 0.1 to 0.8 µg/L. For fipronil, the maximum was 2.1 µg/L observed in DRN waters from Orange County. As expected, maximum chemical concentrations in drain waters were higher than those detected in receiving water bodies (2 to 5x) reflecting the effect of dilution. It is also noted that both chlorpyrifos and diazinon are still being detected despite drastic reduction in urban use resulting from EPA's regulatory actions. As pointed out by the most recent USGS report on trends in pesticides in the US rivers and streams, concentrations of diazinon declined, by nearly two orders of magnitude, in urban streams across the country from the year 2003 to 2008 due to phasing out of its use (*21*). However, the report pointed out

that use of new or alternative pesticides, such as fipronil, caused a widespread increase in fipronil concentrations in urban streams. An observed, trend in fipronil concentrations in 12 locations throughout the U.S. shows concentration increase in 10 locations with a decrease in only one location in NC and no change in one other location in TX.

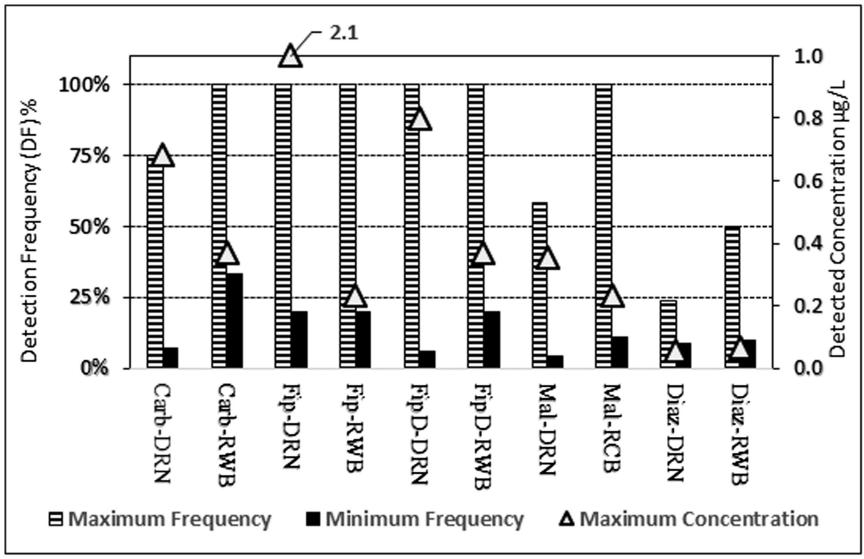

Figure 5. A summary graph for the top five insecticides frequently detected in source drain water (DRN) and receiving water bodies (RWB) in four of the major urban areas of California.

Herbicides Occurrence Frequencies/Concentrations

The top five herbicides that were frequently detected in source and receiving waters were 2,4-D, triclopyr, dicamba, diuron and MCPA (Figure 6). Other herbicides were detected at lower DFs and concentrations.

Data in Figure 6 show that the most frequently detected herbicides in receiving waters were 2,4-D, triclopyr, and diuron (75-100%; N= 6-8). Slightly lower DF were observed for dicamba and MCPA (67-100%; N=3-6). Except of dicamba, the maximum detected concentrations for the top 5 herbicides ranged from 6.7 to 27.6 µg/L. For dicamba, the maximum was 3.1 µg/L observed in DRN waters from the Sacramento area. In drain waters, the maximum concentrations of four of the top five herbicides (MCPA, dicamba, diuron and 2,4-D), in drain waters, were higher than those detected in receiving water bodies (1.1 to 51x) reflecting variable effect of dilution. In contrast, the maximum concentrations of triclopyr in DRN waters were much lower (0.2x). Results obtained for triclopyr may be explained by the possibility that receiving waters at these locations may have been

contaminated with this herbicide before the point of DRN discharge. Although the DFs for herbicides are higher than insecticides, both data show no apparent differences in DFs between source waters (DRN) and receiving waters (RWB).

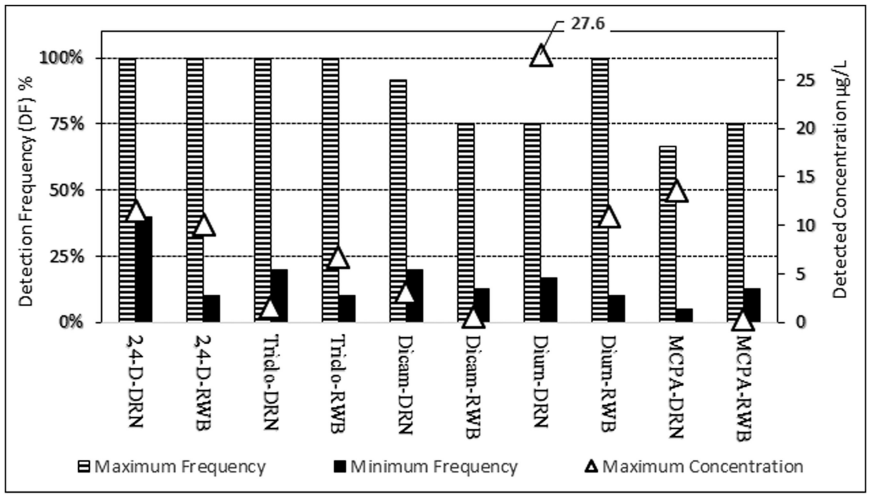

Figure 6. A summary graph for the top five insecticides frequently detected in source drain water (DRN) and receiving water bodies (RWB) in four of the major urban areas of California.

Pyrethroids Occurrence Frequencies/Concentrations

Pyrethroid insecticides that were frequently detected in source and receiving waters included bifenthrin, cyfluthrin, λ-cyhalothrin, cypermethrin, fenvalerate/ esfenvalerate and permethrin (Figure 7). The pyrethroid bifenthrin was detected in all source and receiving water samples with DFs ranging from 56-100% (N= 3-4) followed by permethrin with a range of 20-33% (N= 1-3). DFs for the other pyrethroids were much lower than bifenthrin and permethrin as they were in the range of 0-22% (N= 0-1).

Detected concentrations of pyrethroids in source and receiving waters ranged from 0-203 ng/L. In all of the monitoring events, higher pyrethroid concentrations were observed in source waters (DRNs) as compared to receiving water bodies (RWBs). Source water concentrations were 1.6-7.3 times higher than receiving waters in 4 out of 6 monitoring events and no pyrethroid was detected in the receiving waters of two out of the six events. This is probably a result of partitioning of the pyrethroids to the organic carbon in suspended/underlying sediments of receiving water bodies.

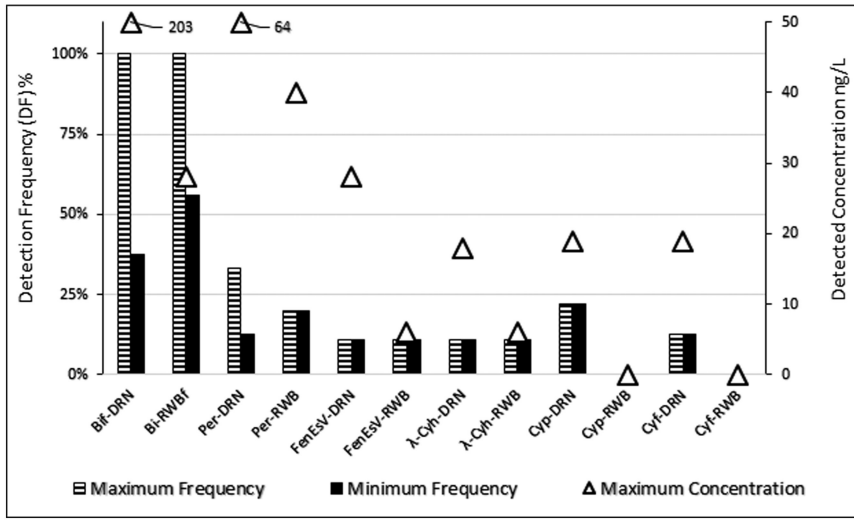

Figure 7. A summary graph for pyrethroid insecticides frequently detected in source drain water (DRN) and receiving water bodies (RWB) in three of the major urban areas in California.

Variations Associated with Geographical Locations

Variations in both concentrations and DFs are summarized in two ways based on the reported monitoring data for the four major urban areas of California. The first is by comparing maximum DFs of the insecticide in all monitoring events (DRN/Dry, DRN/Rain, RCB/Dry and RWB/Rain; referred to as the DFs comparison). The second is by comparing maximum/minimum DFs and maximum concentrations detected in the major source of contamination; that is the storm water drains in the two monitoring events (DRN/Dry and DRN/Rain; referred to as the DRN DF/Concentration comparison). The two types of comparisons are conducted herein for insecticides, herbicides and pyrethroids.

For insecticides, Figure 8 shows differences in the maximum DFs of monitored insecticides between various urban locations in the state of California.

The DFs comparison show that all of the top five insecticides were detected, in varied maximum DFs, in three of the major urban areas of California (SFB, ORN and SND). Diazinon was the only insecticide that was not detected in SAC area. It is also apparent that urban areas of southern California (ORN and SND) show higher maximum DFs, for these five insecticides, compared to the northern urban areas of the State (SAC and SFB). Observed differences could be a reflection of expected higher insecticides usage in the hot climate of the south as compared to the northern part of the State.

Figure 9 shows differences in DFs and concentrations detected in storm waters reflecting the contribution of this important source of insecticides reaching surface waters.

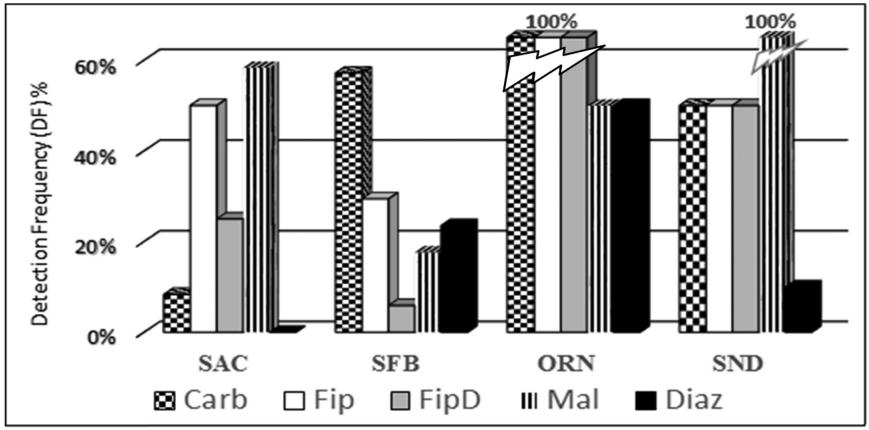

Figure 8. Maximum detection frequencies (DFs) for the top five insecticides detected in source/receiving waters of four of the major urban areas of California (SAC= Sacramento, SFB= San Francisco Bay, ORN= Orange County and SND= San Diego).

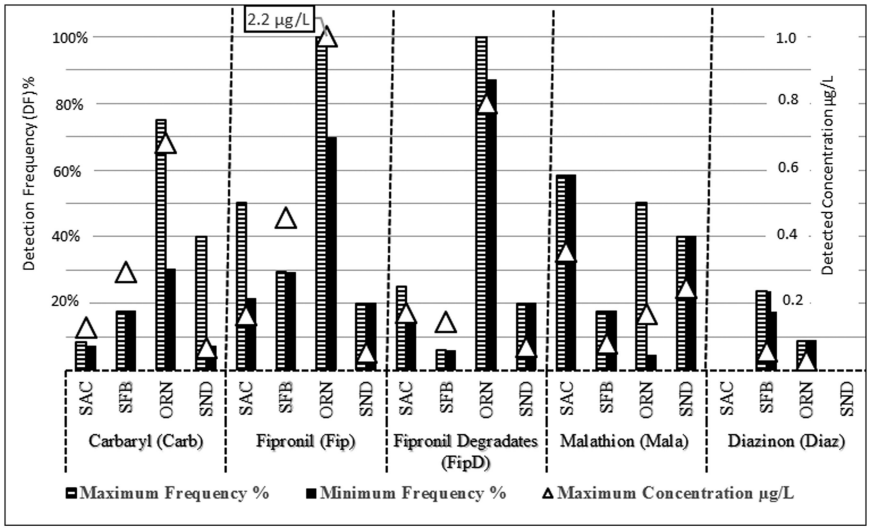

Figure 9. Max/min Detection Frequencies (DFs) and maximum concentrations of major insecticides detected in source drain waters (DRNs) in Sacramento (SAC), San Francisco Bay (SFB), Orange County (ORN) and San Diego (SND) urban areas of California.

The DRN DF/concentration comparison show variations in the insecticide load of the storm water. ORN County appears to have the highest detections for three out of the four insecticides (Carb, Fip, and FipD) and the second highest for the other two insecticides (Mal and Diaz). Data also show that maximum DFs appear to be associated with higher concentrations detected in the storm water in all of the four urban areas.

For herbicides, similar analyses was conducted (not shown) and results show that all of the top five herbicides were detected, in varied maximum DFs, in all of the major urban areas of California. Herbicides were detected at higher DFs than 40%, except for MCPA which was detected at a DF of 13% in ORN, 20% in SND. ORN showed the highest DFs of three herbicides (2,4-D, Triclo, and Diurn) followed by SAC with the lowest being the SND area. The herbicide 2,4-D was the most frequently detected in all of the four area followed by triclopyr in SFB and ORN. MCPA had the least DFs ranging from 13 to 75% with the least DFs in ORN followed by SND, SFB and SAC (highest).

DRN DF/concentration comparison show that ORN county with the highest detections for three out of the four herbicides (2,4,-D, Triclo and Diur) and the 3rd and 4th highest for the other herbicides (Dicam and MCPA). Data also show that maximum DFs do not always coincide with higher concentrations detected in the storm water. For example, SAC had the lowest DF of diuron compared to the other three areas of California but had the second highest observed concentrations and SFB had the 3rd DFs associated with the highest concentrations. Additionally, data on the maximum concentrations observed in source and receiving waters are summarized in Figure 10.

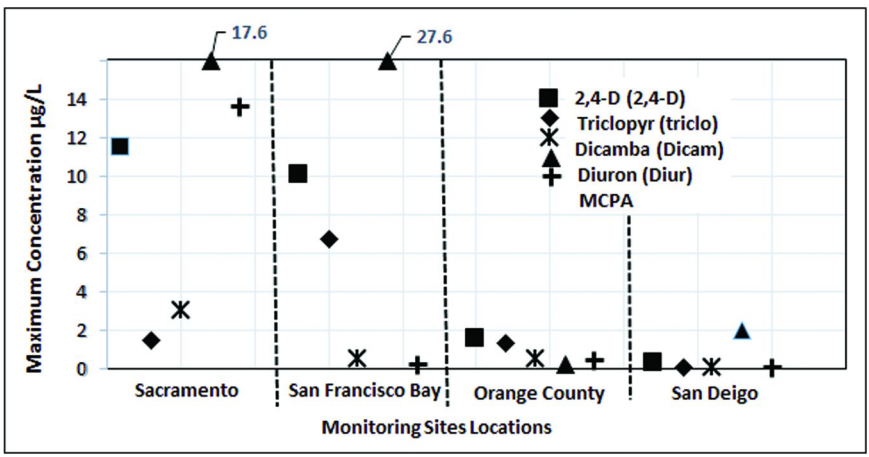

Figure 10. Maximum concentrations of herbicides detected in urban monitoring data from Northern and Southern California.

The summary shows that higher concentrations of the top 5 herbicides (>6.8 to 27.6 µg/L) were observed in source and receiving waters of Northern California urban areas (SAC and SFB) compared to ORN and SND of southern California (<2 µg/L). In Northern California, observed maximum diuron concentrations were the highest (17.6 to 27.6 µg/L) followed by 2, 4-D with maximum concentrations ranging from 10.1 to 11.5 µg/L. The MCPA maximum concentration was highest in SAC area (13.6 µg/L) while triclopyr was highest in SFB area (6.75 µg/L).

