



June 10, 2025

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Via Federal Docket: <https://www.regulations.gov/commenton/EPA-HQ-OPP-2021-0641-0006>

Subject: Comments on the Memorandum Supporting Proposed Decision to Approve
Registration for the New Active Ingredient of Isocycloseram (EPA-HQ-OPP-
2021-0641)

Dear Charles Smith:

On behalf of the Bay Area Clean Water Agencies (BACWA), we thank you for the opportunity to provide comments on the *Memorandum Supporting Proposed Decision to Approve Registration for the New Active Ingredient of Isocycloseram*¹ and its supporting documents, including the *Draft Environmental Fate and Ecological Risk Assessment (draft ERA) for the Proposed FIFRA Section 3 Registration and Biological Evaluation (draft BE) with Associated Effects Determinations for Federally Listed Endangered and Threatened Species and Designated Critical Habitat*².

BACWA is a joint powers agency whose members own and operate publicly owned treatment works (POTWs) and sanitary sewer systems that collectively provide sanitary services to over seven million people in the nine-county San Francisco Bay Area (Bay Area). We take our responsibilities for safeguarding receiving waters seriously.

Every day, BACWA members provide wastewater treatment for millions of gallons of wastewater that is discharged to fresh or saltwater bodies, including local creeks and rivers, bays, and the Pacific Ocean. These waterways provide crucial habitat to a wide array of aquatic species and waterfowl, including several endangered species. In some cases, waters receiving POTW discharges ("receiving waters") may be effluent-dominated in that there is little to no dilution, either because the receiving water is small, or because there is a lack of mixing at certain times due to thermal or saline stratification.

¹ Memorandum Supporting Proposed Decision to Approve Registration for the New Active Ingredient of Isocycloseram, dated May 6, 2025, <https://www.regulations.gov/document/EPA-HQ-OPP-2021-0641-0007>

² Isocycloseram: Draft Environmental Fate and Ecological Risk Assessment (ERA) for the Proposed FIFRA Section 3 Registration and Biological Evaluation (BE) with Associated Effects Determinations for Federally Listed Endangered and Threatened Species and Designated Critical Habitat, dated May 8, 2025, <https://www.regulations.gov/document/EPA-HQ-OPP-2021-0641-0021>

Isocycloseram is a broad-spectrum contact insecticide to be used as a gel, spray, spot, void, or crack-and-crevice treatment with the following proposed urban/suburban uses for cockroaches, bed bugs, ants, and termites:^{3,4}

- Direct sewer linkages: Interior floor drains (to sewers) and outdoor drains leading to sewers.
- Indoor treatments with sewer linkages: between equipment and floors, openings leading into voids and hollow spaces in floors, walls, ceilings, and equipment legs and bases; around plumbing pipes, doors and windows; behind and under appliances, cabinets and sinks; in closets; near garbage collection areas; along baseboards, under counters, cracks and crevices in nightstands and dressers, voids behind headboards, baseboards, moldings, door frames, window frames, closets, and shelving; behind mirrors and picture frames; around edges of carpet or other floor coverings; cracks and joints of bed frames (interior included), headboards, box springs and mattresses; luggage; on structural wood infested with termites, as well as injected into wood infested by termites.

Isocycloseram appears to be more toxic than existing pesticides for the same uses

In the draft ERA, EPA found that isocycloseram is very highly toxic to aquatic invertebrates and toxic to fish. Isocycloseram is particularly toxic to estuarine/marine invertebrates under chronic exposure, with a no observed adverse effect concentration (NOEAC) of 0.00098 µg/L. When comparing aquatic invertebrate toxicity values, isocycloseram is orders of magnitude more toxic than fipronil and imidacloprid, pesticides with many of the same indoor uses (Table 1). The environmental degradation rates listed in Table 5-2 of the draft ERA suggest that isocycloseram and its degradates could persist through the wastewater collection and treatment process, which can be shorter than 1 day. In addition, several of the isocycloseram degradates are also highly toxic to aquatic invertebrates, with toxicity values similar to fipronil.

Urban water bodies in California are already impacted by fipronil, imidacloprid and numerous pyrethroids, with monitoring data that exceed toxicity benchmarks as well as 303(d) listings leading to TMDLs. Pesticides with similar mitigation measures (high dilution ratios for mixing the product prior to application, labeling, and use restrictions) to those of the proposed isocycloseram labels are found in California monitoring data. This indicates that the mitigation measures alone may not be sufficient to prevent improper use. The idea that a new pesticide, with equal or greater chronic toxicity, is being considered for these same urban uses strongly suggests that at a minimum this could become a regrettable substitution in the urban environment.

Additionally, in the Endangered Species Act Draft Biological Evaluation, EPA determined that isocycloseram is likely to adversely affect (LAA) listed species or critical habitat. EPA noted that if the registration of isocycloseram moves forward, that it would “likely need to consult with the Services because the draft effects determinations include may affect determinations” (draft

³ Isocycloseram A21550 400SC Insecticide-Master Label, <https://www.regulations.gov/document/EPA-HQ-OPP-2021-0641-0025>

⁴ Isocycloseram A22128 Cockroach Gel Bait-Master Label, <https://www.regulations.gov/document/EPA-HQ-OPP-2021-0641-0029>

ERA, p. 178). BACWA is particularly concerned with this finding because several of the listed fish species with a predicted potential likelihood of future jeopardy include two species native to the San Francisco Bay Area, Chinook salmon and steelhead (draft ERA, Table 15-8, pg. 210).

Table 1. Acute and Chronic Aquatic Life Benchmarks (ALBs) for Freshwater Aquatic Invertebrates

Pesticide	Acute ALB (µg/L)	Chronic ALB (µg/L)
Isocycloseram	0.007	0.0015
Fipronil	0.11	0.011
Imidacloprid	0.385	0.01
Bifenthrin	0.00024	0.00005
Cyfluthrin	0.0125	0.00012
Permethrin	0.0033	0.0042

Note: Isocycloseram values are based on the draft ERA (p.104). The acute ALB for isocycloseram was calculated based on the LC50 in the draft ERA multiplied by an LOC of 0.5, parallel to the ALBs in the EPA's Aquatic Life Benchmarks website. All other values are from the EPA's Aquatic Life Benchmarks website, <https://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/aquatic-life-benchmarks-and-ecological-risk>

BACWA requests that EPA model indoor and in-sewer uses to ensure that uses affecting POTWs are addressed

In the Draft ERA, EPA did not model indoor uses of isocycloseram including cockroach products applied directly to floor drains connected to sewers, washable fabrics treated for bedbugs, and cockroach and ant sprays used in kitchen areas that will be washed down the drain with mopping. Additionally, EPA did not consider indoor uses in its Biological Evaluation (draft BE) with Associated Effects Determinations for Federally Listed Endangered and Threatened Species and Designated Critical Habitat. The comprehensive conceptual model shown below (from Sutton et al. 2019) identifies the pathways between pesticide uses and POTWs and illustrates how pesticides used indoors flow to the sewer system, to POTWs, and ultimately into the environment via effluent, air emissions, and biosolids.⁵

EPA has been evaluating POTW discharges from indoor pesticide use and discharges to the sewer system in its pesticides risk assessments since the late 1990s. As described by an EPA scientific team (Shamim et al. 2014), 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.⁶ As EPA noted in its pyrethroids ecological risk assessment,⁷ this modeling approach is imperfect, but in combination with monitoring data it has been useful in understanding aquatic risks. Since the mid-2010s, BACWA has been in dialog with EPA scientists to improve the accuracy of EPA's POTW modeling approach, focusing on

⁵ Sutton et al. (2019). Occurrence and Sources of Pesticides to Urban Wastewater and the Environment. In K. Goh (Ed.), Pesticides in Surface Water: Monitoring, Modeling, Risk Assessment, and Management (pp. 63-88). Washington, DC: American Chemical Society.

