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 can contaminate surface waters, 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 down-the-drain transport, both direct and indirect. Review of available studies from the United States (U.S.) indicates 42 current use 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 the water column, with high removal efficiency only observed in the case of highly hydrophobic compounds like 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 (USEPA) 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 water. 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 chemical contaminants – are insufficient to reduce pesticide concentrations below aquatic toxicity thresholds.[9-11]

Treated wastewater effluent continuously discharges to surface water, representing 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 waters.

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 U.S. WWTP influent and effluent; 3) presenting case studies detailing 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 beyond the scope of the monitoring data literature review provided. Furthermore, this review focuses primarily on discharges to indoor drains, which flow to municipal separated sewer systems designed to carry indoor discharges only; it does not address combined sewer systems that mix urban runoff with wastewater from indoor drains.

Because the regulation of pesticides strongly influences use patterns, the scope of this review was limited to the U.S., where there is a 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 (nano or otherwise) or antimicrobial pesticides (e.g., triclosan, triclocarban). Although there are pesticide products that contain metals as an active ingredient, additional non-pesticidal 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 whose regulation is overseen by agencies designed to protect human health. Compounds used as pharmaceuticals as well as pesticides, such as the blood thinner and rodenticide warfarin, were also excluded.

Regulatory Framework Relevant to Urban and Consumer Pesticide Applications

In the U.S., the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) requires all pesticide products to be registered by the USEPA and provides for controls on pesticide sales and use. FIFRA requires pesticide manufacturers to submit supporting studies to demonstrate the efficacy and safety of proposed products. The USEPA then reviews the environmental fate and impact of pesticide products. Following federal registration, additional supporting studies may be required prior to registration in any particular state.

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

Product labels approved by USEPA upon pesticide registration specify approved use patterns and application requirements. Pesticide labels are considered enforceable. Pesticide 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 wastewater, as consumer applications often dominate the pesticide use patterns most likely to result in down-the-drain pesticide transport. In such cases, the more difficult source reduction approach must be used to prevent and mitigate wastewater pesticide contamination, as it is not practical to enforce or to instruct individual consumers on safe pesticide use. Gaining a robust understanding of pesticide use patterns that result in down-the-drain transport and the relative contribution from sources is necessary to develop successful source reduction measures.

Another U.S. federal law, the Clean Water Act, requires California's State and Regional Water Quality Control Boards to implement enforceable effluent pollutant limits on wastewater dischargers including WWTPs. Pesticides in wastewater effluent have posed a significant regulatory challenge for California water quality regulators, particularly after a California study found pyrethroids in the effluents of 28 of 31 municipal WWTPs, in some cases at concentrations higher than USEPA 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]

Wastewater treatment plants 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. In partnership with the USEPA, California's Department of Pesticide Regulation (DPR) has the regulatory authority over use and sale of pesticides in the state. Collaborative efforts between DPR and WWTPs to generate useful data to support 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 can also enable enhanced evaluation of pesticide products during the registration process.[6]

Readily identifiable and direct sources of pesticides to municipal wastewater are topical products, such as pesticidal shampoos, intended to be rinsed down the drain. For humans, examples include treatments for lice (pediculicides) such as over-the-counter shampoos with pyrethrins or permethrin, or prescription-strength products with ivermectin, malathion, or spinosad. For companion animals, examples 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 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 companion animals; 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 companion animals.[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 sporadic, larger 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.[28,32] 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]; for others, this indirect pathway is only suspected, as studies are generally lacking.

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). The vulnerability of a sewer system 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 ng/L concentrations. Any contamination that does not partition to solids or degrade during treatment is discharged to receiving waters via treated wastewater effluent.

For many of the products or use patterns emphasized in this conceptual model, monitoring data are sparse. For example, many sources are associated with non-professional 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-grow 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 current use pesticides. Given the lack of a comprehensive conceptual model describing the potential pathways by which pesticides enter wastewater prior to this publication, this dearth of data is not surprising.

Presented here is a compilation of data from peer-reviewed publications describing U.S. occurrence of current use pesticides in influent and effluent (Table 1). As noted previously, 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. 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. For 39 additional pesticides and degradates, the literature review found no detections. Therefore, 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

Table 1. Occurrence of pesticides in wastewater influent and effluent in the U.S.