Similar analyses was performed on the pyrethroids data which includes only three urban areas SAC, SFB and ORN; SND was not monitored. Results of the DRN DF/concentration comparison show that bifenthrin was detected in DRN waters in the three monitored areas with maximum DFs/concentrations of 56%/26 ng/L), 93%/33 ng/L) and 100%/203 ng/L). The other four pyrethroids were only detected in SAC (cyfluthrin with DF/concentration of 13%/18.9 ng/L and cypermethrin with DF/concentration of 22%/18.9 ng/L), ORN (λ-cyhalothrin with DF/concentration of 11%/18.0 ng/L and fenvalerate/esfenvalerate with DF/concentration of 11%/28.0 ng/L). Additionally, data on the maximum DFs/concentrations observed in source and receiving water are summarized in Figure 11.

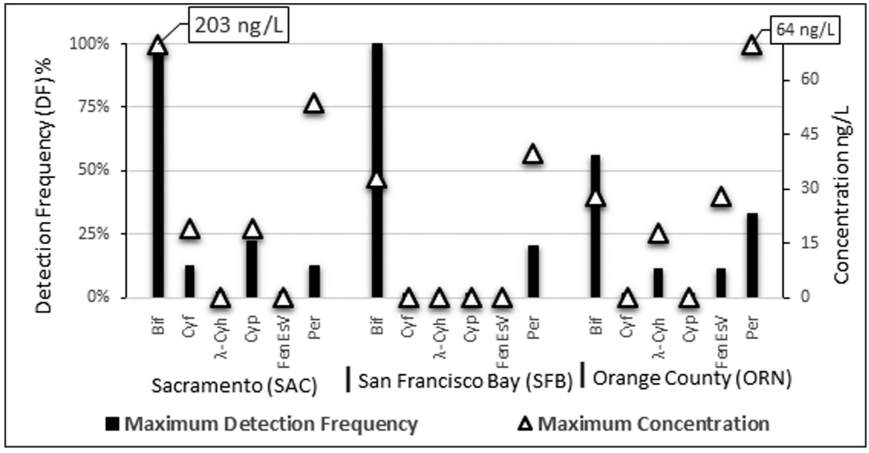

Figure 11. Observed maximum detection frequencies (DFs)/concentrations for pyrethroids detected in source/receiving waters of three major urban areas of California (San Diego (SND) not monitored).

Summary data indicate that the maximum DFs for bifenthrin were 100% in SAC/SFB areas and 56% in ORN County area. In the SAC area, the maximum observed concentrations of bifenthrin, permethrin, cypermethrin and cyfluthrin were 203, 53.9, 18.9 and 18.9 ng/L, respectively. In SFB area, only permethrin and bifenthrin were detected at maximum concentrations of 40 and 33 ng/L. Finally, in ORN County the maximum observed concentrations were 64 ng/L for permethrin, 28 ng/L for bifenthrin, 28 ng/L for fenvalerate/esfenvalerate and 18 ng/L for λ-cyhalothrin.

Variations Associated with Wet/Dry Conditions

Urban pesticides are mainly transported from application sites into surface waters by urban runoff waters resulting from rain storms and/or irrigation. It is thus expected that DFs and concentrations in drain and receiving waters to be related to pesticide properties (persistence and solubility), water availability (rain and irrigation), and timing of application. Additionally, application rate and frequency of application are expected to play a role in determining expected pesticide concentrations in surface waters as these factors are important in determining the pesticide load in quantity and timing. The latter factors can be deduced from usage data.

The results of the monitoring study indicated that most pesticides were detected during wet than dry conditions. One exception was fipronil and its degradates which were detected at higher frequency during dry flow in ORN County. Other reported results included the following: (1) First rainstorm gave the highest DFs in all of monitored site except in ORN county; (2) Detection of fipronil and its degradates with the first storm was similar to dry flow conditions and correlated with usage in Northern California; (3) Pesticides used in urban areas may show continuous load, similar to fipronil, independent of rain; (4) Bifenthrin had high detections associated with rain events although it is mostly applied during the dry season; and (5) Herbicides had more frequency of detections during the rainy season which coincides with timing of its application. Furthermore, the authors used the difference between DFs during wet flow and DFs during dry flow as an indicator for the influence of rain on pesticide detections. The results indicate that most of the pesticides are influenced by rain giving higher detection with the exception of fipronil degradates. Rain appeared to cause the highest detections for bifenthrin followed by diuron, MCPA, 2,4-D, malathion, dicamba, triclopyr, pendimethalin, carbaryl and fipronil (lowest).

The influence of dry and rain conditions on DFs and concentrations was examined based on monitoring data from stormwater ouflows (DRN) using bubble graphs and an example of these graphs is shown in Figure 12 for the top five frequently detected insecticides. DRN data were used because it reflect pesticide load carried out by run-off. In general, Figure 12 shows, that larger number/size and higher positions are for detections following rain compared to small number/size and lower positions for detections associated with dry flow. This is true for almost all of the examined insecticides, except of carbaryl, fipronil and fipronil degradates observed in ORN County.

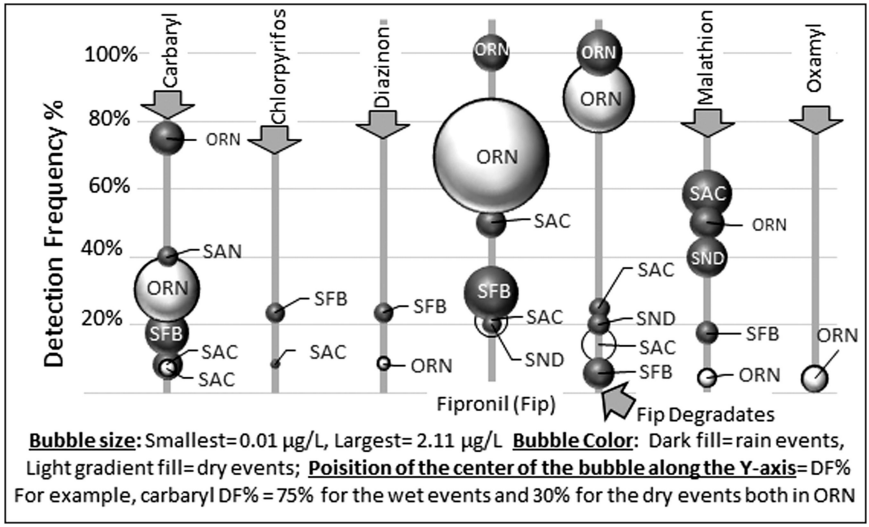

Figure 12. Influence of dry and rain flow conditions on DFs and concentrations of insecticides in the urban areas of Sacramento (SAC), San Francisco Bay (SFB), Orange County (ORN) and San Diego (SND).

Sediment Monitoring

Stream bed sediment samples were collected, during dry flow conditions, in creeks, a river, and a lake receiving waters from identified storm drains of five urban areas in Northern and Southern California (CA-N and CA-S) (*20*). The CA-N site was from Grayson creek receiving stormwater from the mixed residential/commercial urban area of Martinez/Pleasant Hill in the San Francisco Bay area. The CA-S sites were from Salt Creek, Wood Canyon Creek, San Diego River, and Lindo Lake receiving storm waters from the mostly residential or mixed residential/commercial urban areas of Laguna Nigel (Orange Co.), Aliso Viejo (Orange Co.), San Diego and Lakeside cities, respectively (Figure 13). In this California study, sediment samples were analyzed for 9 pyrethroids and chlorpyrifos and only 8 pyrethroids were identified. The pyrethroid fenpropathrin and the insecticide chlorpyrifos were not detected.

In another study, occurances and potential sources of pyrethroids in stream bed sediments from seven U.S. metropolitan areas were assessed. Sediment samples were collected in 2007 from 98 urban streams within the metropolitan areas of Atlanta, GA (ATL); Boston, MA, NH (BOS); Dallas−Fort Worth, TX (DAL); Denver, CO (CO); Milwaukee−Green Bay, WI (MGB); Seattle−Tacoma, WA (SEA); and Salt Lake City, UT (SLC) (*22*) (Figure 13). In this national scale study, sediment samples were analyzed for 14 pyrethroids and reported data were for five pyrethroids.

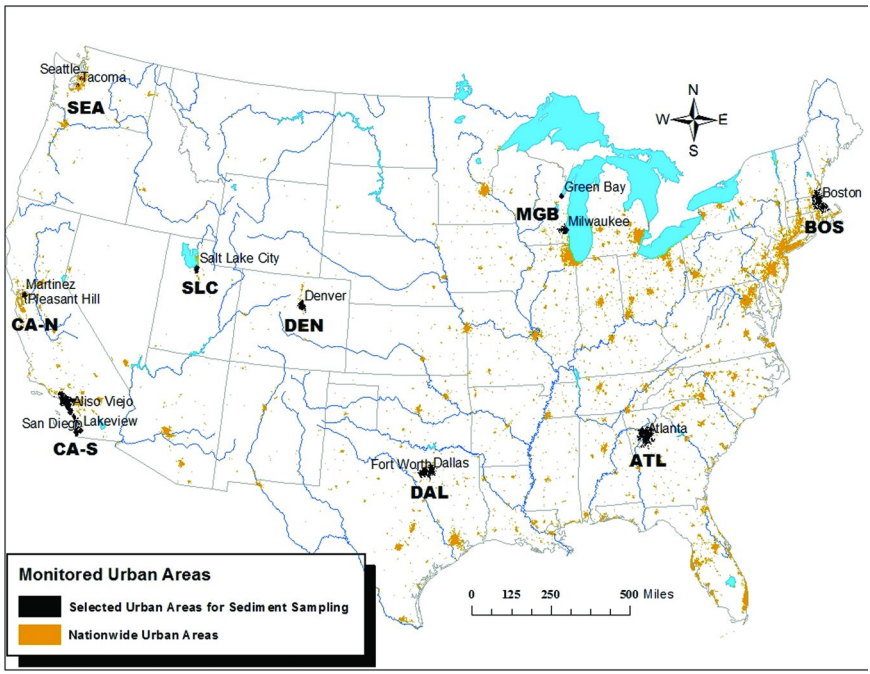

Figure 13. Stream bed sediment sampling sites for the statewide California study by Ensminger and Kelley (20) and the nationwide study by Kuivila et al. (22).

The pyrethroids bifenthrin, λ-cyhalothrin, cypermethrin, permethrin and resmethrin were monitored in both studies. Data from Ensminger and Kelley (*20*) included monitoring data for sediments underlying storm drains in addition to receiving water bodies. The data show relatively high DFs for bifenthrin, cyfluthrin, permethrin deltamethrin, λ-cyhalothrin and cypermethrin (41-97%) with maximum concentrations ranging from 32 to 680 µg/kg dry sediment. Fenvalerate/esfenvalerate maximum DF/concentration was reported to be relatively lower (14% and 24 µg/kg). However, of interest in this section is the pyrethroid chemicals data for sediments underlying receiving water bodies as it can be compared with data obtained for the nationwide bed stream sediments study conducted by Kuivila, *et al.* (*22*) This will permit comparison between bed sediments obtained nationwide from urban areas varied in hydrology, weather, pesticide use, timing of application and land characteristics/use. Figure 14 summarizes the concentration and DF data obtained from both studies for bifenthrin, λ-cyhalothrin, cypermethrin, permethrin.

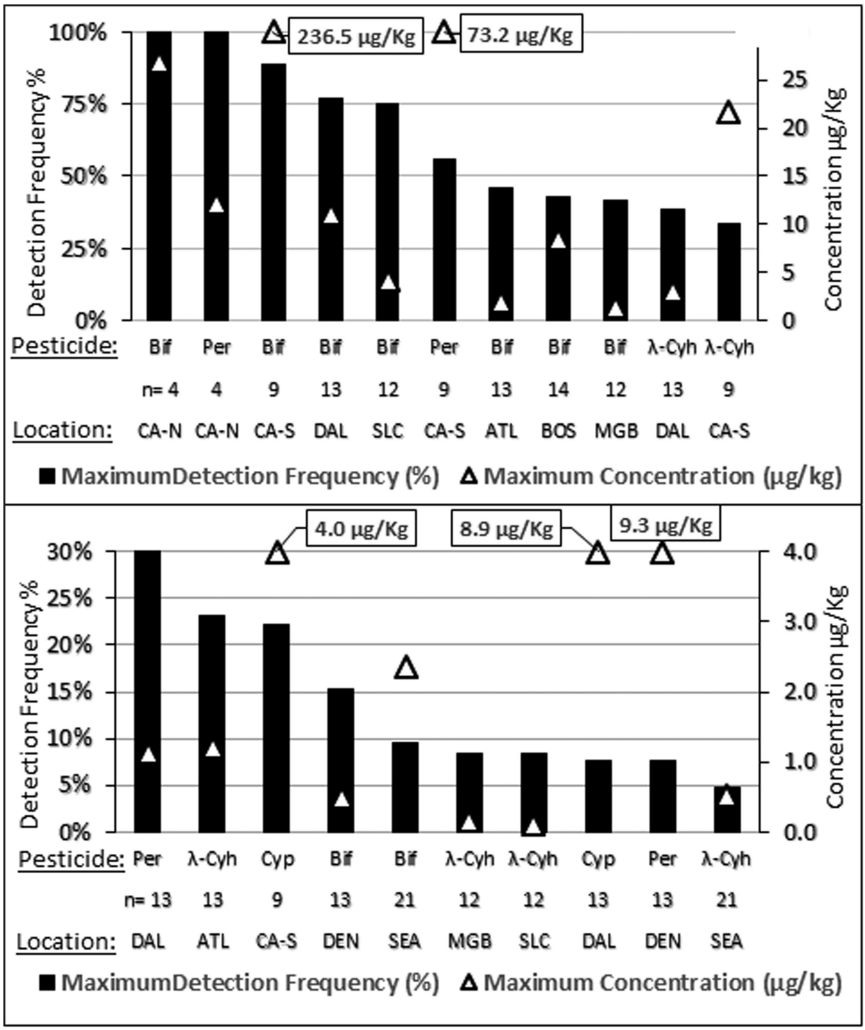

Figure 14. A summary of the sediment concentration/DF data obtained for bifenthrin (bif), λ-cyhalothrin (λ-Cyh), cypermethrin (Cyp) and permethrin (Per) (n = number of samples; for sampling location abbreviation refer to map in Figure 13).

Data show variable occurrence frequencies and concentrations of pyrethroids detected in bed sediment streams across the country. Reported data may be categorized by the frequencies of occurrence into three categories as shown in Table 4.