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.

⁷ EPA OPP EFED (2016). Preliminary Comparative Environmental Fate and Ecological Risk Assessment for the Registration Review of Eight Synthetic Pyrethroids and the Pyrethrins. Part I. Assessing Pyrethroid Releases to POTWs of Pyrethroids and Pyrethrins (DP Barcode D425791).

improvements that can be made with relatively small investments of EPA's scientific staff resources. We appreciate that some of our recommendations, (e.g., effluent dilution factors that recognize the prevalence of "zero dilution" discharges) have been implemented in the current version of the E-FAST model.

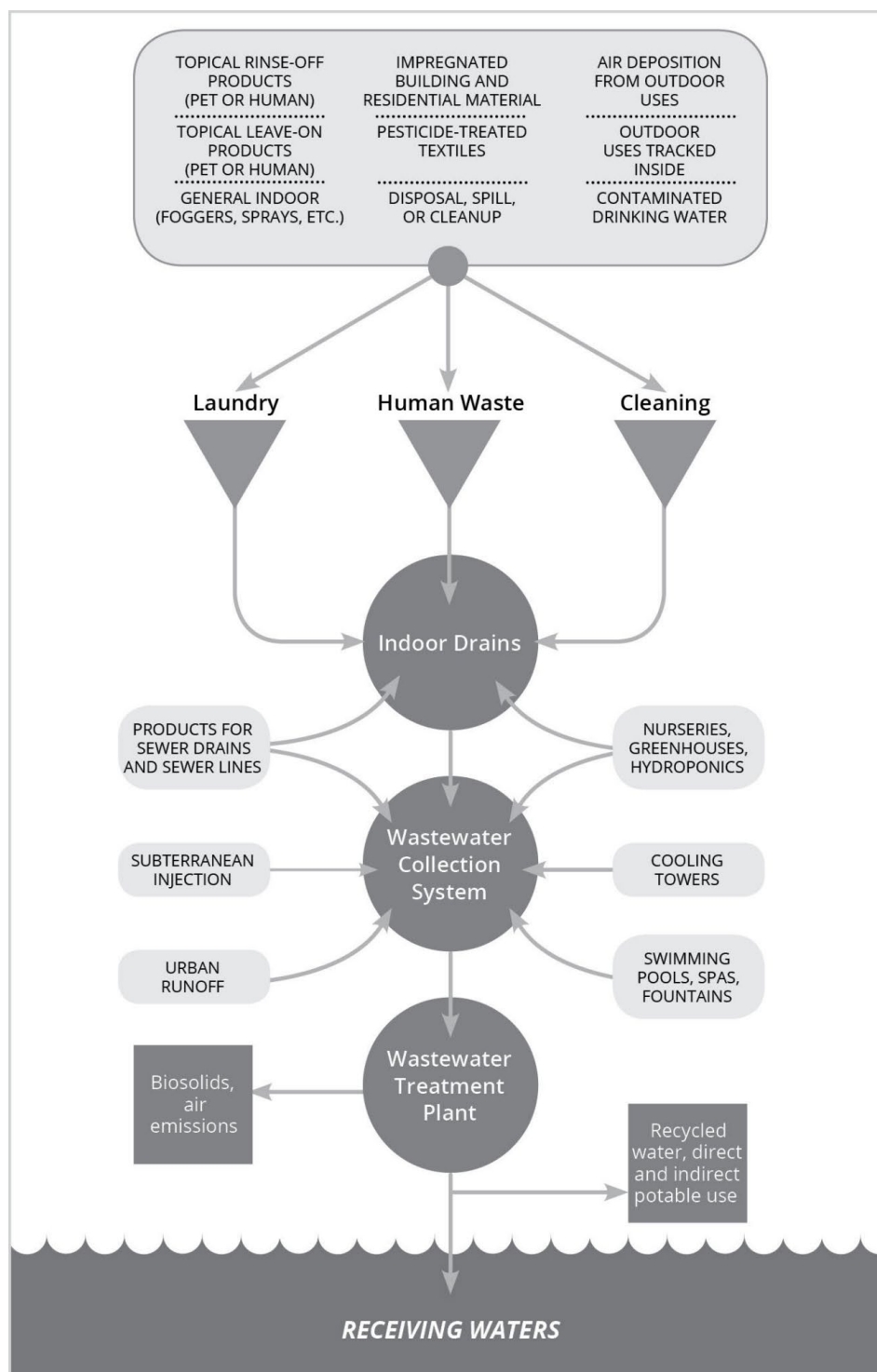


Figure source: Sutton et al., 2019

There are several indoor isocycloseram uses that have a direct down-the-drain pathway including (but not limited to) cockroach product used directly in sewers and sprayable products used on floors, cabinets, and furniture that could later be mopped or washed, as well as washable fabrics treated with isocycloseram for bedbugs. Based on the very limited public data for this new pesticide, we are concerned that the isocycloseram discharges from cumulative residential and commercial uses of these products alone could pass isocycloseram through municipal wastewater treatment plants at concentrations sufficient to be a toxicity concern to aquatic life. The draft ERA does not contain sufficient information for us to estimate these discharges. BACWA asks EPA to model indoor uses of isocycloseram, including these products and that the risk assessment look at not just the parent compound, but also the toxic degradates.

POTW modeling is needed to inform POTW-specific mitigation measures

Local agencies in most states (including California) lack the statutory authority to regulate pesticide use in urban areas. Thus, it is essential that EPA employ the pesticide regulatory and Endangered Species Act consultation processes to assess and prevent urban water pollution as defined by the Clean Water Act and our NDPES permits.

In BACWA's more than ten years of experience reviewing and commenting on EPA's pesticide registration/re-registration process, we have learned that if EPA does not model the specific down-the-drain pathway for a use-type, then it will not propose mitigations for that use-type. We are very concerned that the absence of adequate indoor use modeling and the lack of mitigations will result in direct harm to aquatic life from indoor uses of isocycloseram.

If the pesticides reregistration process fails to identify and implement mitigation, 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, which could increase rates for the general public. 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 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. It is therefore essential that 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 (i.e., uses and/or discharges associated with endangered species impacts do not occur).

BACWA requests that the use of isocycloseram in sewers be removed from all proposed pesticide labels

The use of isocycloseram in and directly around sewers is a direct pathway to the sewer and wastewater treatment plant, as we have discussed above. This puts an undue burden on public agencies to try to remove this pesticide during the wastewater treatment process or bear the burden—in penalty fines from the local and state water boards as well as lawsuits—of discharging this highly toxic pesticide to receiving waters.

BACWA requests that EPA remove the use of isocycloseram in and around sewers from all proposed pesticide labels including the proposed A22128 Cockroach Gel Bait label:

- In Section 3.0 PRODUCT INFORMATION, BACWA requests the following text be removed (see strikethrough):
A22128 Cockroach Gel Bait can be applied indoors or outdoors as a crack-and-crevice, spot, or void treatment in and around residential homes, industrial facilities, offices, warehouses, commercial kitchens, supermarkets, hospitals, schools, nursing homes, hotels/motels, buses, trains, aircraft, retail and commercial establishments, agricultural facilities, ~~sewers~~, and other areas infested with cockroaches.
- In Section 3.2.1 Applications in Non-Food Areas, BACWA requests the following text be removed (see strikethrough):
Non-food/non-feed areas include areas such as garbage rooms, lavatories, ~~floor-drains (to sewers)~~, entries and vestibules, offices, locker rooms, machine rooms, boiler rooms, garages, mop closets, and storage (after bottling or canning). Refer to section below for use directions and restrictions when making applications in food/feed handling areas of Food/Feed-Handling Establishments.
- In Section 4.1.2 Outdoor Use, BACWA requests the following text be removed (see strikethrough):
A22128 Cockroach Gel Bait may also be applied as a spot or thin bead to pest entry sites such as along windows, doors, walls, and between construction elements; ~~drains leading to sewers~~; adjacent trees that can harbor cockroaches; garbage holding areas; or other placement sites where cockroaches harbor.
- In Section 5.1 Use Restrictions, BACWA requests that the following text be added as a use restriction:
DO NOT apply inside sewers or sewer drains.