Pesticide	*Inf./ Eff.*	*Range (ng/L)* [a]	*Median (ng/L)* [b]	*DF (%)*	*No. of Samples*	*No. of Facilities*	*References*
2,4-D	Eff.	<100-1,890	<100	3	102	52	39
2,4-DB	Eff.	<610-7,440	<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	10,48
	Eff.	<0.1-14.1	<1-10.3	71	92	34	10,48-50
Carbaryl	Eff.	<0.49-663	<41	9	140	55	39,41-43

Pesticide	*Inf./ Eff.*	*Range (ng/L)* [a]	*Median (ng/L)* [b]	*DF (%)*	*No. of Samples*	*No. of Facilities*	*References*
Chlorpropham	Eff.	<7.7-72.4	<7.7	3	102	52	39
Chlorpyrifos	Inf.	<1-81.9	15.2	85	13	1	48
	Eff.	<1-24.1	<1-3	40	30	5	41,42,48,50
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	10,48
	Eff.	<0.2-4	<1-0.3	42	90	34	10,48,50
Cypermethrin	Inf.	<0.8-200	18-27.3	99	80	32	10,48
	Eff.	<0.167-17	<1-1.3	56	90	34	10,48,50
DEET [c]	Inf.	413-42,300	413-10,100	100	18	4	44,45,51
	Eff.	<5-13,600	25-675	85	171	69	39,43,44,51-54
Deltamethrin	Inf.	<1.6-210 [d]	<3.33	42	67	31	10
	Eff.	<0.2-2.7	<1	15	81	34	10,50
Diazinon	Eff.	<5-150	<5-38	64	25	22	41,42,47,52
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	10,50
Fenpropathrin	Inf.	<0.8-130 [e]	<1.67	4	67	31	10
	Eff.	<0.167-0.8	<1	2	81	34	10,50
Fipronil	Inf.	<20-146	30-70.5	66	41	33	11,55

Pesticide	*Inf./ Eff.*	*Range (ng/L)* [a]	*Median (ng/L)* [b]	*DF (%)*	*No. of Samples*	*No. of Facilities*	*References*
	Eff.	<0.5-340	30-104	67	57	40	11,41,42,55,56
Fipronil amide	Inf.	<0.3	<0.3	0	8	8	11
	Eff.	<0.3-19.8	1.25-6.7	95	21	13	11,56
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	11,41,42,56
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	11,41,42,56
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	11,41,42,56
Fluridone	Eff.	<7.7-27	<7.7	1	102	52	39
Glyphosate	Eff.	<100–2,000	<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	10,48
	Eff.	<0.167-5.5	<1	41	90	34	10,48,50
Mecoprop	Eff.	<0.28-72	4	80	35	1	43
Metolachlor	Eff.	<0.9-98	<6-75	74	38	3	41-43
Pentachlorophenol	Eff.	<100-300	<100	2	102	52	39
Permethrin	Inf.	30-3,800	180-315	100	80	32	10,48
	Eff.	<1-170	<1-21.4	64	90	34	10,48,50

Pesticide	*Inf./ Eff.*	*Range (ng/L)* [a]	*Median (ng/L)* [b]	*DF (%)*	*No. of Samples*	*No. of Facilities*	*References*
Prometon	Eff.	<4-64	<10	4	105	54	[39,41,42]
Propiconazole	Eff.	<20-9,020	<20	3	102	52	[39]
Simazine	Eff.	<4-56	<4	1	105	54	[39,41,42]
Terbuthylazine	Eff.	<4-61	<4	1	102	52	[39]
Thiabendazole	Eff.	24-27	25.5	100	2	2	[53]
Triclopyr	Eff.	<300-3,900	<300	11	102	52	[39]

Inf. = Influent; eff. = effluent. DF = detection frequency. MDL = method detection limit.

[a] If minimum is non-detect, 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 8,480 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]. References[40-42] 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, which 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 physico-chemical properties. For some compounds, paired influent and effluent data are not available, preventing an estimate of removal efficiency.