Table 4. Categories for the Frequencies of Pyrethroid Occurances in Bed Sediments

Detection Frequencies	*Maximum Concentrations*	*Bed Sediment Location*	*Pyrethroid Detected*	*Exception*	*Reference*
56 - 100%	**11.2 – 237** µg/kg	**CA-S, CA-N, DAL**	Bif	SLC= **4.2** µg/kg	Figure 14 Top Graph
		CA-N	Per		
33 - 46%	**1.4 - 8.4** µg/kg	**BOS, ATL, MGB**	Bif	None	
		DAL	λ-Cyh	CA-S= **22** µg/kg	
5 - 31%	**2.4 - 9.2** µg/kg	**DEN**	Per	None	Figure 14 Bottom Graph
		DAL, CA-S	Cyp		
		SEA	Bif		
	0.1 - 1.2 µg/kg	**ATL, SEA, MGB, SLC**	λ-Cyh		
		DEN	Bif		

Monitoring vs. Modeling

Targeted monitoring data, similar to those discussed earlier, are important resource for regulators of urban pesticides. These type of data are available for pesticides that have been in use for many years. Quality monitoring data can be used as a ground truth for verifying modeled estimated environmental concentrations (EECs) that determine aquatic exposure. EECs are used in ecological and drinking water assessments. In the case of pesticides used in urban setting, monitoring data are much more important due to the usually high uncertainties associated with modeling surface water exposure in the urban environment. In some cases, it was necessary to use EECs from monitoring data instead of modeling due to lack of scenarios that would represent application of a given pesticide and associated processes. For example, application rate/acre, number of applications and timing are required to perform PRZM/EXAMS modeling. Label information is not enough and assumptions had to be made to estimate these key parameters. For example, in the case of house perimeter treatment the label usually gives application rate in lbs a.i/1000 sq. ft and possibly a recommended treatment of 2 ft around the house. A residential area factor is usually estimated in order to arrive at a reasonable application rate for modeling which needs estimates of housing density/acre and area that would be treated (need to assume house dimensions). The assumptions should be reasonably conservative and represent the area where the pesticide is to be applied. The task of arriving at reasonable estimates becomes much more difficult when the pesticide is to be used on a national scale. Many scenarios would be needed to represent housing densities across the U.S. Additionally, other needed parameters, such as timing of application, is assumed conservatively to happen at one time for all houses within a 10-hectare area. PRZM calculates daily load of pesticide transported by water run-off and erosion into 20,000 m^3 pond 2 m deep with no outlet to further simulate degradation. In contrast, urban runoff waters transports pesticides, through urban drainage/pumping systems (in some cases through POTWs), into surface water bodies such as urban creeks, lakes, and rivers. Pesticides arriving to these water bodies may then be transported via running water rather being held into a pond with no outlet. Although EECs estimated in pond, by EXAMS, are expected to be conservative but much higher conservatism may result in unrealistic estimates especially with highly persistent pesticides that accumulates in the pond yielding high EECs.

Monitoring data and examples of previous modeling for surface water EECs are compared for two of the most frequently detected pesticides; Fipronil and bifenthrin (Table 5).

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ACS Symposium Series; American Chemical Society: Washington, DC, 2014.

Table 5. Modeled vs. Monitored EECs for CA

Chemical	*Treatment Type*	*Label Rate* (*lbs ai/A*)	*Modeled rate (No. of Applications)*[1]	*Modeled EECs (ng/L)*			*Observed EECs in CA Monitoring (ng/L)*[2]
				Peak	*21-day*	*60-day*	
Fipronil	House perimeter treatment	2 ft. @ 0.357	0.012 lbs ai/A (1)	41.2	26.7	15.2	Maximum= 232 and 90th%= 83
	Broadcast fire ant treatment	Not Stated	0.014 lbs ai/A (1)	6.3	4.1	2.3	
Fipronil total degradates	House perimeter treatment	Three degradates modeled individually similar to parent using the fate properties of the degradates and the max daily conversion observed in environmental fate studies corrected for differences in molecular weights		19.5	15.5	14.1	Maximum= 372 and 90th%= 125
	Broadcast fire ant treatment			3.2	2.6	2.4	
Bifenthrin	Many residential uses	Varied label rates with calculate range of application rate of 0.001 to 2.2 lbs ai/A and from one application to twelve applications @ 7-180 days intervals		Capped by the solubility limit of 14 ng/L			Maximum= 27.2 and 90th%= 24.2

[1] Modeled rate = Could be different from label rate because it is an adjusted rate based on treated area of the acre. [2] Maximum and 90th percentile values detected in Receiving water bodies (RWB).

Monitored maximum and 90th percentile EECs for both fipronil and bifenthrin are higher than modeled EECs suggesting possible improper parameterization of the model. In the case of fipronil, lower EECs might be related to the application rate calculated for modeling and possibly a reflection of the scenario used. In case of bifenthrin, modeled EECs were capped to the limit of solubility of the chemical which is 14 ng/L. Modeled EECs are higher than the 14 ng/L concentration expected for this insoluble chemical. In fact, bifenthrin was detected to occur at concentration as high as 27.2 ng/L which is almost two times its laboratory determined solubility. The observed relatively high occurrence for bifenthrin in run-off and surface waters may be attributed to factors such as water chemistry, such as presence of dissolved organic carbon or colloids, and possible effects of the formulation that makes bifenthrin more soluble in surface waters than in pure laboratory water.

The above example of comparison between monitored and modeled data is at best an approximation due to many factors such as (1) Modeled EECs were not a result of proper parameterization of the model to represent monitored areas, (2) The summary concentrated on the maximum observed concentrations in order to identify sites having the highest EECs indicating their vulnerability noting that these values may have been influenced by contamination from other sources such as spills and transported pesticides from areas upstream or with airborne particles and/or drift (3) Ideally, only targeted monitoring data, for an identified vulnerable site, may be compared to modeling data using parameters representing the same site. This is not the case for the comparison above, monitoring data were for four different urban areas of the State of California, consisted of 47 values for fipronil and degradates and only 14 values for bifenthrin and the maximum number of values for each site ranged from 1 to 8 (dry + wet events) and only from 1 to 5 for dry event and 1 to 4 for wet events, Monitoring data needed for comparison should represent only one area and should be extensive (daily or weekly). The monitoring data used were with intervals ranging from 24 to 167 days 7 to 118 days. for bifenthrin, (4) It is important to point out that the ultimate maximum exposure EECs in receiving water bodies is dependent on the mass of pesticide transferred into the water body. Winter stormwater high flow with low concentration is expected to contribute more pesticide mass to receiving waters than summer low flow with high concentration, (5) In flowing waters, such as rivers and streams, observed concentrations are expected to be influenced by the flow status of the rivers and streams because higher dilution will occur at high flow compared to low flow, and (3) EECs are also influenced by the pesticide fate and transport properties as well as the receiving water characteristic such as type of suspended matter (content of dissolved/suspended organic carbon and other colloidal materials). Such contents may additionally influence the bioavailability of the pesticide and its toxic effects.

Potential Refinement for Modelling EECs

Currently, the USEPA considers the modeling approaches described above and resultant EECs as crude estimates and provide only a screening-level

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information. This is due to uncertainties regarding: variability in site characteristics that govern runoff, effect of different formulations, types of impervious surfaces, application methods and timing and national representation of regions with varied landscape, housing density and hydrological features. Therefore, refinement of residential and impervious surface exposure scenarios is needed. This can be done by incorporating recent findings that could be used to accurately parameterize the residential and impervious scenarios used in modeling. This information helps in refinement by providing data necessary to establish national representative scenarios for vulnerable sites. The conceptual model for establishing these standard scenarios involves the following steps: (1) identify vulnerable urban watersheds based on available monitoring data and different climatic conditions, pesticide pressure, and hydrology; (2) understand the hydrology of the chosen watersheds especially the drainage system inputs and outputs; (3) classify each of the chosen watersheds according to land use (commercial, industrial, mixed and others), determine fractions of pervious, impervious surfaces and drainage systems for urban runoff waters; (4) choose 10-hectare vulnerable areas of the watershed that represent typical residential, commercial, industrial and mixed developments (that is the catchment area for PRZM); (5) specify the types of surface areas, in the chosen catchments, that would be treated for various label use patterns (i.e., home perimeters patios, driveways, etc.) and the fraction of that area that would be treated (i.e., fraction treated for home perimeters patios, driveways, etc.); (6) determine the application rates for the residential and impervious surface exposure scenarios; (7) adjust the rate for varied impervious surfaces based on available washoff studies (this adjustment would be dependent on the modeled chemicals); (8) establish a pattern for timing of application within the chosen watershed; and (9) run PRZM simulations with outputs processed through mixing cells into varied receiving water bodies (urban streams, lakes and rivers) to arrive at exposure EEC averages needed for risk assessment.

Assessing Adulticide Uses

Mosquito control remains as an important issue in urban environments in the United States due to the need to limit mosquito-borne diseases, such as West Nile virus (affecting human health) (*23*), or dog heartworm (affecting pets) (*24*). Wide area adult mosquito control is accomplished through a different pesticide method of application. In lieu of conventional ground or aerial applications using fine, medium or course droplets (according to American Society of Agricultural and Biological Engineers (ASABE) Standard S-572.1), mosquito adulticides are applied as ground or aerial mists, using extremely fine droplets, known as Ultra-Low Volume (ULV) droplets. Adulticide application rates are usually a very small fraction of the rate of coarser droplet applications used to control other insects (*e.g.*, in the ounces of product per acre range). Conventional pesticide applications are typically intended to hit the crop (*i.e.*, for foliar applications), while the ULV droplets are intended to remain airborne to hit mosquitoes in flight. A critical

review of ULV technology, including efficacy, variables that affect space ULV applications, and some information on non-target impact, has been published (*25*).

Examples of pesticides applied through ULV spray products are permethrin, prallethrin, *d*-phenothrin (commonly known as Sumithrin®), pyrethrins, etofenprox, malathion and naled. These chemicals are often times co-formulated with the synergist piperonyl butoxide (PBO) to enhance their activity. Given that many of these pesticides are considered very toxic to aquatic organisms, an approach to calculate aquatic estimated environmental exposure concentrations (EECs) is required. In this section of the chapter, a brief description of how the USEPA assesses ecological exposure from adulticides is presented, using modeling and open literature data for aerial and ground applications, respectively. The section will provide a synopsis of the use information and modeling, which includes discussions of aquatic and terrestrial exposure. For aerial applications, the AGricultural DISPpersal drift model (AGDISP v.8.26) is used for this purpose. For ground applications, a review of literature information and other lines-of-evidence provided an upper bound deposition level. A short example of an adulticide ecological risk assessment's results will be provided, and compared against monitoring data.

Use of Adulticides

In 2005, a Pesticide Registration (PR) Notice, titled "Labeling Statements on Products Used for Adult Mosquito Control", was issued (PR Notice 2005-1 (*26*)). The PR Notice 2005-1 (*26*) provided recommendations for label language for pesticides products for wide area ground or aerial adult mosquito control products, applied only through ULV spray or fog.

The PR Notice 2005-1 (*26*) included seven major recommendations (*27*). Among the recommendations, adult mosquito control applications should be limited to trained personnel and users should consult their State and Tribal agency to determine if permits or regulatory requirements exist. Additionally, adulticide applications should be clearly distinguished from conventional applications of insecticides in the label directions. The "Environmental Hazards" section of the labels should be clear and direct applications over bodies of water should be allowed under certain circumstances. Bee precautionary language should allow adulticide applications in order to respond to threats to public health that might be identified. As of October 15, 2005, registrants were expected to submit label amendments reflecting recommended label language; however, some labels were changed after this date. This language also provided more consistent instructions across different products relative to the quality of spray droplet, application rate, seasonal or annual rate, *etc*. Adulticide application parameters are also highly dependent on actual weather conditions, such as wind speed and direction. PR Notice 2005-1 (*26*) addresses such issues as well. The labels for mosquito adulticides now include restrictions surrounding the size of the droplets from the applications. According to the recommendation, two droplet dimensions should be specified: one is the Dv0.5 (the volume median diameter: half of the volume of spray contains droplets which are smaller than the stated value), and the other is the Dv0.9 (90% of the spray is contained in droplets smaller than this value),

both expressed in microns (*e.g.*, Dv0.5 <60 µm and Dv0.9 <115 µm, for aerial applications). Furthermore, labels now indicate the frequency and timing of applications, and the maximum annual application rate. This information is very useful and allows the assessor to determine which conditions should be assessed for risk of aquatic (and terrestrial) exposure. Moreover, the altitude of aerial applications is oftentimes also specified (*e.g.*, ≥75 ft).

Modeling Approach for Adulticide Assessment

As indicated earlier, the modeling approach for the aerial adulticide use includes calculations of spray drift using the exposure model AGDISP. This computer program estimates the deposition of the pesticide to the treated area, which is the application efficiency. Further, by means of its toolbox "Deposition Assessment," the deposition to adjacent bodies of water (*i.e.* the standard pond), the value of spray drift can be obtained. AGDISP provides a prediction of spray drift under circumstances where a mosquito adulticide is used. Besides the Dv0.5, Dv0.9, and boom height, other parameters of importance in modeling in AGDISP include the spray volume (usually expressed in gallons per acre), wind speed range (miles per hour), wind direction, spray material (*e.g.*, oil or water based), and specific gravity. The spray volume, material, and specific gravity, are specified or can be estimated from the label or the material safety data sheet (MSDS) for the product, or from product chemistry submissions. To model aerial applications, the lowest boom height allowed in the label is selected, which is expected to result in the highest deposition and drift. The model output of AGDISP includes the spray drift fraction (obtained from the "Deposition Assessment" tool of the model's Toolbox), and application efficiency (fraction of the material that deposits in the target area under the aircraft, which is expected to be much lower than the default values for typical agricultural applications). In order to obtain aquatic EECs, these values are utilized as input parameters in the aquatic models PRZM/EXAMS. To obtain terrestrial EECs, the application efficiency can be used to correct the application rate in T-REX (Terrestrial Residue Exposure, v.1.5.2). The "adjusted application rate", based on application efficiency estimated by AGDISP, is the rate that is entered into T-REX for estimating exposure and risk to non-target terrestrial animals. The model can also be used to estimate exposure to wildlife off the field, by means of the terrestrial point estimate of the "Deposition Assessment" tool.

The AGDISP model has been used for aerial applications; however, it has not been approved for wide use in EFED for ground applications. Recently, in response to a request to amend certain labels, and a petition by the Health Effects Division (HED), EFED evaluated aerial ULV applications using the model AGDISP (*28*). The model chemical was etofenprox. Given the same application parameters (*i.e.*, drop size distribution, application material, application height), model results indicated that the deposition value is sensitive to wind speed as an input parameter. For etofenprox the wind speed range allowed by the label is 1-10 mph. Based on AGDISP modeling of aerial applications, at wind speeds of 1 mph the application efficiency (percent of the chemical that deposits on the crop) was

estimated to be ~33%. Additionally, the application efficiency decreases with increasing wind speeds.

For ground applications, eight open literature studies (Table 6) and a dissertation focused on the mechanistic aspects of drift from ground-based adulticide applications (Schleier III (*29*), Schleier III *et al.* (*30*)). EFED evaluated these articles and detected that peak deposition rates, measured in a variety of dosimeters, and at different wind speeds and distances from the application sites were similar to aerially based ULV applications. Consensus of the studies indicated that ground ULV pesticide deposition is similar to that from aerial ULV pesticides. For ground applications, the deposition is expected to range from 0 to 33% of the applied (Table 6).

Table 6. Summary of Peak Deposition Rates Reported in Literature Studies [1]

Reference	*Material*	*Peak deposition (ng/cm²)*	*Peak deposition (% applied)[2]*	*Distance from application source to peak deposition (m)*	*Wind speed (mph)[2]*
Tucker *et al.* (*31*)	Fenthion	2.92	2	8	NR
	Malathion	85.8	15	8	NR
	Naled	57.3	20	8	NR
Moore *et al.* (*32*)	Malathion	84.1	14	30.4	0.9–3.4
Tietze *et al.* (*33*)	Malathion	50	9	5	2.1–4.0
Knepper *et al.* (*34*)	Malathion	9,222	NA	7.6	1
	Permethrin	14,389	NA	7.6	1
Tietze *et al.* (*35*)	Malathion	473	NA	Unknown	0–2.5
Schleier & Peterson (*36*)	Naled	74	33	50	1.5
	Permethrin	4.6	5.9	25	4.3
Pierce *et al.* (*37*)	Permethrin	5.1	10	Unknown	6−12
Preftakes *et al.* (*38*)	Permethrin	8	10	25−50 m	4.8

[1] Source: USEPA (*28*). [2] NA – insufficient information to assess; NR – not reported.