BACWA requests that isocycloseram pesticides labels include drain discharge prohibition language in both English and Spanish as well as simple graphic, as adopted for all pyrethroid products

BACWA suggests the use of a simple graphic on product packages to show that the product should not be poured down the drain. This graphic was adopted by EPA for all of the pyrethroid labels in 2021⁸. BACWA recommends that a clear graphic be used, such as this one provided by the Dublin San Ramon Services District:



BACWA would be pleased to work with EPA and registrants on determining an appropriate

⁸ Updated Label Language for the Pyrethroids and Pyrethrins Revised Ecological Risk Mitigation and Response to Comments on the Ecological Risk Mitigation Proposal For 23 Chemicals, September 30, 2020, memorandum dated February 17, 2021.

graphic, along with the details for using the graphic on product packages, such as size and placement. Along with the graphic, BACWA supports a drain discharge prohibition label language in both English and Spanish, and recommends the following language for products labeled for use directly inside pipes or sinks:

“Do not pour down the drain or sewer. Call your local solid waste agency for local disposal options.”

BACWA requests that the use of isocycloseram be forbidden on washable fabrics or textiles.

The proposed isocycloseram label allows for its use on fabrics and textiles. Many fabrics and textiles are washable. These washable fabrics and textiles create a direct down-the-drain pathway for isocycloseram to reach the sewers and wastewater treatment plant from washing machine drains, as shown above in the Sutton et al., 2019 figure. BACWA asks EPA to request that the registrant add clarifying language in the proposed label for A21550 400SC INSECTICIDE to make it clear that users should not use the pesticide on *washable* fabrics and textiles.

- In Section 6.2 Bed bugs, BACWA requests the following text be added: Only apply to non-washable fabrics and textiles.
- In Section 6.2 Bed bugs, BACWA requests the following text be added to the existing sentence in this section (added text shown with underline):
Remove all washable items in area such as bed linens, pillows, pet bedding, and rugs, before treating mattresses and allow spray to dry before remaking the bed.
- In Section 5.0 USE RESTRICTIONS AND PRECAUTIONS, BACWA requests that the following text be added as a use restriction:
DO NOT apply to washable textiles and fabrics, including bed linens, washable rugs, etc.

BACWA requests a minimum of 60-day comment periods for future pesticide registration comment periods

BACWA requests that EPA allow a sixty-day comment period in the future for all new pesticide registrations, draft environmental risk assessments, and draft biological evaluations. In particular, this product registration contains more information than previous product registrations, including a draft Biological Evaluation Determination as well as a draft Environmental Risk Assessment. These extra assessments take additional time to review. Public agencies, cities, counties, and others need at least sixty days to review documents from EPA and route them through their approval process. Like many public agencies and non-profits, BACWA’s signatory process requires that all letters be reviewed by a subcommittee, and then once revised are routed to the Board and Executive Team. The letters are then revised again to incorporate comments and finalized. A thirty-day comment period is not sufficient for this process.

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

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Respectfully Submitted,



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Attachments:

- 1) 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.
- 2) Sutton et al. (2019). Occurrence and Sources of Pesticides to Urban Wastewater and the Environment. In K. Goh (Ed.), Pesticides in Surface Water: Monitoring, Modeling, Risk Assessment, and Management (pp. 63-88). Washington, DC: American Chemical Society.

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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.

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

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

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

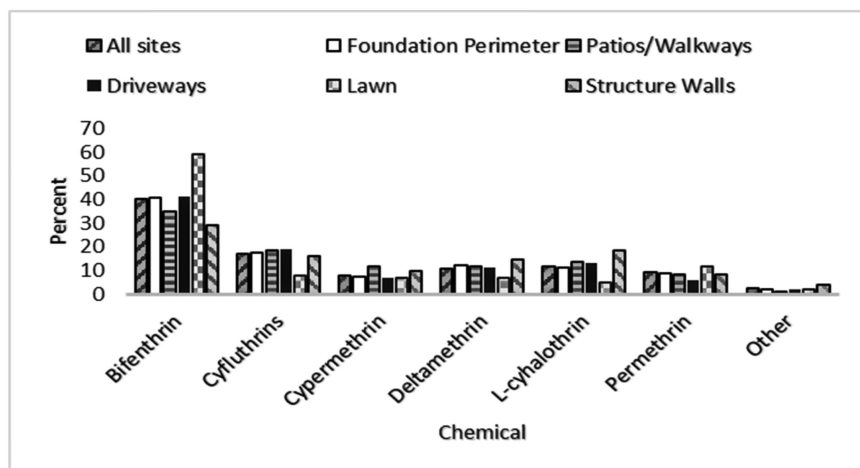


Figure 1. Percent of Respondents' Pyrethroid Active Ingredient Use in Outdoor Applications by Selected Use Sites, Excluding California.

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.

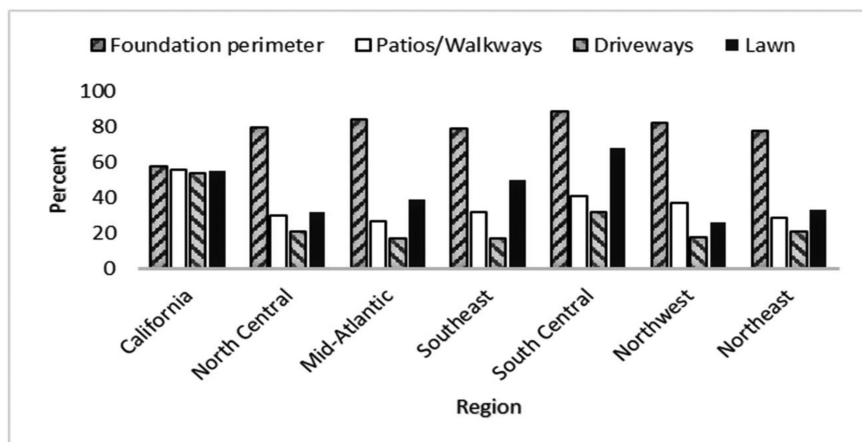


Figure 2. Percent of PCOs and LCOs Applying Pyrethroids to Selected Sites by Region.

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

<i>Use Site Type of Surface</i>	<i>Average Number of Treatments Per Year</i>	<i>Fraction of Use Site Surface Area Treated</i>	<i>Most Commonly Used Active Ingredient</i>
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

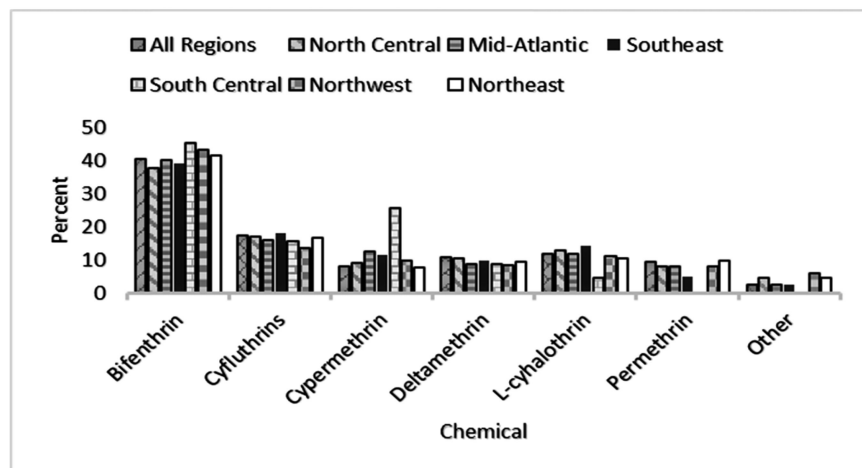


Figure 3. Percent of Respondents' Pyrethroid Active Ingredient Use in Outdoor Applications by Region, Excluding California.