The review concluded, based on EFED's analysis and guidance provided in the label, that a deposition rate of 33% for sprays reaching agricultural crops is a conservative estimate for both ground (based on submitted literature data) and aerial (based on AGDISP modeling) ULV applications for etofenprox.

Adulticide Insecticides Monitoring Data

Monitoring data for adulticides is scarce. Given that they are applied at extremely low rates, and some of these pesticides have other uses, monitoring results can be confounded with other uses. For example, permethrin can be used as an adulticide; however, it can be used on agricultural crops, in residential settings, and industrial sites, and it has uses that may lead to residues in wastewater discharges, and consequently in treatment plant effluents.

In 2000, Milam *et al.* (*39*) published a report of monitoring for toxicity of ground and aerial permethrin adulticidal applications (product Biomist®) in Arkansas. Toxicity was performed *in situ* in 10 replicate test chambers plus controls. Test organisms included *Daphnia pulex*, *Ceriodaphnia dubia*, and *Pimephales promelas*. Five test organisms were placed in each chamber. Once permethrin was allowed to settle, the chambers were transferred to the laboratory for the remainder of the exposure period (24 or 48 hours). *P. promelas* did not appear to be susceptible to aerial or ground ULV permethrin applications, showing 100% survival in all instances. Both *D. pulex* and *C. dubia* appeared to be more susceptible to aerial than to ground applications and showed variable survival rates from ground applications of permethrin.

Weston *et al.* (*40*) reported their results from monitoring of aerial applications of pyrethrins and PBO in August 2005, using the product Evergreen Crop Protection EC 60-6 (containing 6% pyrethrins and 60% PBO), on ~50,000 hectares over the densely populated area of Sacramento, CA. (across the American River). Treated areas were primarily commercial and residential. Water and sediments from six creeks draining the treatment area were sampled and tested for toxicity (water *C. dubia* test (~6-8-day tests); sediment *Hyalella azteca* (10-day test) and chemistry (pyrethrins, chlorpyrifos, diazinon and PBO in water; pyrethroids, pyrethrins, PBO and chlorpyrifos in sediment). Additionally, two separate experiments were performed to determine the effect of PBO on sediment sorbed pyrethroids: one was conducted with a sediment that showed near total lethality to *H. azteca*, and another with a sediment spiked with bifenthrin. The sediment's LC_{50}s were determined, with PBO present in the overlaying water at 0, 4, and 25 µg/L. Water analysis indicated that the sum of pyrethrins I and II, were not detected above the reporting limit of 0.01 µg/L, which was attributed to degradation via photolysis and adsorption by bed sediments; however, PBO was undetected prior to application and reached a maximum level of 3.92 µg/L after application. Sediment sample analyses revealed that pyrethrins I were present at a concentration of up to 403 µg/kg dry weight after application and PBO concentrations were up to 61.4 µg/kg dry weight. There was no evidence of aquatic toxicity due to the application of pyrethrins and PBO alone. The additional testing indicated that PBO concentrations of 2-4 µg/L in the overlaying water were sufficient to enhance previously present sediment pyrethroid toxicity

to *H. azteca* by a factor of up to two. Even though there is uncertainty about the PBO actual exposure duration in the environment, at the treatment site PBO was applied on three consecutive nights. This could cause prolonged PBO concentrations in the environment. Water sampling occurred at 10 and 34 hours after application and the difference in PBO concentration between samplings was not appreciable. This article was the first to show that the synergist PBO could pose additional risk to aquatic animals, compared to risk posed by individual insecticide active ingredients, at an environmentally realistic PBO concentration.

The Sacramento-Yolo Mosquito and Vector Control District provided a water quality monitoring effort for the same applications by Weston *et al.* (*40*) (Ziegler (*41*)). No sediment samples were taken for analysis. Water samples were analyzed for pyrethrins and PBO, with respective reporting limits of 0.2 and 1.0 µg/L. Since applications were made in the evening (usually after 8:00 pm), for each application event water samples were taken three times, which represented before application (baseline), in the morning on the day after application (representing immediate post-application), and in the afternoon on the day after application (next day post-application, taken approximately 15 hours after the immediate post-application samples). For the first application event, immediate post-application samples were not taken. Results indicated that the pre-application (baseline) samples were non-detects at the reporting limit for both pyrethrins and PBO. For the immediate post-application samples, 35% and 56% of the water samples were reported as detects for pyrethrins and PBO, respectively. For the next day post-application samples, pyrethrins were not detected in any samples and PBO was detected in 35% of the samples. The maximum pyrethrins concentration reported was 3.77 µg/L and PBO was at a maximum concentration of 20 µg/L.

Schleier and Peterson (*42*) derived LC_{50}s for permethrin, permethrin synergized with PBO, permethrin in the product Permenone®, Permanone® plus PBO, technical naled, and naled in the product Trumpet®, towards the representative medium–to-large ground-dwelling non-target insect, the house cricket (*Acheta domesticus* (L.)). Using ground ULV applications, there were no significant differences in mortalities of caged house crickets exposed to Permanone® or naled, compared to controls. The authors calculated EECs using the Industrial Source Complex Short-Term (ISCST3) dispersion model, which resulted in exceedance of the levels of concern (LOCs) for the house cricket in all cases, except for technical grade permethrin. However, using actual environmental concentrations, only the risk quotient (RQ) for technical grade naled exceeded the LOC. RQs were 10- to 100-fold lower using the measured environmental concentrations than using modeling.

In another monitoring effort, Kuivila *et al.* (*22*) reported sampling for several synthetic pyrethroids in 7 metropolitan areas across the U.S., which excluded California. Among the pyrethroids analyzed, resmethrin was included, which has been used primarily for mosquito abatement. The study reported a frequency of detection of resmethrin in sediment samples of 4% and a highest concentration of 38.3 µg/kg dry weight, a median 5.3 µg/kg, with a method detection limit of 0.5 µg/kg dry weight. According to the article, given that resmethrin is used primarily as an adulticide, the source of the chemical for the site that showed the maximum resmethrin concentration at a site within Estes Park, Colorado (an undeveloped

watershed), is aerial applications of resmethrin for mosquito control. According to this article, a previous study had reported a maximum resmethrin concentration in suspended sediment of a San Joaquin Valley, California watershed of 19 µg/kg (*43*).

Phillips *et al.* (*44*) incorporated toxicity testing to monitoring relative to mosquito adulticide applications. As a requirement of a National Pollutant Discharge Elimination System (NPDES) General Permit to comprise discharges to waters from mosquito control applications in California in 2011, the California State Water Resources Control Board and the Mosquito Vector Control Association of California conducted chemical and toxicity analyses in the water column and sediment pre- and post-applications of malathion, naled (and its degradate dichlorvos), permethrin, *d*-phenothrin, pyrethrins, etofenprox, and PBO (plus a suite of other pyrethroids), during 15 mosquitocide applications in 2011 and 2012. Settings included and were labeled as urban, agricultural and wetland environments. Pre-application water and sediment samples were collected in the evening of each application day. Post-application water samples were collected in the early morning hours (12-hr post-application) and evenings of the day after each application (24-hr post-application). The post-application sediment samples were taken 4-7 days post-applications, to allow time for partitioning with the sediments. The toxicity of malathion and naled was assessed using *Ceriodaphnia dubia*, while the toxicity of pyrethroids and pyrethrins was assessed using *Hyalella azteca*.

Only four post-application sediment samples were more toxic than their corresponding pre-application samples; however, the toxicity could not be attributed to the spray events and there was a limited number of chemicals tested (Table 7).

Toxicity of nine out of 16 toxic water samples was related to applications of naled and attributed to it's degradate dichlorvos. Given the limited number of adulticide chemicals available in the market, and that naled is only one of two organophosphate pesticides used for this purpose, the authors recommended best management practices to prevent toxicity due to naled applications. They indicated that some practices are already being implemented (Table 7).

Table 7. Summary of Sampling Results from Monitoring Mosquitocide Applications. (Source: Phillips *et al.* (*44*))

Chemical	*Toxicity*	*Concentrations and Other Notes*
Sediment		
Pre-App Samples	Out of 17 samples, only one exhibited significant toxicity (*H. azteca*), taken before a *d*-phenothrin application.	The corresponding post-application sample exhibited the same mean survival (74%), and it was not found to be significant.
Permethrin	Only one urban site was sampled for permethrin, which exhibited significant toxicity pre-application (*H. azteca*). See above.	The permethrin concentration was below the toxicity threshold.
Pyrethrins	Two of the urban sites exhibited toxicity post-application (*H. azteca*).	There were no detections of pyrethrins and no sample exceeded the PBO toxicity threshold.
d-phenothrin	Five wetland and five agricultural sites were sampled for *d*-phenothrin, all of which did not exhibit significant toxicity pre- and post-application (*H. azteca*).	No sample had concentrations of *d*-phenothrin or PBO exceeding their toxicity thresholds.
Water Column		
Pre-App Samples	Out of 53 samples, only one exhibited significant toxicity (*H. azteca*), taken before a *d*-phenothrin application.	The corresponding post-application sample was not significantly toxic at the same site.
Malathion	Two sites were tested, which did not exhibit significant toxicity (*C. dubia*).	The concentrations of malathion were below the organism threshold.
Naled	Six urban, two wetland and one agricultural sites were tested. Significant toxicity was observed in both wetland and all six urban sites (*C. dubia*).	Naled was not detected in any of the sites but its degradate, dichlorvos, was observed at concentrations exceeding the organism threshold in both wetland and four of the urban sites. Trichlorfon, another precursor of dichlorvos, was noted at levels exceeding thresholds in one of the wetland sites.

Continued on next page.

Table 7. (Continued). Summary of Sampling Results from Monitoring Mosquitocide Applications

Chemical	*Toxicity*	*Concentrations and Other Notes*
Etofenprox	The 24-hr post-application sample exhibited significant toxicity (*H. azteca*).	The chemical's concentration was below the reporting limit.
Permethrin	Six agricultural, one wetland and five urban sites were sampled. Three permethrin post-application sites exhibited significant toxicity (one agricultural and two urban) (*H. azteca*).	Permethrin, bifenthrin and PBO concentrations were all below toxicity thresholds in these samples (*H. azteca*) with the exception of one bifenthrin concentration exceeding the threshold in one of the urban sites that exhibited toxicity (12- and 24-hours post-application).
Pyrethrins	Six urban and six wetland sites were monitored, of which only one urban site exhibited toxicity (*H. azteca*).	Even though the concentration of pyrethrins and PBO were below their toxicity thresholds, it turned out that the concentrations of PBO were the highest reported for the samples that exhibited toxicity. The authors speculated that the PBO may have synergized the toxicity of other pyrethroids present in the samples.
d-phenothrin	None of the six agricultural, six wetland and six urban sites monitored exhibited significant toxicity post-application (*H. azteca*).	The concentrations of *d*-phenothrin and PBO were below their toxicity thresholds.

Example Ecological Risk Assessment

In 2008, EFED issued an analysis of the ecological risk assessment for permethrin for the following endangered or threatened species in California (*45*): California red-legged frog *(Rana aurora draytonii*), California clapper rail (*Rallus longirostris obsoletus*), Salt marsh harvest mouse (*Reithrodontomys raviventris*), San Francisco garter snake (*Thamnophis sirtalis tetrataenia*), and Bay checkerspot butterfly (*Euphydryas editha bayensis*). One of the assessed uses of permethrin was for vector control through ULV applications. In the assessment, aquatic and terrestrial species were evaluated. At the time of the review, some labels did not comply with PR Notice 2005-1 (*26*), and therefore, analyses were performed using both pre- and post-PR Notice 2005-1 labels. Table 8 provides the urban aquatic EECs. Compared to a peak water EEC of 0.221 µg/L (post-CFR 2005-1), the single monitoring study that provided water column concentrations of permethrin (*44*) presented a maximum concentration of 0.03 µg/L. The ecological risk assessment did not provide sediment concentrations for comparison; however, they can be estimated based upon the value of organic/carbon partition coefficient (K_{OC} = 76800 L/kg). An estimated conversion factor of 3073 from pore water concentration to sediment concentration is calculated using a spreadsheet and the constants that define the EXAMS ecological pond. The peak pore water concentration was 0.0515 µg/L. The estimated peak sediment concentration is 158 µg/kg, which is above 2-fold higher than the monitored concentration of 65.9 µg/kg.

Table 8. Water Column EECs (µg/L) for Permethrin Uses in California

Scenario	*App Rate (lb a.i./A)*	*Peak (µg/L)*
Recreational areas (Pre-CFR 2005-1)	0.007x7	0.496
Recreational areas (Post-CFR 2005-1)	0.007x7	0.221

In the past, EFED has based its adulticide evaluations on existing turf Pesticide Root Zone Model (PRZM) scenarios for modeling aquatic exposure (*e.g.*, FL, PA or CA turf). These scenarios are used as surrogates for areas such as, but not limited to parks, campsites, woodlands, athletic fields, golf courses, garden playgrounds, and recreational areas; however, for uses in other urban sites, such as residential, the combination of the residential and impervious scenario, run in tandem may be utilized in upcoming assessments. It is expected that the development of new scenarios depicting residential sites and/or impervious surfaces may be further used in the future.

Assessing Pesticide Releases to POTWs

In the context of ecological risk assessment of conventional pesticides at USEPA, the issue of household wastewater releases of pesticides was first raised by public stakeholders from California during the Re-registration Eligibility

Decision (RED) process of the pyrethroid insecticide permethrin (*46*). Concerns were raised that clothes pretreated with permethrin may cause adverse water quality impacts due to releases to POTWs when washed and result in subsequent discharges to receiving waters by POTWs. It is noteworthy that potential releases of antimicrobial pesticides to POTWs have routinely been considered in OPP environmental risk assessments due to their widespread use in consumer care products that result in substantive 'down the drain' releases (*e.g.,* antibacterial ingredients in hand soaps). In contrast, this issue is relatively new for conventional pesticides where exposure from outdoor uses has traditionally been assumed to dominate environmental risk concerns. Monitoring data described later in this section indicates that for some pesticides, releases to (and from) POTWs may be significant to the extent that this exposure pathway requires consideration in USEPA environmental risk assessments. More recently as part of OPP's pesticide Registration Review process, the aforementioned concerns were echoed and additional concerns were identified regarding the potential for environmental exposure to pesticides resulting from their sorption onto biosolids and subsequent biosolid application to land (*47*).

In this section, we summarize the currently available information regarding conventional pesticide releases to POTWs in the U.S. and approaches being considered for evaluating these exposure pathways in OPP's forthcoming ecological risk assessments. We first discuss sources and pesticide uses associated with releases to POTWs. Following this, we describe approaches and data that are being used to model the fate of these releases in POTWs. Finally, we summarize available monitoring data which have been generated specifically to characterize potential pesticide exposure to and from POTWs.

Pesticide Sources to POTWs

In response to the concerns raised by the public regarding the potential release of conventional pesticides to POTWs, OPP reviewed indoor uses of conventional pesticides and identified those that present a high potential for "down the drain" (DtD) releases (Table 9). Generally, these include pesticidal treatments of fabric, clothing and carpets, pet shampoos, and drains with hydrologic connections to sewer systems. Selected uses in greenhouses have been evaluated previously in the context of pesticide releases to both POTWs (assuming connectivity with sewer systems) and surface waters (assuming direct discharge to bodies of water). These uses are therefore being considered as exposure pathways of potential concern in current and forthcoming environmental risk assessments by OPP.