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

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)) synthesizes 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

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 $\frac{1}{4}$ 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 $\frac{1}{4}$ 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 $\frac{1}{4}$ -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 ($\leq 0.011\%$ 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, Aliso Viejo, 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.

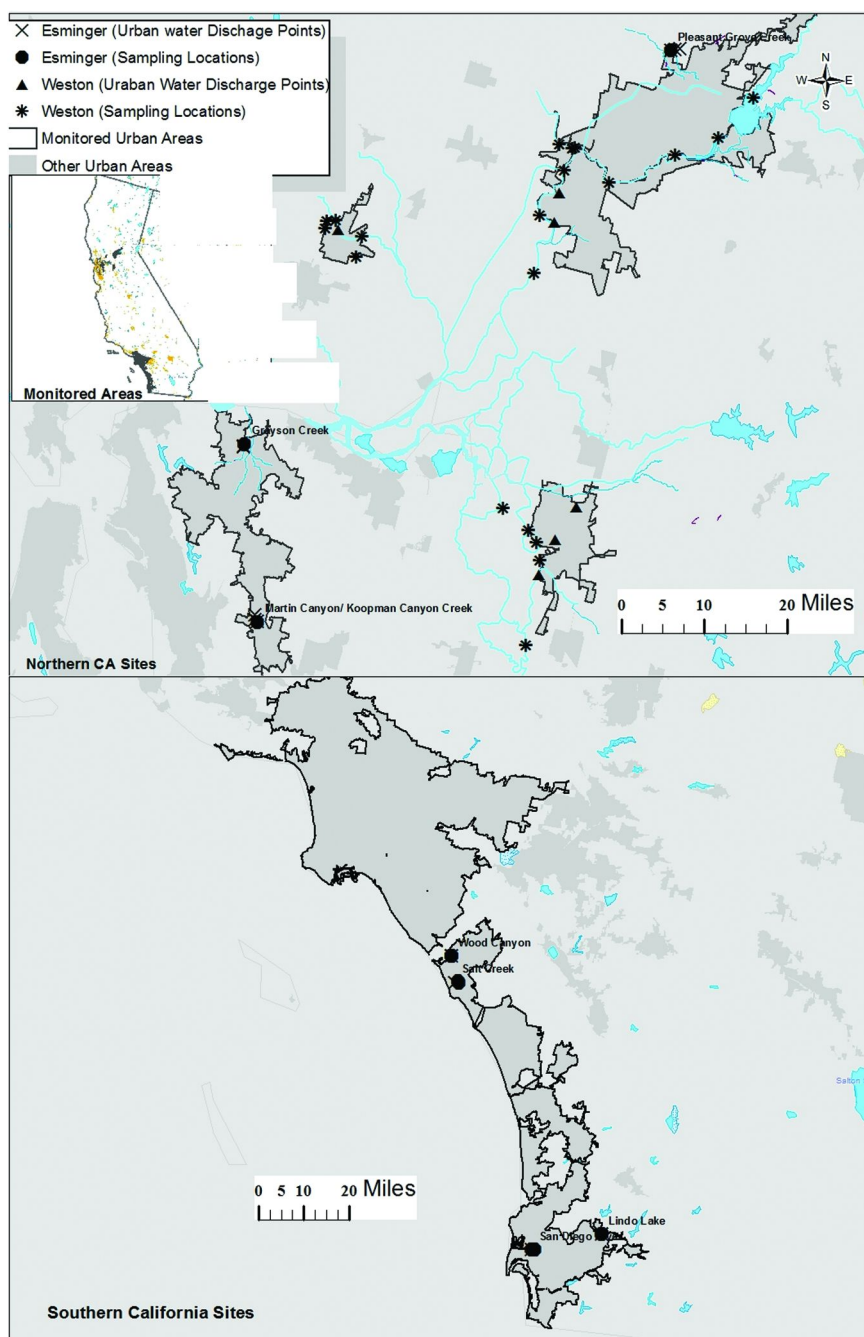


Figure 4. Monitored urban areas in Northern and Southern California (Weston and Lydy (19); and Ensminger and Kelley (20)).

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, desulfinylfipronil 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), fenvalerate/fenvalerate (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, desulfinylfipronil 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 ($N = 8 = 2 \times 4$; 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 $\mu\text{g/L}$. For fipronil, the maximum was 2.1 $\mu\text{g/L}$ 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.

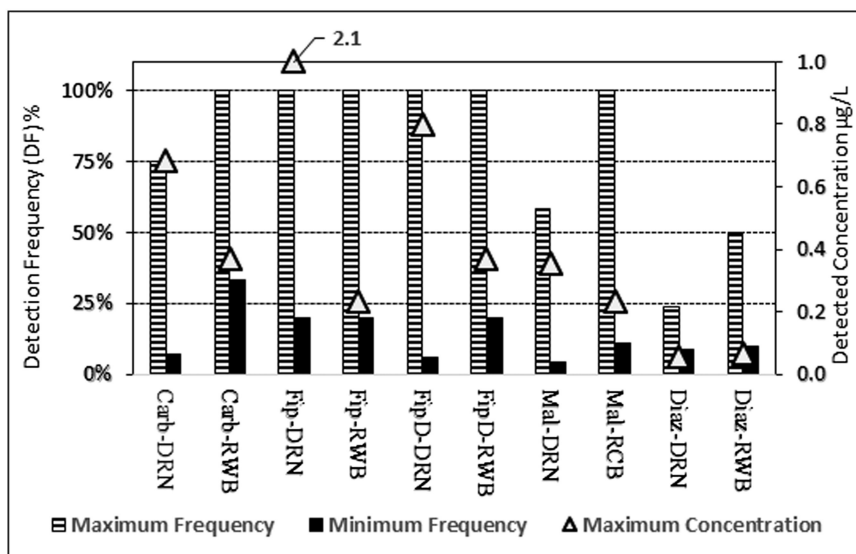


Figure 5. A summary graph for the top five insecticides frequently detected in source drain water (DRN) and receiving water bodies (RWB) in four of the major urban areas of California.

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).

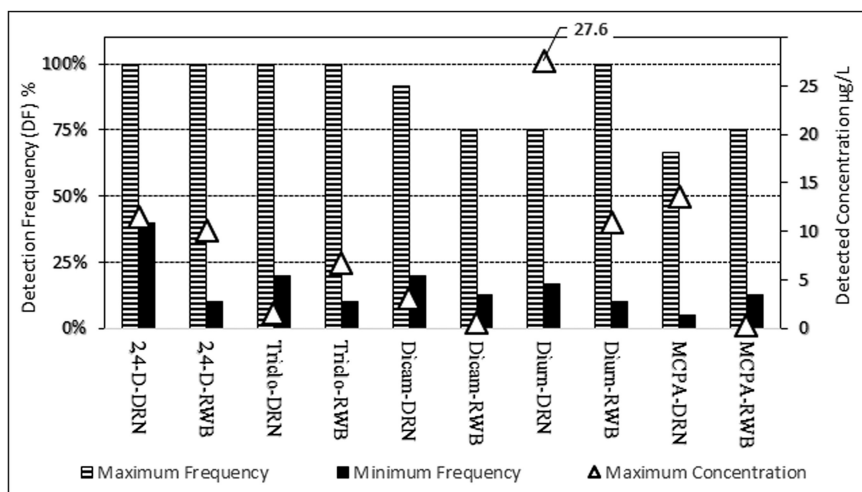


Figure 6. A summary graph for the top five insecticides frequently detected in source drain water (DRN) and receiving water bodies (RWB) in four of the major urban areas of California.

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.