A number of indoor pesticide uses are considered to have lower potential for substantive releases to POTWs based on labeled uses. These include labeled applications of indoor foggers, baits, crack and crevice treatment, and bed and mattress treatments where a hydrological connection to sewer systems is considered highly unlikely or at most, rare. Considerable discussion arose around the use of 'spot on' treatments for pets (*e.g.,* flea and tick control) as well as insecticide-impregnated collars. With spot on treatments, it is expected (and advised on some pesticide labels) that shampooing soon after application of spot on treatments would reduce the efficacy of such treatments, and those would not

be cost effective and discouraged. Regarding pet collars, the potential substantive releases to POTWs are considered low based on their expected slow release rate of pesticides from the collars.

Table 9. Indoor Uses of Conventional Pesticides and Their Potential for 'Down the Drain' Release to POTWs

Uses With High Potential for Substantive Release to POTWs
• Pet lotions or shampoos (*e.g.*, treatment for fleas and ticks)
• Products for the treatment of shoes/clothing/textiles (*e.g.*, miticides, sanitizers, deodorizers)
• Pre-treated clothes/textiles, bed sheets, linens, etc.
• Drain treatments that convey water to sanitary sewer systems (root herbicides)
• Storm drain/storm system treatments connected to sewer systems (*e.g.*, root herbicides and filtration media for storm water filtration systems)
• Sewage system treatments (*e.g.*, filtration media for municipal wastewater filtration)
• Carpet treatments (except materials preservatives) removed from carpets during shampooing then subsequently disposed with wash water down-the-drain
• Lice shampoos, skin lotion treatments (*e.g.*, for mites)[1]
• Selected greenhouse uses with drains connected to sewer systems
• Pool treatment[2]
Uses With Lower Potential for Substantive Release to POTWs
• Pesticide-containing pet collars and spot-on treatments
• Bed and mattress treatments (except products to treat bed sheets)
• Storm water system treatments not connected to sewer systems
• Crack and crevice treatment
• Indoor foggers
• Indoor baits

[1] Although this is considered a pharmaceutical use, EPA in agreement with FDA is assessing exposure from down the drain releases. [2] Even though pools are typically considered outdoor use patterns, generally localities require discharging their water to sanitary sewers.

It is important to note that the pesticide uses identified in Table 9 do not represent *all* potential sources of pesticide input to POTWs. Rather, they represent those uses that are currently being assessed as part of DtD modeling in OPP environmental risk assessments. For example, pesticides may potentially be released by industrial discharges to POTWs from pesticide manufacturers. However, such releases are subject to regulation under other environmental statutes and regulatory programs (*e.g.,* state and federal pretreatment programs

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under the authority of the Clean Water Act), and not under FIFRA. It is recognized that certain outdoor residential uses of pesticides may contribute to pesticide loadings to storm water systems which are connected to POTWs. Modeling of outdoor residential use of pesticides in OPP environmental assessments is presently focused on direct loadings to surface water. Information from the open literature suggests that some POTWs may experience greater flow during wet weather events even when direct connections to storm water inputs are not apparent (*19*). Presumably, such inputs represent groundwater intrusion and/or fugitive inputs from storm water runoff. For these and other sources of pesticides to POTWs unaccounted for in Table 9, OPP is relying on targeted monitoring data to ascertain inputs to and discharges from POTWs.

Modeling Approach for POTW Assessment

In order to address the issue of releases to domestic wastewater, OPP has relied on the consumer exposure model, *Exposure and Fate Assessment Screening Tool* (E-FAST, v.2.0) that was developed for assessing industrial chemicals in EPA's Office of Pollution Prevention and Toxics (*48*). The 'Down-the-Drain' module (DtD) of E-FAST v.2.0 is specifically designed to address sources of a chemical that could potentially be disposed into domestic wastewater from a DtD application. The DtD module can be used to represent residential, domestic and certain commercial facilities (*e.g.*, supermarkets, storage facilities and warehouse uses likely to end up in drains). This model provides screening-level estimates of chemical residues in surface water that may result from household uses and the disposal of consumer products into wastewater.

Conceptually, the E-FAST's DtD module assumes that in a given year the entire production volume of a chemical (*i.e.*, the amount of pesticide) is parceled out on a daily basis to the entire U.S. population and converted to a mass release per capita, and subsequently, a daily per capita release to a wastewater treatment facility (*i.e.,* g/person/day). This mass is then diluted into the average daily volume of wastewater released per person to arrive at an estimated concentration of the chemical in wastewater prior to entering a treatment facility. The underlying equations used by the DtD module are shown below. The daily per capita release is defined as follows.

$$H_R = \frac{PV}{Pop} \times \frac{1000\ g}{1\ kg} \times \frac{1\ year}{365\ days}$$

where,

i. H_R is the daily per capita release of the chemical (g/person/day);
ii. P_V is the production volume of the chemical being evaluated that is produced annually in the USA that is discharged into domestic wastewaters (kg/year); and
iii. *Pop* is the 2003 U.S. resident population (2.908×10^8 persons) (U.S. Bureau of the Census, 2004-2005).

The chemical's concentration in untreated wastewater is then reduced by the fraction removed during wastewater treatment processes. The remaining chemical is discharged into surface water (*e.g.,* a river or stream), where it is assumed that it is instantaneously diluted, with no further removal. The surface water concentration is calculated using the following general equation.

$$SWC = \frac{H_R \times \frac{1}{Q_H} \times \left(1 - \frac{WWT}{100}\right) \times \frac{10^6\ \mu g}{g}}{SDF}$$

where,

i. *SWC* is the surface water concentration (μg/L);
ii. Q_H is the household wastewater volume released daily (it is estimated to be 388 L per person per day), it includes only domestic and residential POTWs;
iii. *WWT* is the wastewater treatment removal (percent removed prior to discharging into a body of water, %); and
iv. *SDF* is the stream dilution factor.

The Stream Dilution Factor (SDF) is the volume of the receiving stream flow divided by the volume of the wastewater released from the POTW or effluent flow (SDF = SF/EF). There are four types of stream flows that the developers of the model have deemed adequate for the protection of aquatic life and human health (acute and chronic). Additionally, flows have been characterized to represent mid-sized receiving bodies of water and smaller streams. It should be noted that the DtD module of E-FAST is a screening-level model and the results should be treated as such. It does not take into account processes such as degradation prior to treatment at the facility, or partitioning (*i.e.,* sorption by sediment or particulate matter).

Model Inputs

There are two main input values in the E-FAST's DtD module: the production volume (PV), and the percent removal from wastewater treatment (WWT). (The BCF is an input parameter, which the model uses for calculations that are not relevant to EFED's purpose to calculate aquatic EECs.) The PV can be obtained from the registrant(s) sources or can be supplied by the Biological and Economic Analysis Division (BEAD). Model results are sensitive to the WWT, which in turn is dependent on the physicochemical properties of the active ingredient of concern and the extent of wastewater treatment (*e.g.,* primary, secondary, tertiary, or ultrafiltration). An estimate of WWT is available from the Sewage Treatment Plant Fugacity Model (STPWIN™) of EPI Suite v.4.11 (*49*). This model provides estimates of the fate of organic chemicals in conventional wastewater treatment plant that uses activated sludge secondary treatment. According to the STPWIN™ Help manual, EPI Suite's STP program was conservative predicting removal percent (WWT) 88% of the time using its default half-lives of 10,000

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hours for 29 of 33 chemicals evaluated, for primary clarifier, aeration vessel and settling tank; however, the evaluation was based on a set chemicals which are not pesticides. A more suitable and reliable alternative, is data derived from a bench scale study (described further below) that may be required either during the registration process of the chemical or during registration review, to further refine this input parameter. Finally, for a few chemicals, WWT can be obtained from actual monitoring studies of influent and effluent from POTWs. This has been used in the past to refine estimates of permethrin.

Table 10 provides a summary of removals by various mechanisms for eight pyrethroid insecticides predicted by STPWIN™. As shown in the table, the module predicts that for these chemicals, the main removal mechanism is sludge adsorption. The total biodegradation is low while the release to air is minimal.

Model Outputs

In the past, EFED has conducted preliminary DtD screens of a pesticide to determine the need for a bench scale POTW treatability study. In some cases the modeling results indicated that the study is not needed (*e.g.*, pyrethrins, spinosad). The modeling is possible if the production volume or its estimate, is available to the assessor. The assessor models the chemical with the aid of the EPI Suite v.4.11 model and gets an estimate of the level of removal (*i.e.*, WWT) from the module 'Sewage Treatment Plant Fugacity Model (STP)' using the default half-lives of 10,000 hours (~417 d) in the primary tank, the aeration tank, and the settling tank. This may be considered a conservative value (alternatively EPI Suite provides the second option to enter half-lives derived from monitoring experiments, or the third option to use model-estimated half-lives for the above mentioned processes). Suitable flows and the 10th percentile concentrations are used to derive RQs. The RQs derived from this process are compared against the LOCs. If they are well below the LOCs, it may be determined whether a treatability study is required using best professional judgment and considering the conservativeness of the preliminary risk assessment.

The most recent assessment for which the E-FAST's DtD module was used was an ecological risk assessment for deltamethrin. Uses assessed included sewage systems treatments (*50*). It was assumed that the upper bound value of the production volume is 50 kg a.i./year. After running the chemical using the DtD module, the acute concentration was found to be 0.000425 ppb and the chronic concentration was 0.000425 ppb (the same value). For freshwater and estuarine/marine fish and vascular and non-vascular plants there were no exceedances of LOCs. A summary of the findings on invertebrates is shown in Table 11.

Table 10. Removal Percent of Eight Pyrethroids in Wastewater Treatment Plants Obtained from EPISUITE v.4.11 and Its STPWIN Module[1]

Process	*Bifent.*	*Fenprop.*	*Cyhalot.*	*Permet.*	*Cyflut.*	*Cypermet*	*Esfenval.*	*Deltamet.*
Sludge Adsorption	93.2	91.4	93.1	92.7	91.2	93.0	92.1	92.1
Total Biodegradation	0.78	0.77	0.78	0.78	0.77	0.78	0.77	0.77
Total to Air	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
Total Removal	94.0	92.2	93.8	93.4	91.9	93.8	92.9	92.8

[1] All results were rounded to two decimal places or three significant figures.

Table 11. Summary of Acute and Chronic RQs for Aquatic Freshwater and Estuarine/Marine Invertebrates Exposed to Deltamethrin

Use	*App Rate*	*Peak EEC (µg/L)*	*21-day EEC (µg/L)*	*Acute RQ*	*Chronic RQ*
Freshwater Invertebrates[2]	50 kg/yr	0.000425	0.000425	0.11[1]	>16.3[1]
Estuarine/Marine Invertebrates[3]	50 kg/yr	0.000425	0.000425	0.11[1]	0.58

[1] RQs that exceed the EPA's levels of concern. [2] Acute RQ = use-specific peak EEC/0.004 ppb [for the amphipod *G. fossarum*]. Chronic RQ = use-specific 21-day EEC/10-d NOAEC of $<2.6x10^{-5}$ ug a.i./L [for the amphipod, *H. azteca*]. Chronic RQ values are expressed as ">" values because the NOAEC is non-definitive ("<") [3] Acute RQ = use-specific peak EEC/0.0037 ppb [for mysid shrimp, *Americamysis bahia*]. Chronic RQ = use-specific 21-day EEC/0.00073 ppb [from data for *A. bahia*].

Refinement of E-FAST (Bench Scale Study)

Based on experience with DtD modeling with pyrethroids, OPP requested additional data from registrants to improve modeling of the fate and removal efficiency of pyrethroids in POTWs. In response, registrants conducted a bench scale study simulating four processes that occur in POTWs: primary settling, aerobic biological treatment, anaerobic digestion, and ultra-filtration (Cleary and McGrath, MRID 48762906 (*51*)). Pyrethroids studied in these processes included: permethrin, deltamethrin, bifenthrin, cyfluthrin, *lambda*-cyhalothrin, cypermethrin, esfenvalerate, and fenpropathrin. Although in treatment plants, they occur simultaneously, these processes were evaluated separately from each other (*i.e.*, they were treated as modules). First, primary settling, anaerobic digestion, and ultrafiltration were measured in batch mode (*i.e.*, a set amount of sample was submitted to the process and evaluated after a period of time, *e.g.*, two hours for primary settling, up to 35 days for anaerobic digestion). Meanwhile, the aerobic biological treatment was evaluated in a continuous process (*i.e.*, process was continuously circulated and sample was evaluated throughout the procedure for 50 days, with a target solids retention time (SRT) of 10 days). Table 12 provides a results synopsis of the study. Note that the estimated removals are for specific modules and not overall removals. The percentages are not additive.

Wastewater from a treatment plant in Ridgewood, New Jersey, was spiked with known levels of the eight pyrethroids, well above background levels (5 µg/L of each pyrethroid, with the exception of permethrin at 50 µg/L), in order to characterize each process. This study was not conducted in compliance with Good Laboratory Practice Standards set forth in Title 40, Part 160 of the Code of Federal Regulations.

Table 12. Results Synopsis: Removal Percent of Eight Pyrethroids in Certain Treatment Processes Simulated in a Bench Scale Wastewater Treatability Study[1]

Process	*Bifent.*	*Fenprop.*	*l-Cyhal.*	*Permet.*	*Cyflut.*	*Cyperme.*	*Esfenval.*	*Deltamet.*
Primary Settling	LR[2]	LR[2]	LR[2]	LR[2]	LR[2]	LR[2]	LR[2]	LR[2]
Aerobic Chamber	51.9	80.1	48.6	86.6	73.2	76.3	56.1	59.1
Anaerobic Digestion	32.1	45.5	57.0	43.5	81.2	78.1	79.2	77.1
Ultrafiltration	91.7	95.7	93.1	96.9	95.7	95.4	93.6	92.6

[1] The percent shown is for each of the individual modules (refer to text). [2] LR means limited removal was achieved in this process.

Primary Settling

The primary settling experiment was conducted in batch mode. In primary settling, incoming wastewater (primary influent), was kept in a quiescent state for a specific period of time (in this study it was 2 hours), to allow heavy particles to settle. The result of the process was primary effluent (the supernatant) and primary sludge. Pyrethroids were measured in the primary influent wastewater and in the primary effluent and sludge. The primary effluent had concentrations of pyrethroids that were very similar to the concentrations in the primary influent. Primary settling did not appear to be effective to remove substantial amounts of pyrethroids from the primary influent.

Aerobic Biological Treatment

The primary effluent was added to the aerobic biological treatment system to reduce its organic content. The aerobic system was kept at *ca.* 20°C and it consisted of two submodules: the aeration system in which dissolved oxygen promotes aerobic biological degradation, and secondary settling. This part of the experiment was run for 50 days, where secondary sludge and primary effluent were fed to the aerobic chamber, in a continuous flow system. The target SRT was 10 days, which was reported to represent a likely best case scenario. Pyrethroids were removed moderately from the secondary influent (or primary effluent from the primary settling module), in the aerobic chamber. Removals ranged from 52 to 87 percent, for bifenthrin and permethrin, respectively.

Anaerobic Digestion

A specific amount of primary sludge (*i.e.*, sludge from primary settling) was submitted to digestion and run in batch mode for 35 days at *ca.* 35°C under anaerobic conditions. Pyrethroids were also removed moderately from primary sludge under these testing conditions in the anaerobic chamber. Among eight pyrethroids tested, removals ranged from 32 to 81 percent, for bifenthrin and cyfluthrin, respectively, attributed to anaerobic biological digestion.

Ultrafiltration

In ultrafiltration, the supernatants from the secondary settling were filtered and remaining solids were removed, reducing further the suspended particles, and thus the organic matter associated with those particles, and its associated pyrethroids. This process was run in batch mode, using an apparatus and method similar to the one used to measure total suspended solids. Removal represents the amount remaining in the effluent minus the amount applied of each pyrethroid in the influent. Ultrafiltration appeared to be the process that removed the highest percentage of pyrethroids from the secondary effluent, with over 90 percent of

pyrethroid removed from the final effluent. It is noted, however, that ultrafiltration is not a process employed by all WWTPs nationwide. Results presented in Table 12 are the means of two values, using a 0.1 μm filter.

Utility of the Bench Scale Study

The bench scale treatability study is useful in understanding the relative contributions of the different processes that occur at a treatment facility. Removal processes include primary settling, which shows very limited removal, and aerobic and anaerobic digestion, which show moderate levels of removal. Only ultrafiltration appeared to remove over 90% of the material in the bench scale study. Results from modeling (using EPISUITE giving total removal) and monitoring data (as discussed below) indicate levels of removal of above 90%. However, direct comparison of the bench scale study results to modeling and monitoring data is confounded by the fact that the bench scale study design does not enable determination of an overall removal efficiency based on the sum of the simulated treatment processes. Therefore, the utility of the bench scale study mostly relates to how separate processes affect pyrethroid removal and not for an estimate of the overall removal efficiency of pyrethroids from POTWs.

POTW Monitoring Data

The available information on the occurrence of pesticides in U.S. POTW influent, effluent and biosolids was reviewed and is summarized here with a focus on the following questions:

1. Which pesticides are most commonly detected in POTWs and how does this relate to their intended uses?
2. What is the removal efficiency of pesticides by wastewater treatment processes and how does this compare to estimates based on modeling and bench scale treatability studies?

Although a number of country-wide surveys of pesticides and other micropollutants in POTW wastewater have been conducted in Europe (*e.g.,* Loos *et al.* (*52*); Luo *et al.* (*53*)), an analogous U.S. wide survey was not identified in this review. Instead, several state-wide and POTW-specific surveys were identified and are summarized below.

Pesticides in POTW Influent and Effluent

Oregon POTWs

In one of the most comprehensive surveys of chemical contaminants in POTW effluent in the U.S., Hope *et al.* (*54*) analyzed effluents from 52 POTWs throughout Oregon once during the summer and during the fall of

2010. Of the 406 chemicals included in the survey, 149 were categorized as pesticides or pesticide-related chemicals (pesticide precursors, degradation products). The most frequently detected pesticide-related compounds include: 2,6-dichlorophenol (93%), arsenic (86%), DEET (78%), 2,4,6-trichlorophenol (72%), 2,4-dichlorophenol (62%), diuron (46%) 2,4,5-trichlorophenol (16%) and 2,3,4,5-tetrachlorophenol (13%) (Table 13). However, the presence of many of these compounds cannot be unambiguously traced to pesticide use. Specifically, the chlorinated phenols may be used as chemical intermediaries, are no longer registered as pesticides, and/or may be produced as a byproduct of effluent chlorination. Arsenic has some remaining commercial and industrial uses (*e.g.,* as a component of the chromated copper arsenate wood preservative) but also occurs naturally in the environment and may be released to POTWs via other commercial or industrial processes.

On the contrary, the presence of the insect repellant DEET most likely results from its widespread application to skin and subsequent washoff into household drains. DEET, the third most frequently detected pesticide, has the second greatest median concentration (232 ng/L and the greatest maximum concentration detected (13,600 ng/L). Diuron, the 6th most frequently detected pesticide, is a pre- and post-emergent herbicide with numerous agricultural and residential use sites, including application to water bodies for aquatic weed control. Particularly relevant to its occurrence in POTW effluent is its use as a mildewcide in certain paints and stains. This use could conceivably lead to down-the-drain releases to POTWs through washing of brushes and other painting equipment. Diuron and DEET were also among the most commonly detected pesticides in POTW effluent across Europe (*52*).

Triclopyr (detected in 11% of the samples), is used for broadleaf control in a variety of agricultural and residential settings. With no registered indoor uses in the U.S., direct release of triclopyr to POTWs via household drains is not expected. However, its use for weed control in residential settings could result in releases into stormwater runoff and subsequently to POTWs with hydrologically-connected stormwater conveyances. Interestingly, the herbicide 2,4-DB has no registered indoor or residential uses. Potential reasons for occurrence in 10% of the Oregon POTW effluent samples are not clear. Imidacloprid (10%) and imazapyr (9%), both have widespread residential uses for insect and weed control, respectively. Imidacloprid is also commonly used for flea control on pets via pet collars and spot-on treatments. It seems possible that its presence in POTWs could relate to pet washing or inappropriate disposal down the drain.

Hope *et al.* (*54*) report that detection of the fungicide propiconazole, used to prevent mold on wood, may have been related to discharge from a wood processing facility that discharged to a POTW. Propiconazole is also an ingredient in paints and stains which may also lead to releases to POTWs, possibly through washing of painting equipment and/or runoff into storm water connected to POTWs. The authors also note that fluridone, imazapyr and terbutylazine are applied directly to surface water for algae and macrophyte control and speculate that surface water intrusion into POTW conveyance systems may be occurring.

Table 13. Pesticides and Related Compounds Detected in a Survey of 52 Oregon POTWs. Source: Hope *et al.* (*54*)

Chemical	*CAS*	*LOQ (ng/L)*	*% Detect. (n=102)*	*Min. (ng/L)*	*Median (ng/L)*	*Max. (ng/L)*	*Category*
2,6-Dichlorophenol	87-65-0	7.7	93	10.3	82.4	864	other [1]
Arsenic (TR)	7440-38-2	250	86	260	620	4320	other [2]
DEET (*N,N*-diethyl-*m*-toluamide)	134-62-3	5	78	53	232	13600	other (insect repellant)
2,4,6-Trichlorophenol	88-06-2	19	72	25	55.6	339	wood preservative [3]
2,4-Dichlorophenol	120-83-2	19	62	19.8	68.5	470	other [1]
Diuron	330-54-1	4	46	38	89	775	herbicide
2,4,5-Trichlorophenol	95-95-4	19	16	21.4	42.4	300	other [3]
2,3,4,5-Tetrachlorophenol	4901-51-3	19	13	43.6	48.3	200	other [1]
Triclopyr	55335-06-3	300	11	310	620	3900	herbicide
2,4-DB	94-82-6	610	10	660	127	7440	herbicide
Imidacloprid	138261-41-3	20	10	202	237	387	insecticide
Imazapyr	81334-34-1	40	9	534	1670	17200	herbicide
Azobenzene	103-33-3	19	7	55	108	178	other [3]
Carbaryl	63-25-2	5	7	66	137	663	insecticide
2,4-D	94-75-7	100	3	1600	1630	1890	herbicide
Chlorpropham (CIPC)	101-21-3	7.7	3	17	46.1	72.4	herbicide

Continued on next page.

Table 13. (Continued). Pesticides and Related Compounds Detected in a Survey of 52 Oregon POTWs

Chemical	*CAS*	*LOQ (ng/L)*	*% Detect. (n=102)*	*Min. (ng/L)*	*Median (ng/L)*	*Max. (ng/L)*	*Category*
Dicamba	1918-00-9	300	3	380	700	760	herbicide
Prometon	1610-18-0	4	3	55	63	64	herbicide
Propiconazole	60207-90-1	20	3	387	7210	9020	fungicide
Pentachlorophenol	87-86-5	100	2	220	260	300	fungicide
Baygon	127779-20-8	4	1	42	42	42	insecticide
Dichloroprop (2,4-DP)	120-36-5	300	1	370	370	370	herbicide
Fluridone	59756-60-4	7.7	1	27	27	27	herbicide
Pentachlorobenzene	1825-21-4	380	1	416	416	416	other (PCP degradate)
Pentachlorophenol	87-86-5	380	1	700	700	700	fungicide
Simazine	122-34-9	4	1	56	56	56	herbicide
Terbutylazine	5915-49-3	4	1	61	61	61	herbicide

[1] Pesticide precursor or other chemical intermediary. [2] Organo arsenate and residential CCA uses no longer registered in the U.S. [3] Pesticide is no longer registered in the U.S.

In another comprehensive state-wide survey, Markle *et al.* (*55*) sampled 31 POTWs in California for the presence of eight pyrethroids in influent, effluent, and/or biosolids. This effort was conducted by the Pyrethroid Working Group (PWG), a consortium of registrants representing eight pyrethroids, in response to pyrethroid re-evaluation activities by both the California Department of Pesticide Regulation and the USEPA. The POTWs the surveyed represent approximately 40% of the treated municipal wastewater in California and include primary, secondary and tertiary treatment as terminal wastewater treatment processes. Samples were taken from January through March, 2013 during dry weather period. Consecutive grab samples were taken from influent, effluent and biosolids (when available) and did not account for hydrologic retention time between entry to the POTW and discharge. Extensive quality control measures were instituted including separate analytical measurement by two laboratories.

Results indicate high detection frequencies (*e.g.*, 43% to 100%) for 7 of the 8 pyrethroids sampled in POTW influent (Table 14). Frequencies of detection exceeded 80% for bifenthrin, cyfluthrin, *lambda*-cyhalothrin, cypermethrin and permethrin. Fenpropathrin was the least detected pyrethroid in effluent at 4.5% and is the only pyrethroid sampled that is not registered for residential uses in California. This suggests residential uses of these products are contributing to their loadings to California POTWs. By far the highest maximum and median influent concentrations reported are for permethrin (3,800 and 230 ng/L, respectively), which may be related to its topical use to treat lice infestations.

In POTW effluent, the greatest detection frequencies are observed for bifenthrin (82%), followed by cypermethrin (81%), permethrin (65%), cyfluthrin (60%), *lambda*-cyhalothrin (48%) and esfenvalerate (32%; Table 15). Comparatively, the rates of detection for deltamethrin and fenpropathrin are much lower (16% and 3% respectively) in effluent than influent. Consistent with the influent sampling results, the greatest maximum and median concentrations in POTW effluent are observed for permethrin (170 and 9.4 ng/L, respectively). Cypermethrin showed the next highest effluent concentrations with maximum and median values of 13 and 1.3 ng/L, respectively. Maximum and median concentrations for the other six pyrethroid are 2 orders of magnitude below that for permethrin.

It is instructive to compare the results of POTW monitoring to that predicted by down-the-drain modeling (DtD) using E-FAST described earlier, as a way of evaluating model predictions. Previous DtD assessments were conducted with permethrin and deltamethrin (USEPA (*45*) and USEPA (*50*), respectively) and are shown in Table 16 along with the monitored concentrations in effluent summarized in Table 15. With permethrin, the predicted concentrations in POTW effluent is 0.09 ppb, which is an order of magnitude above the median concentration measured in California POTWs by Markle *et al.* (*55*) However, it is about 2X below the maximum concentration detected in California POTW effluent (0.17 ppb). With deltamethrin, the predicted concentration (0.0004 ppb) is comparable to the median and maximum measured concentrations (0.0003 and 0.001 ppb, respectively).

Table 14. Summary of Pyrethroid Measurements in Influent from 31 California POTWs. (Source: Markle *et al.* (*55*))

Chemical	*# of Detects*	*% Detected*	*LOQ (ng/L)*	*Max. (ng/L)*	*Min. (ng/L)*	*Average[1] (ng/L)*	*Median[1] (ng/L)*
Bifenthrin	64	96%	5	74	ND	15	9.7
Cyfluthrin	59	88%	5	55	ND	11	7.4
Lambda-Cyhalothrin	54	81%	5	72	ND	5.6	2.8
Cypermethrin	54	81%	5	200	ND	35	21
Deltamethrin	29	43%	10	210	ND	8	3.3
Esfenvalerate	31	46%	5	360	ND	8.1	1.7
Fenpropathrin	3	4.5%	5	130	ND	4.6	1.7
Permethrin	67	100%	50	3800	30	330	230

ND = Not detected. A total of 67 influent samples were collected (62 samples + 5 repeats). [1] Median and average values were calculated assuming the limit of quantitation for non-detects.

Table 15. Summary of Pyrethroid Measurements in Effluent from 31 California POTWs. (Source: Markle *et al.* (*55*))

Chemical	*# of Detects*	*% Detected*	*LOQ (ng/L)*	*Max. (ng/L)*	*Min. (ng/L)*	*Average[1] (ng/L)*	*Median[1] (ng/L)*
Bifenthrin	51	82%	0.5	3.9	ND	0.89	0.6
Cyfluthrin	37	60%	0.5	4	ND	0.6	0.3
Lambda-Cyhalothrin	30	48%	0.5	1.6	ND	0.3	0.2
Cypermethrin	50	81%	0.5	13	ND	2.11	1.3
Deltamethrin	10	16%	1.0	1.2	ND	0.31	0.3
Esfenvalerate	20	32%	0.5	0.6	ND	0.25	0.2
Fenpropathrin	2	3.2%	0.5	0.8	ND	0.22	0.2
Permethrin	40	65%	5.0	170	ND	20	9.4

ND = Not detected. A total of 67 effluent samples were collected. [1] Median and average values were calculated assuming the limit of quantitation for non-detects.

Table 16. Estimated Environmental Exposure Concentrations of Permethrin and Deltamethrin, from POTW Discharges

Chemical	*Production Volume (kg)*	*WWT (%)*[1]	*Predicted Conc. (ppb)*	*Measured Conc. (ppb) (min, med, max)*
Permethrin	60,900	93.4	0.09	ND, 0.009, 0.17
Deltamethrin	50	65	0.0004	ND, 0.0003, 0.001

[1] WWT = percent removal from wastewater treatment.

It is also of interest to evaluate the removal of pyrethroids by POTW treatment, since this information can help inform modeling approaches for estimating pyrethroid loadings from POTWs. Influent and effluent data from Markle *et al.* (*55*) were used to calculate percent removal of pyrethroids using the following equation:

$$\%\ \text{Removal} = \left(1 - \frac{\text{Effluent Concentration}}{\text{Influent Concentration}}\right) \times (100\%)$$

When the effluent concentration was reported below limits of quantitation (LOQ), the concentration was equated to the LOQ. When the influent was reported to be below the LOQ, no calculation was made. On average, pyrethroid concentrations measured in POTW effluent are approximately 10% those measured in influent, representing a reduction of approximately 90% (Figure 15). The higher mean % removal indicated for esfenvalerate (97%) and fenpropathrin (99%) are based on very few samples and are therefore considered highly uncertain.

In terms of POTW-specific factors affecting pyrethroid concentrations, there was typically a large reduction in pyrethroid concentrations in effluent from primary to secondary treatment, although only one plant sampled had primary treatment as its terminal treatment process. The relationship between secondary and tertiary treatment was less clear, whereby some POTWs containing secondary treatment had higher concentrations in effluent compared to those with tertiary treatment and vice versa.

It is noted that the study by Markle *et al.* (*55*) was not specifically designed to estimate % removal efficiency of pyrethroids because samples were taken concurrently from influent and effluent without regard to the retention time of treated water in the POTW. Therefore, differences between concentrations of pyrethroid in influent and effluent may reflect, not only partitioning and degradation processes associated with wastewater treatment, but also variation in pesticide loadings over time. Nonetheless, average % removal efficiencies based on the monitoring data (90-99%) are quite similar to those calculated using the STPWIN™ model summarized in Table 10 (91-93%).