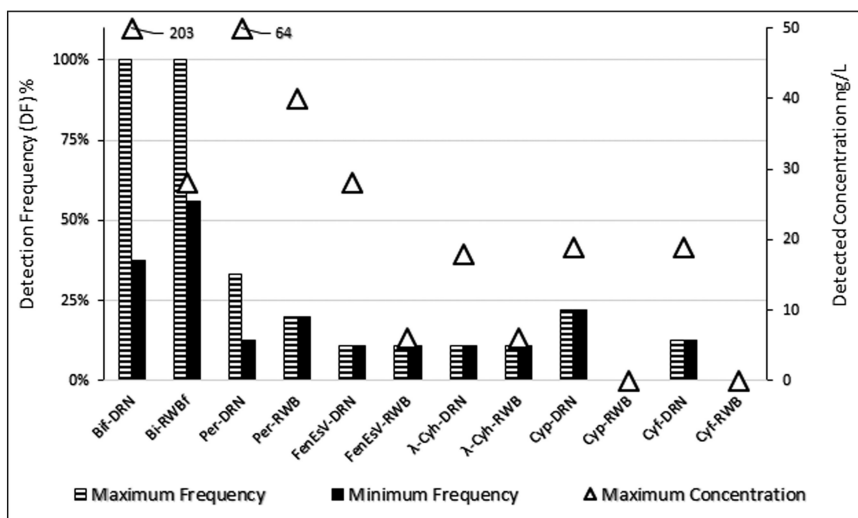


Figure 7. A summary graph for pyrethroid insecticides frequently detected in source drain water (DRN) and receiving water bodies (RWB) in three of the major urban areas in California.

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.

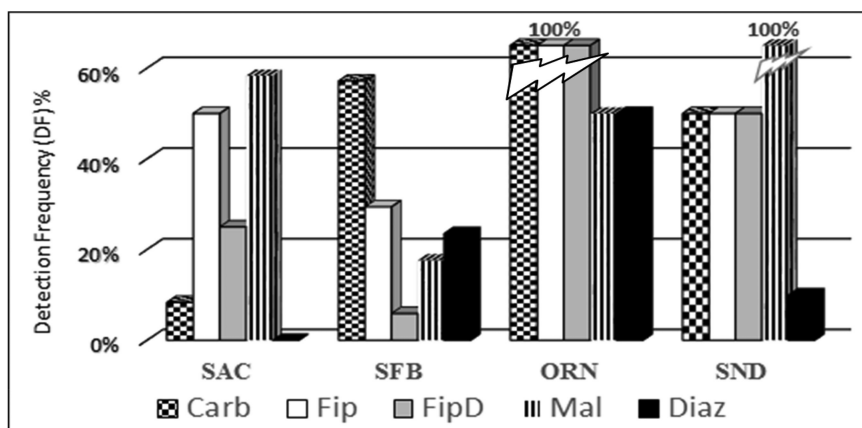


Figure 8. Maximum detection frequencies (DFs) for the top five insecticides detected in source/receiving waters of four of the major urban areas of California (SAC= Sacramento, SFB= San Francisco Bay, ORN= Orange County and SND= San Diego).

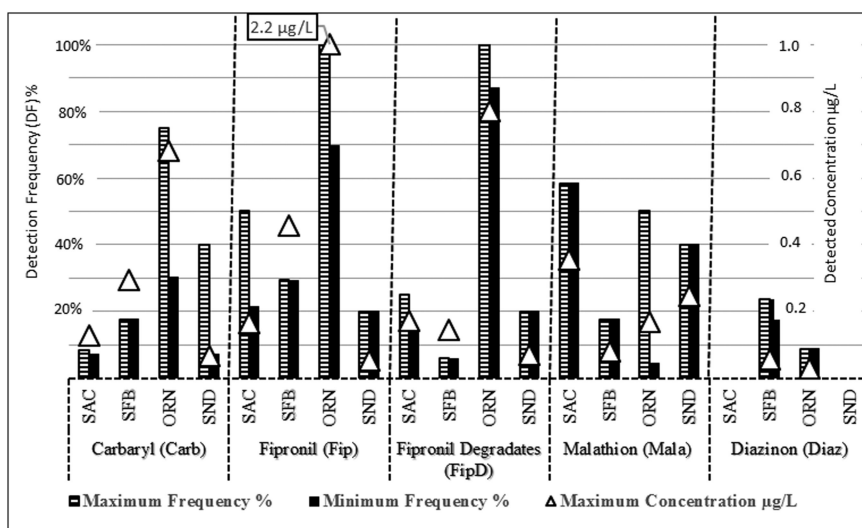


Figure 9. Max/min Detection Frequencies (DFs) and maximum concentrations of major insecticides detected in source drain waters (DRNs) in Sacramento (SAC), San Francisco Bay (SFB), Orange County (ORN) and San Diego (SND) urban areas of California.

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.

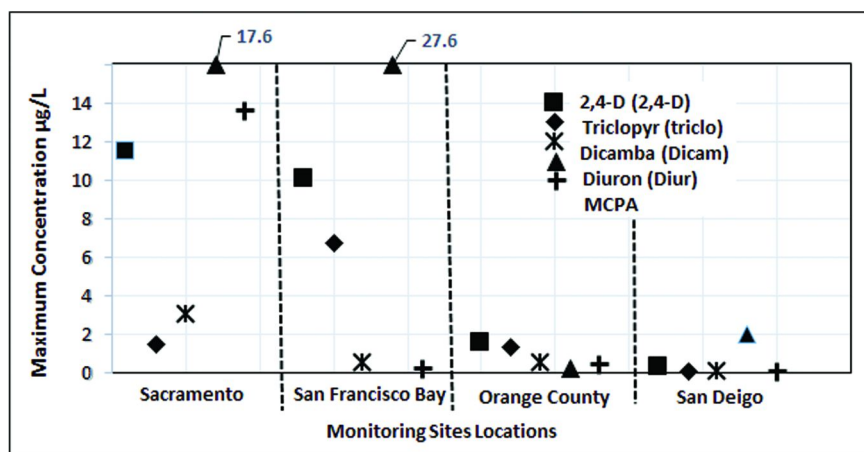


Figure 10. Maximum concentrations of herbicides detected in urban monitoring data from Northern and Southern California.

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

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 $56\%/26 \text{ ng/L}$, $93\%/33 \text{ ng/L}$ and $100\%/203 \text{ ng/L}$. The other four pyrethroids were only detected in SAC (cyfluthrin with DF/concentration of $13\%/18.9 \text{ ng/L}$ and cypermethrin with DF/concentration of $22\%/18.9 \text{ ng/L}$), ORN (λ -cyhalothrin with DF/concentration of $11\%/18.0 \text{ ng/L}$ and fenvalerate/esfenvalerate with DF/concentration of $11\%/28.0 \text{ ng/L}$). Additionally, data on the maximum DFs/concentrations observed in source and receiving water are summarized in Figure 11.

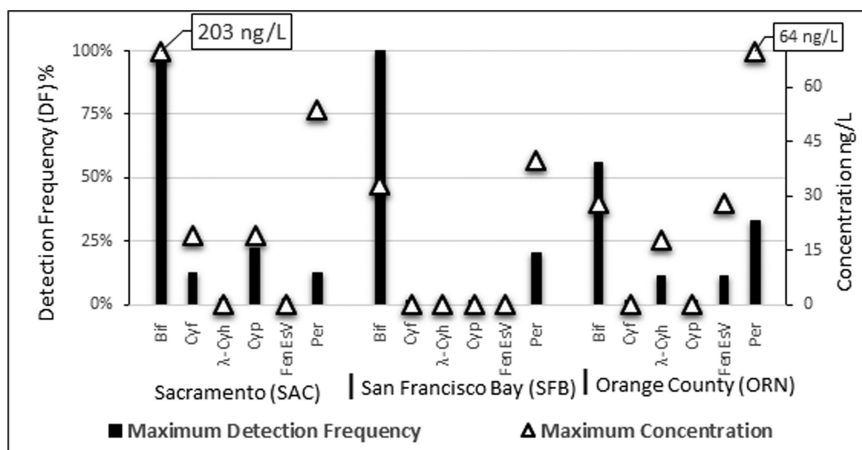


Figure 11. Observed maximum detection frequencies (DFs)/concentrations for pyrethroids detected in source/receiving waters of three major urban areas of California (San Diego (SND) not monitored).

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 outflows (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.

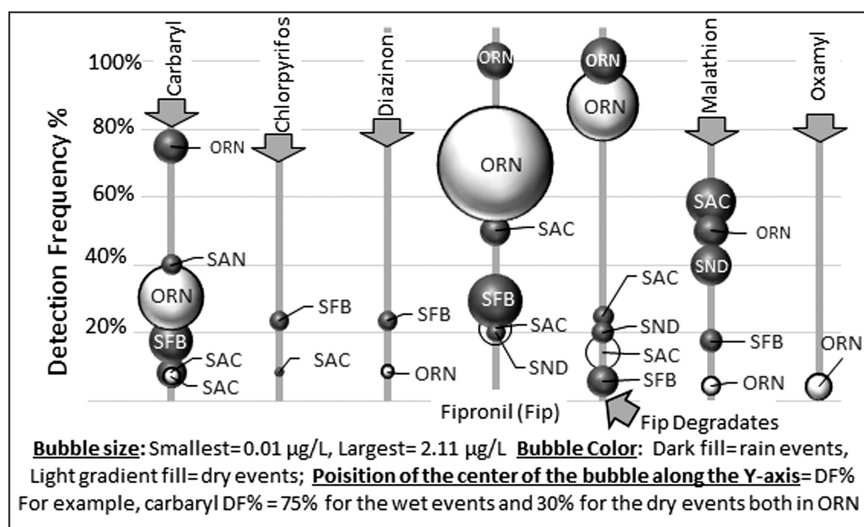


Figure 12. Influence of dry and rain flow conditions on DFs and concentrations of insecticides in the urban areas of Sacramento (SAC), San Francisco Bay (SFB), Orange County (ORN) and San Diego (SND).

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, occurrences 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.

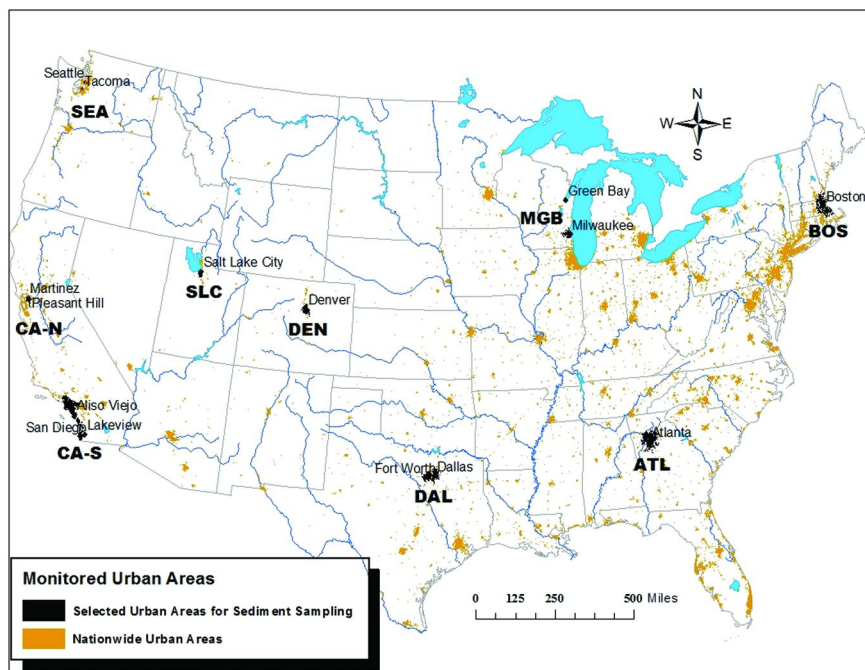


Figure 13. Stream bed sediment sampling sites for the statewide California study by Ensminger and Kelley (20) and the nationwide study by Kuivila *et al.* (22).

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 $\mu\text{g/kg}$ dry sediment. Fenvalerate/esfenvalerate maximum DF/concentration was reported to be relatively lower (14% and 24 $\mu\text{g/kg}$). 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.

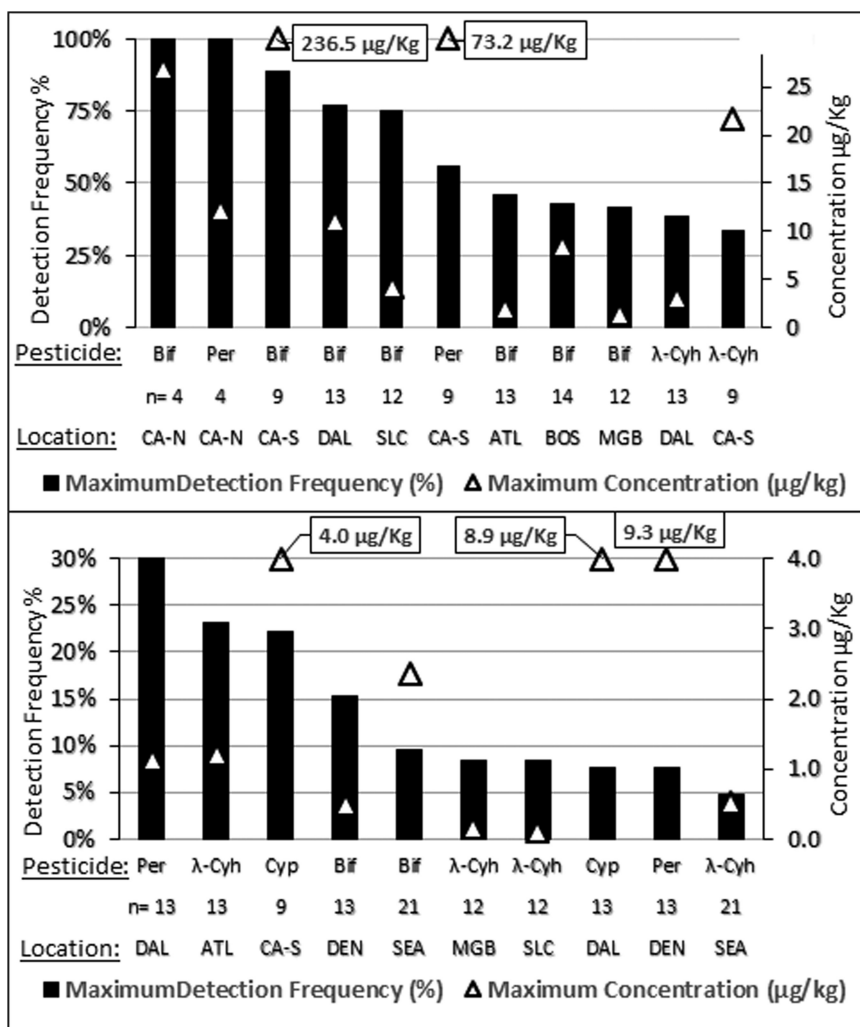


Figure 14. A summary of the sediment concentration/DF data obtained for bifenthrin (bif), λ-cyhalothrin (λ-Cyh), cypermethrin (Cyp) and permethrin (Per) (n = number of samples; for sampling location abbreviation refer to map in Figure 13).

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

<i>Detection Frequencies</i>	<i>Maximum Concentrations</i>	<i>Bed Sediment Location</i>	<i>Pyrethroid Detected</i>	<i>Exception</i>	<i>Reference</i>
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 m³ 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).