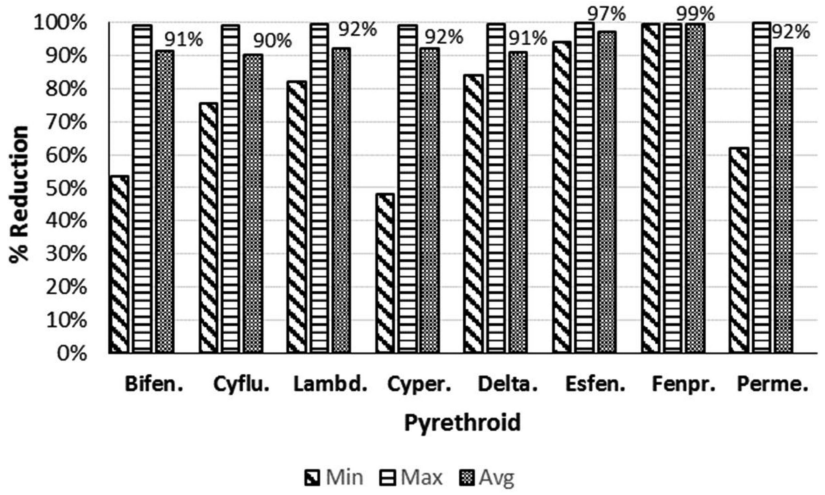

Figure 15. Percent reduction in pyrethroid concentrations in POTW effluent relative to influent. (Source: Markle et al. (55))

Sacramento POTW

In contrast to the previous two studies which conducted limited sampling of POTW wastewater across many facilities, Weston *et al.* (*56*) focused their efforts on a single facility, the Sacramento Regional County Sanitation District Treatment Plant. Concentrations of eight pyrethroids in influent and effluent were sampled over multiple time periods from November 2010 to January 2012. Twelve, 24-h composite samples were taken monthly from influent and seven 24-h, flow-weighted composite samples were taken from effluent (4 during rain events and 3 during dry events). Importantly, the timing of effluent samples was adjusted to account for the retention time of the wastewater in the plant. This facilitates more accurate estimation of % removal efficiency compared to the previous study by Markle *et al.* (*55*) Weston *et al.* (*56*) also sampled three POTW wastewater interceptors during the course of this study, one of which (City interceptor) received both municipal sewage and storm water runoff while the other two (Folsom and Laguna interceptors) received only municipal sewage.

Results from this study indicate that four pyrethroids were detected in all (100%) of the 12 monthly POTW influent samples (permethrin, bifenthrin cypermethrin, and *lambda*-cyhalothrin). Among these, permethrin was the dominant pyrethroid detected in terms of overall concentration and typically ranged between 200 and 400 ng/L. Cypermethrin and bifenthrin were generally found between 20 and 40 ng/L in influent while cyhalothrins were found up to 30 ng/L. Cyfluthrin was detected once in influent during the study, while deltamethrin, fenpropathrin and esfenvalerate were not detected in any of the 12 influent samples. Attempts to correlate temporal peaks in influent concentrations with known use pattern or sales data were not successful. Analysis of pyrethroids

in the wastewater interceptor upstream of the treatment plant suggest that storm water runoff was not the dominant source of pyrethroids to the plant. Concentrations of permethrin in the City interceptor (receiving stormwater) were slightly lower than those which did not receive stormwater. Furthermore, all the interceptors sampled contained substantially lower concentrations of permethrin than what was found in the POTW influent, suggesting that other sources of permethrin to the plant are likely. The other pyrethroids were found in similar concentrations in the three interceptors compared to POTW influent. The authors speculate that indoor uses of pyrethroids, container washing and possibly improper disposal of unwanted pesticide may be leading to the loadings to the Sacramento POTW.

In terms of effluent quality, permethrin was again the dominant pyrethroid detected in all but one of the seven effluent samples, ranging from 12-45 ng/L. Bifenthrin and cyhalothrins ranged from 1-5 ng/L in effluent and were detected 43% and 29% of the time, respectively. Concentrations of permethrin, bifenthrin and cyhalothrin were up to 2 times the respective 96-h EC_{50} values reported for the freshwater amphipod, *Hyalella azteca*. However, attempts to correlate observed toxicity to *H. azteca* in effluent samples with toxic units or TIE procedure were not definitive in terms of the cause of toxicity. Removal efficiencies of the pyrethroids from the POTW influent generally ranged from 90-95%, which is similar to the findings reported by Markle *et al.* (*55*) in their California-wide POTW survey.

Weston and Lydy (19)

In this study, Weston and Lydy sampled three California POTWs (Sacramento, Stockton, and Vacaville) for the presence of 8 pyrethroids and chlorpyrifos during three dry and three wet seasons in 2008 and 2009. The authors indicate that except for a small portion of the Sacramento POTW influent, all plants contained sanitary sewer systems that were separate from stormwater systems. They further note that the Stockton POTW included tertiary treatment via routing secondary treated wastewater through 240 ha of treatment ponds which yielded a retention time of about 30 days. Results above 1 ng/L are considered by the authors to be reliable. A total of 18 POTW samples were taken. Other samples of agricultural drains and urban runoff were also analyzed but are not discussed here.

Weston and Lydy (*19*) report that of all the samples, quantifiable concentrations of one or more pyrethroids were found in 67% of the samples taken. Across all three facilities, chlorpyrifos (40%), bifenthrin (39%) and permethrin (33%) were most commonly detected (Table 17). Generally, the highest concentrations of pyrethroids and chlorpyrifos are seen with the Sacramento POTW. In terms of toxicological relevance, 22% of the effluent samples containing bifenthrin, 17% containing *lambda*-cyhalothrin, and 6% of the samples containing cypermethrin exceeded the respective EC_{50} or LC_{50} values for *H. azteca*. The authors note that the presence of pyrethroids is surprising especially given the low levels of suspended solids in the effluent (< 8 mg/L). They suggest that sewer disposal of household pesticides, use of pet and lice control shampoos and laundering of permethrin-treated clothing may be

potential sources of pyrethroids to the POTWs. Despite 25-50% greater flows in wet weather, Weston and Lydy (*19*) report similar concentrations in effluent during dry and wet weather flows, which indicates that pesticide loadings from urban/residential runoff may be contributing to loadings to POTWs.

Pesticides in POTW Biosolids

Section 405(d) of the Clean Water Act (CWA) requires the U.S. Environmental Protection Agency (EPA) to identify and regulate toxic pollutants that may be present in biosolids (sewage sludge) at levels of concern for public health and the environment. Historically, the focus of identification and regulatory efforts has been on industrial chemicals, pharmaceuticals, metals, and selected antimicrobial chemicals. (*57*). However, recent studies have raised attention on the occurrence of conventional pesticides in biosolids, which often are treated and applied to land. Potential consequences of land-applied biosolids that contain appreciable amounts of pesticides include alteration of soil and terrestrial biota, runoff to surface waters and contamination of ground water.

In addition to quantifying pyrethroid concentrations in POTW influent and effluent, the previously summarized study conducted Markle *et al.* (*55*) also measured pyrethroids in biosolids from 24 of the POTWs included in the survey (Table 18). In terms of overall detection frequency, results mirror those described previously for influent and effluent, with the highest detection frequencies reported for bifenthrin (96%), permethrin (92%), cypermethrin (90%), and cyfluthrin (87%). The maximum concentration of permethrin (11,000 ng/g d.w.) is 10X that of the pyrethroids with the next highest maxima concentrations (bifenthrin, cypermethrin). Median concentrations are greatest for permethrin (1,200 ng/g d.w.), bifenthrin (120 ng/g d.w.) and cypermethrin (79 ng/g d.w.). Permethrin was also reported in sewage sludge from the U.K. (*58*) and Switzerland (*59*).

As a consequence of these and other reports of conventional pesticides in POTW biosolids, OPP has undertaken efforts along with counterparts in the Office of Water to develop approaches to screen uses of conventional pesticides for their potential to end up and persist in biosolids. The initial efforts focused on identifying pesticide uses with the greatest potential for releases down the drain (Table 9). Subsequently, efforts have focused on developing screening level models for evaluating the potential risks associated with pesticides in land-applied biosolids. One approach being evaluated is adapting the current Office of Water Biosolids Core Risk Assessment Model (BCRAM) for a screening level assessment. Other approaches being investigated include adapting existing OPP models (*e.g.*, PRZM) and exposure scenarios for evaluation of land applied biosolids.

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ACS Symposium Series; American Chemical Society: Washington, DC, 2014.

Table 17. Pyrethroids and Chlorpyrifos in Effluent from Three California POTWs. (Source: Weston and Lydy (*19*))

POTW[1]	*Bifen.*	*Cyfl.*	*Cyp.*	*Delt.*	*Esfen.*	*Fenp.*	*L. Cyh*	*Perm.*	*Chlor.*
Maximum Concentration Detected (ng/L)									
Sacr.	2.7	1.7	17.0	0	3.7	0	5.5	17.2	24.1
Stock.	4.8	0	0	1.3	0	0	0	7.9	5.5
Vaca.	6.3	0	0	2.7	0	0	2.8	7.6	0
Overall Detection Frequency (n=18) [2]									
	39%	6%	6%	11%	6%	0%	17%	33%	40%
Frequency exceeding EC_{50} or LC_{50} [3]									
	22%	0	6%	NA	NA	NA	17%	0	0

[1] Sacr. = Sacramento; Stock. = Stockton; Vaca. = Vacaville. [2] Detection frequency = # samples > 1 ng/L/total samples from all 3 plants (n=18). [3] Frequency of exceeding EC_{50} or LC_{50} for *H. azteca* (Bif =3.3 ng/L; Cyf = 1.9 ng/L; Cyp = 1.7 ng/L; L. Cyh = 2.3 ng/L; Per =21.1 ng/L and chlor = 96 ng/L).

Table 18. Summary of Pyrethroid Measurements in Biosolids from 24 California POTWs. (Source: Markle *et al.* (*55*))

Chemical	*# of Detects*	*% Detected*	*LOQ (ng/g)*	*Max. (ng/g)*	*Min. (ng/g)*	*Average[1] (ng/g)*	*Median[1] (ng/g)*
Bifenthrin	50	96%	2.5	1100	ND	150	120
Cyfluthrin	45	87%	2.5	190	ND	34	29
Lambda-Cyhalothrin	27	52%	2.5	200	ND	29	28
Cypermethrin	47	90%	2.5	1000	ND	110	79
Deltamethrin	16	31%	5.0	78	ND	28	24
Esfenvalerate	16	31%	2.5	42	ND	15	14
Fenpropathrin	3	5.8%	2.5	71	ND	12	6.8
Permethrin	48	92%	25	11000	30	1500	1200

ND = Not detected. A total of 52 influent samples were collected. [1] Median and average values were calculated assuming the limit of quantitation for non-detects.

Conclusions

As part of the Registration Review Program in USEPA, the first pyrethroid ecological risk assessments are less than two years away. Their widespread and diverse urban use patterns present many challenges in conducting a national scale ecological risk assessment. The problem formulations and public comment process has been extremely valuable in focusing on issues that need to be addressed. The Pyrethroid Working Group (PWG) has conducted a number of studies in response to the Data-Call-In (DCI) from USEPA and California Department of Pesticide Regulation (CADPR). Analysis of data from some of these studies is presented in this chapter while other studies are currently being reviewed. These data along with a wealth of information from public literature would be used in conducting ecological risk assessments for urban use pesticides.

To assess the exposure estimates from outdoor urban uses, EFED is currently using the residential and impervious scenarios in PRZM/EXAMS which only provide screening level information. To further refine these urban scenarios, results obtained from studies submitted for pathway identification, impervious surfaces washoff/runoff, turfgrass runoff and others could be used. Additionally, quality monitoring data may be used in verifying modeled EECs. Other factors that should be considered in improving these urban scenarios include characteristics of the pesticide to be modeled such as expected solubility in natural/urban drainage waters and washability from varied types of impervious surfaces. Any other significant pesticide load from sources such as ground water, drift and airborne dust contaminated with pesticides should also be considered.

The available evidence indicates that uses of conventional pesticides are resulting in relevant loadings to and from POTWs in the U.S. Information on use patterns can be used to identify those uses which are more likely to result in releases down the drain. However, POTW monitoring studies have also identified the presence of some pesticides for which the occurrence in POTW effluents is not easily explained by their labeled use patterns. Less obvious practices such as container washing, pet washing and possibly improper disposal of unwanted pesticide may be leading to pesticide loadings to POTWs. Efforts to date to model pesticide loadings to POTWs have relied on coarse, screening level models (*e.g.,* E-FAST). Information to refine critical model input parameters (*e.g.,* % removal efficiency) has been collected for some pesticides and suggest reasonable agreement between predicted and measured model parameters. The need for more comprehensive surveys of pesticides in U.S. POTW effluent is clear, as no national level survey information was identified to date. Information from such surveys in Europe (*e.g.*, Loos *et al.* (*52*)) and pesticide use pattern can provide useful information for identifying candidate pesticides for additional monitoring.

DISCLAIMER: The content of this chapter does not necessarily represent the official views of the U.S. EPA.

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ACS Symposium Series; American Chemical Society: Washington, DC, 2014.

References

1. Pesticide Use Reporting (PUR). California Department of Pesticide Regulation. http://www.cdpr.ca.gov/docs/pur/purmain.htm.
2. Gilliom, R. I., Barbash, J. E., Crawford, C. G., Hamilton, P. A., Martin, J. D., Nakagaki, N., Nowell, L. H., Scott, J. C., Stackelberg, P. E., Thelin, G. P., Wolock, D. M. *The Quality of Our Nation's Waters: Pesticides in the Nation's Streams and Ground Water, 1992–2001*; Circular 1291; U.S. Geological Survey, Revised February 17, 2007. http://pubs.usgs.gov/circ/2005/1291/.
3. Wilen, C. A. *Survey of Residential Pesticide Use and Sales in the San Diego Creek Watershed of Orange County, California*; University of California Statewide IPM Program, UC Cooperative Extension. Prepared for the California Department of Pesticide Regulation, October 16, 2001. http://www.ipm.ucdavis.edu/PDF/PUBS/sdcrk.pdf.
4. Wilen, C. A. *Survey of Residential Pesticide Use in the Chollas Creek Area of San Diego County and Delhi Channel of Orange County, California*; University of California Statewide IPM Program. Prepared for the California Department of Pesticide Regulation, September 2, 2002. http://www.ipm.ucdavis.edu/PDF/PUBS/chollas_survey.pdf.
5. Flint, M. L. *Residential Pesticide Use in California: A Report of Surveys Taken in the Sacramento (Arcade Creek), Stockton (Five-Mile Slough) and San Francisco Bay Areas with Comparisons to the San Diego Creek Watershed or Orange County, California*; University of California Statewide IPM Program. Prepared for the California Department of Pesticide Regulation, March 15, 2003. http://www.ipm.ucdavis.edu/PDF/PUBS/ncalifsurvey_1.pdf.
6. Kreidich, N., Flint, M. L., Wilen, C. A., Zhang, M. *Tracking Non-Residential Pesticide Use in Urban Areas of California*; DPR Agreement Number 02-0198C; Conducted by the University of California. Prepared for the California Department of Pesticide Regulation, June 10, 2005. http://www.ipm.ucdavis.edu/PDF/PUBS/ucdavisrep.pdf.
7. *California 2009 Urban Pesticide Use Pattern Study*; Published study conducted by the Pyrethroid Working Group (PWG) and Meta Research, Inc., Sacramento, CA, and sponsored by PWG; Laboratory Project ID CDPR Study ID Number 256489; December 1, 2010 (MRID 48762913).
8. Winchell, M. F., Cyr, M. J. *Residential Pyrethroid Use Characteristics in Geographically Diverse Regions of the United States*; An unpublished study performed by Stone Environmental, Inc., Montpelier, VT and Kline & Company, Inc., Parsippany, NJ, and sponsored by the Pyrethroid Working Group, Valdosta, GA; Laboratory Project ID PWG Number PWG-ERA-02a; Study completed November 30, 2013, Submitted January 6, 2014 (MRID 49292101).
9. Fugate, D., Hall, K. *Consumer Markets for Pesticides and Fertilizers: U.S. Market Analysis and Opportunities*, 17th ed.; Kline & Company: Parsippany, NJ, 2012.