Table 5. Modeled vs. Monitored EECs for CA

<i>Chemical</i>	<i>Treatment Type</i>	<i>Label Rate (lbs ai/A)</i>	<i>Modeled rate (No. of Applications)¹</i>	<i>Modeled EECs (ng/L)</i>			<i>Observed EECs in CA Monitoring (ng/L)²</i>
				<i>Peak</i>	<i>21-day</i>	<i>60-day</i>	
Fipronil	House perimeter treatment	2 ft. @ 0.357	0.012 lbs ai/A (1)	41.2	26.7	15.2	Maximum= 232 and 90 th %= 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 90 th %= 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 90 th %= 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

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 coarse 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 DISPersal 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

<i>Reference</i>	<i>Material</i>	<i>Peak deposition (ng/cm²)</i>	<i>Peak deposition (% applied)²</i>	<i>Distance from application source to peak deposition (m)</i>	<i>Wind speed (mph)²</i>
Tucker <i>et al.</i> (31)	Fenthion	2.92	2	8	NR
	Malathion	85.8	15	8	NR
	Naled	57.3	20	8	NR
Moore <i>et al.</i> (32)	Malathion	84.1	14	30.4	0.9–3.4
Tietze <i>et al.</i> (33)	Malathion	50	9	5	2.1–4.0
Knepper <i>et al.</i> (34)	Malathion	9,222	NA	7.6	1
	Permethrin	14,389	NA	7.6	1
Tietze <i>et al.</i> (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 <i>et al.</i> (37)	Permethrin	5.1	10	Unknown	6–12
Preftakes <i>et al.</i> (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 LC₅₀s were determined, with PBO present in the overlying 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 overlying 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 $\mu\text{g/L}$. 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 $\mu\text{g/L}$ and PBO was at a maximum concentration of 20 $\mu\text{g/L}$.

Schleier and Peterson (42) derived $\text{LC}_{50\text{s}}$ 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 $\mu\text{g/kg}$ dry weight, a median 5.3 $\mu\text{g/kg}$, with a method detection limit of 0.5 $\mu\text{g/kg}$ 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 $\mu\text{g/kg}$ (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 its 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))

<i>Chemical</i>	<i>Toxicity</i>	<i>Concentrations and Other Notes</i>
Sediment		
Pre-App Samples	Out of 17 samples, only one exhibited significant toxicity (<i>H. azteca</i>), taken before a <i>d</i> -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 (<i>H. azteca</i>). See above.	The permethrin concentration was below the toxicity threshold.
Pyrethrins	Two of the urban sites exhibited toxicity post-application (<i>H. azteca</i>).	There were no detections of pyrethrins and no sample exceeded the PBO toxicity threshold.
<i>d</i> -phenothrin	Five wetland and five agricultural sites were sampled for <i>d</i> -phenothrin, all of which did not exhibit significant toxicity pre- and post-application (<i>H. azteca</i>).	No sample had concentrations of <i>d</i> -phenothrin or PBO exceeding their toxicity thresholds.
Water Column		
Pre-App Samples	Out of 53 samples, only one exhibited significant toxicity (<i>H. azteca</i>), taken before a <i>d</i> -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 (<i>C. dubia</i>).	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 (<i>C. dubia</i>).	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

<i>Chemical</i>	<i>Toxicity</i>	<i>Concentrations and Other Notes</i>
Etofenprox	The 24-hr post-application sample exhibited significant toxicity (<i>H. azteca</i>).	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) (<i>H. azteca</i>).	Permethrin, bifenthrin and PBO concentrations were all below toxicity thresholds in these samples (<i>H. azteca</i>) 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 (<i>H. azteca</i>).	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.
<i>d</i> -phenothrin	None of the six agricultural, six wetland and six urban sites monitored exhibited significant toxicity post-application (<i>H. azteca</i>).	The concentrations of <i>d</i> -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 $\mu\text{g/L}$ (post-CFR 2005-1), the single monitoring study that provided water column concentrations of permethrin (44) presented a maximum concentration of 0.03 $\mu\text{g/L}$. 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 ($K_{OC} = 76800 \text{ L/kg}$). 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 $\mu\text{g/L}$. The estimated peak sediment concentration is 158 $\mu\text{g/kg}$, which is above 2-fold higher than the monitored concentration of 65.9 $\mu\text{g/kg}$.

Table 8. Water Column EECs ($\mu\text{g/L}$) for Permethrin Uses in California

<i>Scenario</i>	<i>App Rate (lb a.i./A)</i>	<i>Peak ($\mu\text{g/L}$)</i>
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

<i>Uses With High Potential for Substantive Release to POTWs</i>
<ul style="list-style-type: none">• 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 treatment²
<i>Uses With Lower Potential for Substantive Release to POTWs</i>
<ul style="list-style-type: none">• 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

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.

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

where,

- i. H_R is the daily per capita release of the chemical (g/person/day);
- ii. PV 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 ($\mu g/L$);
- 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

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 STPWINTM. 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 Module¹

<i>Process</i>	<i>Bifent.</i>	<i>Fenprop.</i>	<i>Cyhalot.</i>	<i>Permet.</i>	<i>Cyflut.</i>	<i>Cyperm.</i>	<i>Esfenval.</i>	<i>Deltamet.</i>
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

<i>Use</i>	<i>App Rate</i>	<i>Peak EEC (μg/L)</i>	<i>21-day EEC (μg/L)</i>	<i>Acute RQ</i>	<i>Chronic RQ</i>
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 $<2.6 \times 10^{-5}$ 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 Study¹

<i>Process</i>	<i>Bifent.</i>	<i>Fenprop.</i>	<i>I-Cyhal.</i>	<i>Permet.</i>	<i>Cyflut.</i>	<i>Cyperme.</i>	<i>Esfenval.</i>	<i>Deltamet.</i>
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 repellent 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)

<i>Chemical</i>	<i>CAS</i>	<i>LOQ (ng/L)</i>	<i>% Detect. (n=102)</i>	<i>Min. (ng/L)</i>	<i>Median (ng/L)</i>	<i>Max. (ng/L)</i>	<i>Category</i>
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 (<i>N,N</i> -diethyl- <i>m</i> -toluamide)	134-62-3	5	78	53	232	13600	other (insect repellent)
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

<i>Chemical</i>	<i>CAS</i>	<i>LOQ (ng/L)</i>	<i>% Detect. (n=102)</i>	<i>Min. (ng/L)</i>	<i>Median (ng/L)</i>	<i>Max. (ng/L)</i>	<i>Category</i>
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 degradata)
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))

<i>Chemical</i>	<i># of Detects</i>	<i>% Detected</i>	<i>LOQ (ng/L)</i>	<i>Max. (ng/L)</i>	<i>Min. (ng/L)</i>	<i>Average¹ (ng/L)</i>	<i>Median¹ (ng/L)</i>
Bifenthrin	64	96%	5	74	ND	15	9.7
Cyfluthrin	59	88%	5	55	ND	11	7.4
<i>Lambda</i> -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))

<i>Chemical</i>	<i># of Detects</i>	<i>% Detected</i>	<i>LOQ (ng/L)</i>	<i>Max. (ng/L)</i>	<i>Min. (ng/L)</i>	<i>Average¹ (ng/L)</i>	<i>Median¹ (ng/L)</i>
Bifenthrin	51	82%	0.5	3.9	ND	0.89	0.6
Cyfluthrin	37	60%	0.5	4	ND	0.6	0.3
<i>Lambda</i> -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

<i>Chemical</i>	<i>Production Volume (kg)</i>	<i>WWT (%)¹</i>	<i>Predicted Conc. (ppb)</i>	<i>Measured Conc. (ppb) (min, med, max)</i>
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%).

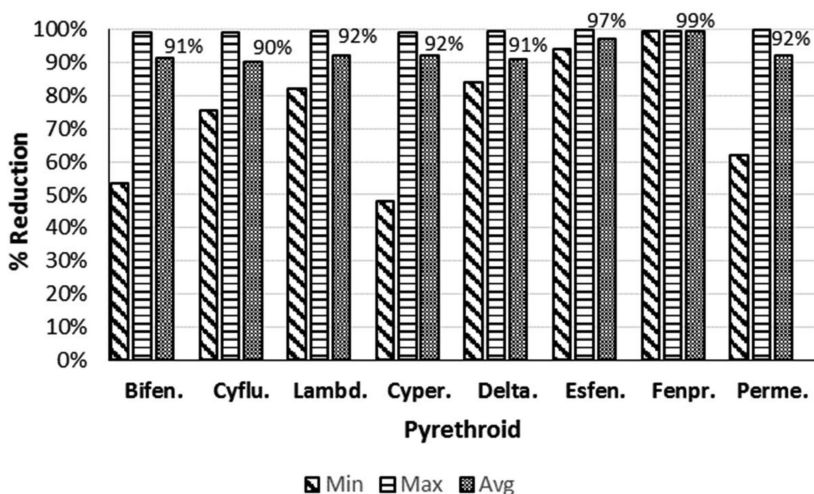


Figure 15. Percent reduction in pyrethroid concentrations in POTW effluent relative to influent. (Source: Markle *et al.* (55))

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.

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

<i>POTW¹</i>	<i>Bifen.</i>	<i>Cyfl.</i>	<i>Cyp.</i>	<i>Delt.</i>	<i>Esfen.</i>	<i>Fenp.</i>	<i>L. Cyh</i>	<i>Perm.</i>	<i>Chlor.</i>
<i>Maximum Concentration Detected (ng/L)</i>									
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
<i>Overall Detection Frequency (n=18)²</i>									
	39%	6%	6%	11%	6%	0%	17%	33%	40%
<i>Frequency exceeding EC₅₀ or LC₅₀³</i>									
	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 EC₅₀ or LC₅₀ 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))

<i>Chemical</i>	<i># of Detects</i>	<i>% Detected</i>	<i>LOQ (ng/g)</i>	<i>Max. (ng/g)</i>	<i>Min. (ng/g)</i>	<i>Average¹ (ng/g)</i>	<i>Median¹ (ng/g)</i>
Bifenthrin	50	96%	2.5	1100	ND	150	120
Cyfluthrin	45	87%	2.5	190	ND	34	29
<i>Lambda</i> -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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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

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).

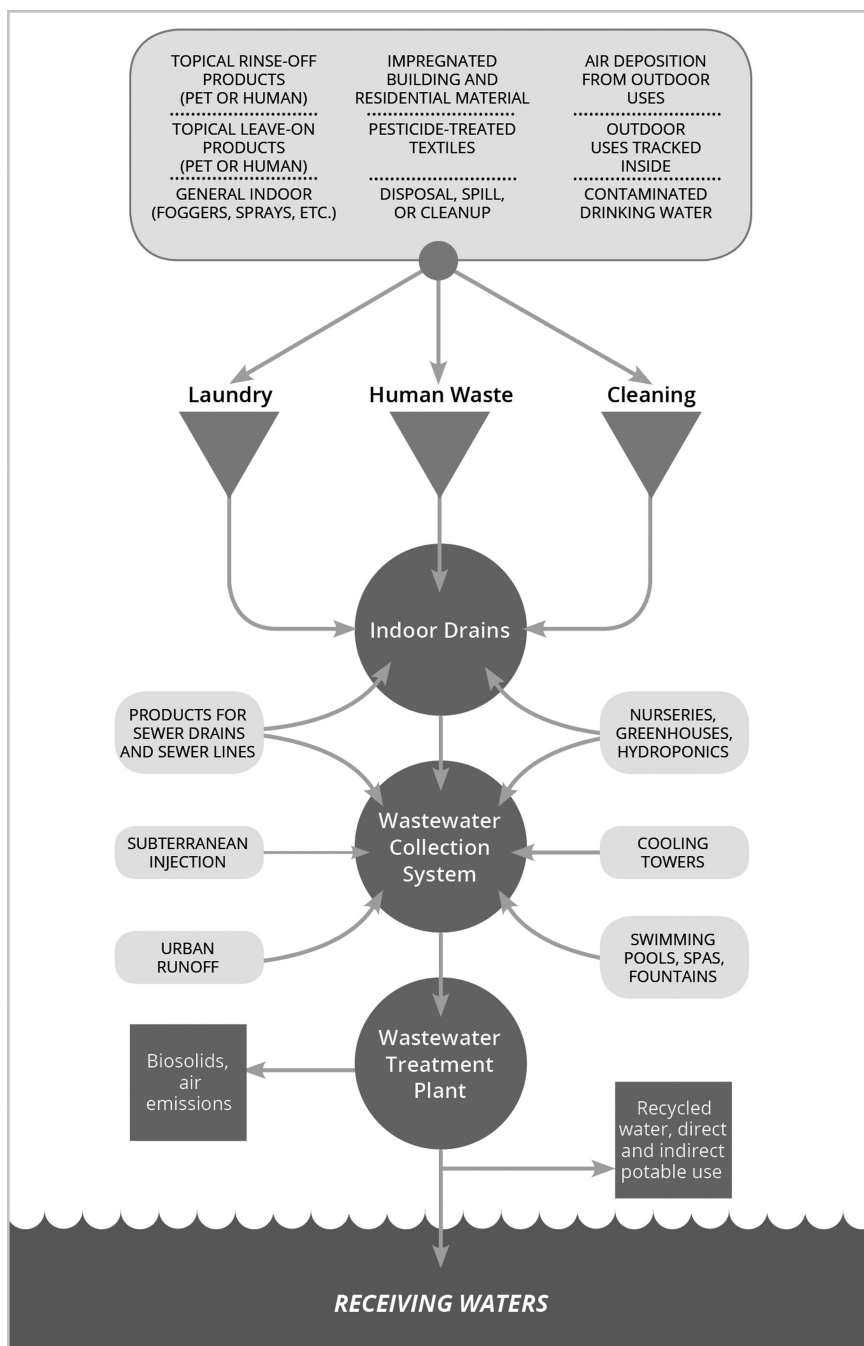


Figure 1. Conceptual model of sources of current-use pesticides to municipal wastewater. Black text is used to describe sources.

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.

<i>Pesticides & Degradates</i>	<i>Inf./Eff.</i>	<i>Range (ng/L)^a</i>	<i>Median (ng/L)^b</i>	<i>DF (%)</i>	<i>No. of Samples</i>	<i>No. of Facilities</i>	<i>References</i>
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.

<i>Pesticides & Degradates</i>	<i>Inf./Eff.</i>	<i>Range (ng/L)^a</i>	<i>Median (ng/L)^b</i>	<i>DF (%)</i>	<i>No. of Samples</i>	<i>No. of Facilities</i>	<i>References</i>
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)

<i>Pesticides & Degradates</i>	<i>Inf./Eff.</i>	<i>Range (ng/L)^a</i>	<i>Median (ng/L)^b</i>	<i>DF (%)</i>	<i>No. of Samples</i>	<i>No. of Facilities</i>	<i>References</i>
	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.

<i>Pesticides & Degradates</i>	<i>Inf./Eff.</i>	<i>Range (ng/L)^a</i>	<i>Median (ng/L)^b</i>	<i>DF (%)</i>	<i>No. of Samples</i>	<i>No. of Facilities</i>	<i>References</i>
	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)
Terbutylazine	Eff.	<4–61	<4	1	102	52	(39)

<i>Pesticides & Degradates</i>	<i>Inf./Eff.</i>	<i>Range (ng/L)^a</i>	<i>Median (ng/L)^b</i>	<i>DF (%)</i>	<i>No. of Samples</i>	<i>No. of Facilities</i>	<i>References</i>
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 \pm 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 subwatershed 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.

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Disclaimer

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