10. Winchell, M. F. *Pyrethroid Use Characteristics in Geographically Diverse Regions of the United States: Parameterization of Estimated Pyrethroid Treatment Extent and Frequency for Urban Exposure Modeling*; Unpublished study performed by Stone Environmental, Inc., Montpelier, VT, and sponsored by Pyrethroid Working Group, Valdosta, GA; Laboratory Project ID PWG Number PWG-ERA-02b; Study completed November 30, 2013, Submitted January 6, 2014 (MRID 49292102).
11. Davidson, P. C., Jones, R. L., Harbourt, C. M., Hendley, P., Holscher, J. A., Sliz, B. A., Goodwin, G. E., Zwilling, L. F., Jacobson, A. S., Brown, S., Mason, B. J. *Pathway Identification Study*; Unpublished study performed by Waterborne Environmental, Inc., Leesburg,VA, Morse Laboratories, LLC, Sacramento, CA, and Agvise Laboratories, Inc., Northwood, ND, and sponsored by the Pyrethroid Working Group, Valdosta, GA; Laboratory project IDs PWG Number 11-02; Waterborne Number 794.15; Morse Number 67525; and Agvise Number 11-02(794.15); May 24, 2013 (MRID 49137401).
12. Davidson, P. C.; Jones, R. L.; Harbourt, C. M.; Hendley; Goodwin, G. E.; Sliz, B. A. Major transport mechanisms of pyrethroids in residential settings and effects of mitigation measures. *Environ. Toxicol. Chem.* **2014**, *33*, 52–60.
13. Trask, J. R.; Harbourt, C. M.; Miller, P.; Cox, M.; Jones, R.; Hendley, P.; Lam, C. Washoff of cypermethrin residues from slabs of external building material surfaces using simulated rainfall. *Environ. Toxicol. Chem.* **2014**, *33*, 302–307.
14. Harbourt, C., Trask, J., Miller, P., Miller, P., Cox, M., Jones, R., Hendley, P, Lam, C. *Washoff/Runoff of Cypermethrin Residues from Slabs of External Building Material Surfaces Using Simulated Runoff: Final Report*; Project Number 08/01, 794/10; Unpublished study prepared by Waterborne Environmental, Inc. (WEI) and Bayer CropScience; Study completed March 4, 2009 (MRID 48072902).
15. Hanzas, J. P., Jr.; Jones, R. L.; White, J. W. Runoff transport of pyrethroids from a residential lawn in central California. *J. Environ. Qual.* **2011**, *40*, 587–597.
16. Hanzas, J. P., Jr., Stone, C. T., Toth, B., White, J. *Bifenthrin and Beta-Cyfluthrin Quantification of Pyrethroid Runoff Losses from Treated Turfgrass under Over-irrigation Conditions and Simulated Rainfall*; Final Report; Unpublished study performed by Stone Environmental, Inc., Montpelier, VT, CRG Marine Laboratories, Inc., Torrance, CA, and AGVISE Laboratories, Northwood, ND, and sponsored by the Pyrethroid Working Group, Greensboro, NC; Stone Environmental Study Number 082018; Study completed December 23, 2008 (MRID 476478-01).
17. Giddings, J. M., Wirtz, J. R., Campana, D. *Analysis of Monitoring Data for Synthetic Pyrethroids in Surface Water and Sediment of the United States*; Prepared for the Pyrethroid Working Group, Landis International, Inc., Valdosta, GA; PWG Report No. PWG-ERA-05; Study completed February 4, 2014 (MRID 49314703).

18. Ruby, A., *Review of Pyrethroid, Fipronil and Toxicity Monitoring Data from California Urban Watersheds*; Prepared for the California Stormwater Quality Association (CASQA) by Armand Ruby Consulting, Santa Cruz, CA; July 10, 2013 (MRID 49354001).
19. Weston, D.; Lydy, M. Urban and agricultural sources of pyrethroid insecticides to the Sacramento-San Joaquin Delta of California. *Environ. Sci. Technol.* **2010**, *44*, 1833–1840.
20. Ensminger, M., Kelley, K. *Monitoring Urban Pesticide Runoff in California 2008–2009*; California Environmental Protection Agency, California Department of Pesticide Regulation, Environmental Monitoring Branch, Surface Water Protection Program, Sacramento, CA; Report 249; March 2011. http://www.cdpr.ca.gov/docs/emon/pubs/ehapreps/study_249_ensminger.pdf.
21. *Trends in Nutrients and Pesticides in the Nation's Streams and Rivers*; U.S. Congressional Briefing April 11, 2014, USGS 2014. https://water.usgs.gov/nawqa/headlines/nut_pest/.
22. Kuivila K. M., Hladik M. L., Ingersoll, C. G., Kemble, N. E, Moran, P. W., Calhoun D. L., Nowell, L. H, Gilliom, R. J. Occurrence and potential sources of pyrethroid insecticides in stream sediments from seven U.S. metropolitan areas. *Environ. Sci. Technol.* **2012**, *46* (8): 4297–4303.
23. Mosquito-Borne Diseases. National Center for Infectious Diseases (NCID). http://www.cdc.gov/ncidod/diseases/list_mosquitoborne.htm (accessed March 6, 2014).
24. Mosquito-Borne Diseases. American Mosquito Control Association. http://www.mosquito.org/mosquito-borne-diseases (accessed March 6, 2014).
25. Bonds, J. A. S. Ultra-low-volume space sprays in mosquito control: A critical review. *Med. Vet. Entomol.* **2012**, *26*, 121–130.
26. Pesticide Registration (PR) Notice 2005 -1. U.S. Environmental Protection Agency. http://www.epa.gov/PR_Notices/pr2005-1.pdf (accessed March 6, 2014).
27. Pesticide Registration (PR) Notice 2005-1: Labeling Statements on Products Used for Adult Mosquito Control. U.S. Environmental Protection Agency. http://www.epa.gov/PR_Notices/pr2005-1qa.htm (accessed March 6, 2014).
28. *Spray Drift Analysis for the Etofenprox Label Amendment*; Memorandum from Charles Peck to Andrew Ertman (Registration Division) and Kristin Rury (Health Effects Division), approved by Marietta Echevarria, March 28, 2013, and associated Data Evaluation Record; Office of Pesticide Programs, Environmental Fate and Effects Division, U.S. Environmental Protection Agency, 2013 (DP Barcode 407817).
29. Schleier, J., III *Development of an Environmental Fate Model for Risk Assessment of Ultra-Low Volume Insecticides*; Dissertation submitted in partial fulfillment of the requirements for the degree of Doctoral of Philosophy in Ecology and Environmental Sciences, Montana State University, April 2012.
30. Schleier, J. J., III, Peterson, R. K. D., Irvine, K. M., Marshall, L. M., Weaver, D. K., Preftakes, C. J. Environmental fate model for ultra-low-volume

insecticide applications used for adult mosquito management. *Sci. Total Environ.* **2012**, *438*, 72–79.
31. Tucker, J.; Thompson, C.; Wang, T.; Lenahan, R. Toxicity of organophosphorus insecticides to estuarine copepods and young fish after field applications. *J. Florida Anti-Mosq. Assoc.* **1987**, *58*, 1–6.
32. Moore, J. C.; Dukes, J. C.; Clark, J. R.; Malone, J.; Hallmon, C. F.; Hester, P. G. Downwind drift and deposition of malathion on human targets from ground ultralow volume mosquito sprays. *J. Am. Mosq. Control Assoc.* **1993**, *9*, 138–142.
33. Tietze, N. S.; Hester, P. G.; Shaffer, K. R. Mass recovery of malathion in simulated open field mosquito adulticide tests. *Arch. Environ. Contam. Toxicol.* **1994**, *26*, 473–477.
34. Knepper, R. G.; Walker, E. D.; Wagner, S. A.; Kamrin, M. A.; Zabic, M. J. Deposition of malathion and permethrin on sod grass after single, ultra-low volume applications in suburban neighborhood in Michigan. *J. Am. Mosq. Control Assoc.* **1996**, *12*, 45–51.
35. Tietze, N. S.; Hester, P. G.; Shaffer, K. R.; Wakefield, F. T. Peridomestic deposition of ultra-low volume malathion applied as a mosquito adulticide. *Bull. Environ. Contam. Toxicol.* **1996**, *56*, 210–218.
36. Schleier, J., III; Peterson, R. Deposition and air concentrations of permethrin and naled used for adult mosquito management. *Arch. Environ. Contam. Toxicol.* **2010**, *58*, 105–111.
37. Pierce, R. H.; Henry, M. S.; Blum, T. C.; Mueller, E. M. Aerial and tidal transport of mosquito control pesticides into the Florida Keys National Marine Sanctuary. *Rev. Biol. Trop.* **2005**, *53*, 117–125.
38. Preftakes, C. J.; Schleier, J. J., III; Peterson, R. K. D. Bystander exposure to ultra-low volume insecticide applications used for adult mosquito management. *Int. J. Environ. Res. Public Health* **2011**, *8*, 2142–2152.
39. Milam, C. D.; Farris, J. L.; Wilhide, J. D. Toxicity and risk of permethrin and naled to non-target insects after adult mosquito management. *Ecotoxicology* **2000**, *19*, 1140–1146.
40. Weston, D. P.; Amweg, E. L; Mekebri, A.; Lydy, M. J. Aquatic effects of aerial spraying for mosquito control over an urban area. *Environ. Sci. Technol.* **2006**, *40*, 5817–5822.
41. Zeigler, E. *Sacramento/Yolo Mosquito and Vector Control District Pyrethrin Water Quality Monitoring Data Summary*; Memorandum from Eric Zeigler to Gary Goodman, February 10, 2006, Davis, CA; Published study conducted by Larry Walker Associates and directed by the Sacramento-Yolo Mosquito and Vector Control District. http://www.up3project.org/documents/FinalMemo+att02-10-06.pdf (accessed March 5, 2014).
42. Schleier, J. J., III; Peterson, R. K. D. Toxicity and risk of permethrin and naled to non-target insects after adult mosquito management. *Ecotoxicology* **2010**, *19*, 1140–1146.
43. Hladik, M. L.; Kuivila, K. M. Assessing the occurrence and distribution of pyrethroids in water and suspended sediments. *J. Agric. Food Chem.* **2009**, *57*, 9079–9085.

44. Phillips, B. M.; Anderson, B. S.; Voorhees, J. P.; Siegler, K.; Denton, D.; TenBrook, P.; Larsen, K.; Isorena, P.; Tjeerdema, R. S. Monitoring the aquatic toxicity of mosquito vector control spray pesticides to freshwater receiving waters. *Integr. Environ. Assess. Manage.* **2014**, 1–7.
45. *Risks of Permethrin Use to the Federally Threatened California Red-legged Frog (Rana aurora draytonii) and Bay Checkerspot Butterfly (Euphydryas editha bayensis), and the Federally Endangered California Clapper Rail (Rallus longirostris obsoletus), Salt Marsh Harvest Mouse (Reithrodontomys raviventris), and San Francisco Garter Snake (Thamnophis sirtalis tetrataenia)*; Pesticide Effects Determination; Office of Pesticides Program, Environmental Fate and Effects Division, U.S. Environmental Protection Agency, 2008. http://www.epa.gov/oppfead1/endanger/litstatus/effects/redleg-frog/index.html#permethrin (accessed March 6, 2014).
46. *Response to Permethrin RED Public Comments, EFED Ecological Risk Assessment and Mitigation*; Office of Pesticides Program, Environmental Fate and Effects Division, U.S. Environmental Protection Agency, 2006 (DP Barcode D333756).
47. *Response to Public Comments on the EFED Registration Review Problem Formulation for Permethrin*; Office of Pesticides Program, Environmental Fate and Effects Division, U.S. Environmental Protection Agency, 2011 (DP Barcode D393883).
48. *Exposure and Fate Assessment Screening Tool (E-FAST) Version 2.0 Documentation Manual*; Prepared for the U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics; Prepared by Versar, Inc., Springfield, VA, October 2007. http://www.epa.gov/oppt/exposure/pubs/efast.htm (accessed March 7, 2014).
49. *Estimations Programs Interface (EPI) Suite™ v. 4.11*; Developed by the U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics and Syracuse Research Corporation (SRC). http://www.epa.gov/oppt/exposure/pubs/episuite.htm (accessed March 7, 2014).
50. *Risks of Deltamethrin Use to Federally Threatened Bay Checkerspot Butterfly (Euphydryas editha bayensis), Valley Elderberry Longhorn Beetle (Desmocerus californicus dimorphus), California Tiger Salamander (Ambystoma californiense), Central California Distinct Population Segment, and Delta Smelt (Hypomesus transpacificus), and the Federally Endangered California Clapper Rail (Rallus longirostris obsoletus), California Freshwater Shrimp (Syn caris pacificus), California Tiger Salamander (Ambystoma californiense) Sonoma County Distinct Population Segment and Santa Barbara County Distinct Population Segment, San Francisco Garter Snake (Thamnophis sirtalis tetrataenia), and Tidewater Goby (Eucyclogobius newberryi)*; Pesticide Effects Determination; Office of Pesticides Program, Environmental Fate and Effects Division, U.S. Environmental Protection Agency. http://www.epa.gov/oppfead1/endanger/litstatus/effects/redleg-frog/index.html#deltamethrin (accessed March 7, 2014).
51. Cleary, J. G., McGrath, J. *Laboratory Investigation of the Fate of Pyrethroid Insecticides in Wastewater Treatment Processes*; Unpublished

study performed by HDR|HydroQual, Mahwah, NJ and submitted by the Pyrethroid Working Group, Greensboro, NC; HDR|HydroQual Project Identification PYWG-153304.005' January 2012 (MRID 48762906).
52. Loos, R.; Carvalho, R.; António, D. C.; Comero, S.; Loroco, G.; Taravazzi, S.; Paracchini, B.; Ghiani, M.; Lettieri, T.; Blaha, L.; Jarosova, B.; Voorspoels, S.; Servaes, K.; Haglund, P.; Fick, J.; Lindberg, R. H.; Schwesig, D.; Gawlik, B. M. EU-wide monitoring survey on emerging polar organic contaminants in wastewater treatment plant effluents. *Water Research* **2013**, *47*, 6475–6487.
53. Luo, Y.; Guo, W.; Ngo, H. H.; Nghiem, L. D.; Hai, F. I.; Zhang, J.; Liang, S.; Wang, X. C. A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment. *Sci. Total Environ.* **2014**, *473-474*, 619–641.
54. Hope, B. K.; Pillsbury, L.; Boling, B. A state-wide survey in Oregon (USA) of trace metals and organic chemicals in municipal effluent. *Sci. Total Environ.* **2012**, *417–418*, 263–272.
55. Markle, J. C., van Buuren, B. H., Moran, K. D., Barefoot, A. C. *Pyrethroid Pesticides in Municipal Wastewater: A Baseline Survey of Publicly Owned Treatment Works Facilities in California in 2013*; Technical Report sponsored by the Pyrethroid Working Group; January 22, 2014.
56. Weston, D. P.; Ramil, H. L.; Lydy, M. J. Pyrethroid insecticides in municipal wastewater. *Environ. Toxicol. Chem.* **2013**, *32*, 2460–2468.
57. *Targeted National Sewage Sludge Survey Overview Report*; EPA-822-R-08-014; Office of Water, U.S. Environmental Protection Agency. http://water.epa.gov/scitech/wastetech/biosolids/tnsss-overview.cfm#appA.
58. Rogers, H. R.; Campbell, J. A.; Crathorne, B.; Dobbs, A. J. The occurrence of chlorobenzenes and permethrins in twelve U.K. sewage sludges. *Water Res.* **1989**, *2*, 913–921.
59. Plagellat, C.; Kupper, T.; de Alencastro, L. F.; Grandjean, D.; Tarradellas, J. Biocides in sewage sludge: Quantitative determination in some Swiss wastewater treatment plants. *Bull. Environ. Contam. Toxicol.* **2004**, *73*, 794–801.