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 USEPA chronic invertebrate aquatic life pesticide benchmarks[57]: 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 within 50% of the lowest available USEPA 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 in itself 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, and few reference values like USEPA 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 like USEPA pesticide aquatic life benchmarks or other aquatic toxicity thresholds signals the need for a closer examination of its sources and uses, and the pathways by which it can enter 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, including those of residential and key commercial or industrial facilities, to the sewer system. Two case studies illustrate this approach, which can provide evidence to guide management actions designed to reduce pesticide presence in surface waters.

Case Study: Diazinon and Chlorpyrifos

In the late 1980s, toxicity testing 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.[58]

DPR partnered with Central Contra Costa Sanitary District to conduct wastewater sampling to better understand potential sources. Sampling included influent and sub-sewershed sites (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 ng/L and 190 ng/L respectively. Pesticide concentrations reported in residential sewage ranged from ND–4,300 ng/L and ND–1,200 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%).[58] This sub-sewershed 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 USEPA conducts registration reviews for actively-registered products. In the early 2000s, as a part of the re-registration review process, 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.[59,60]

Limited available long-term monitoring data suggest a general reduction in chlorpyrifos and diazinon WWTP influent concentrations resulting from 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 USEPA WWTP survey conducted in 2005-2008 was <10 ng/L.[61] 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.[58] were not included in Table 1, as they primarily represent contributions from products no longer in current use. Current replacement insecticidal products for consumers now typically contain active ingredients like pyrethroids, and more recently fipronil and imidacloprid. Unfortunately, the use reduction of organophosphates 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 USEPA aquatic life benchmarks.

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

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

While occurrence data for both fipronil and its degradates (collectively fiproles) and imidacloprid in WWTP influent and effluent are sparse, these compounds are typically detected in available studies (Table 1). In one such study, the per capita influent loads for fiproles (54 ± 9 nmol/person/d, mean ± standard deviation) and imidacloprid (190 ± 80 nmol/person/d) for 7 Northern California WWTPs had low load variability, suggesting ubiquitous, low-level contributions from sources within the service areas.[11] The authors outlined a conceptual model specific to fiproles and imidacloprid, which 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 fipronil-containing spot-on products 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.[62]

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 like 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,[63] 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.[11,55] As noted previously, concentrations in effluent commonly exceed USEPA aquatic life benchmarks.[57] 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 USEPA highlighting the need to include pet products in models used in pesticide risk assessment and regulation.[64,65] BACWA has distributed consumer education materials and findings from recent studies[11,19] 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, suggesting 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 sub-sewershed contributions, characterizing sewage concentrations and loadings from residential and commercial sites.[58] Study calculations to fill this data gap revealed low-level, ubiquitous residential sources to be of greater importance than large mass pulses.[58] 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.

In the case of fipronil- and imidacloprid-based flea and tick control, a refined conceptual model[11] identified the need to confirm suggested contamination pathways, an important data gap. A study of the most direct contamination pathway, 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 1,000 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.[30,66] However, these techniques may not be sufficiently sensitive to rule out the presence of pesticides at parts-per-trillion 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 where plants are temporarily held before sale) has received little study. Legalization of cannabis cultivation in many states may lead to an increase in hydroponic indoor grows 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, commercial laundering of uniforms for large groups (e.g., the military) that utilize clothing impregnated 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, including impregnated building and construction materials, foggers, and sprays, that is dislodgeable and available for transport down the drain.

Developing advanced engineering solutions to expand the capacity of wastewater treatment to reduce trace organic chemicals, present in the parts-per-billion to sub parts-per-trillion concentrations, has been an area of intense research over the past twenty to thirty years.[67] 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. Such data can inform improved predictive modeling.

Addressing data gaps concerning pesticide wastewater treatment removal efficiency and incorporating this information into modeling tools, such as the USEPA Exposure and Fate Assessment Screening Tool (E-FAST) model currently used for risk evaluation,[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[68] 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.[69] 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. For the municipal wastewater pathway, pollution prevention is a key strategy to improve water quality.

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References

1. Gilliom, R. J.; Barbash, J. E.; Crawford, C. G.; Hamilton, P. A.; Martin, J. D.; Nakagaki, N.; Nowell, L. H.; Scott, J. C.; Stackelburg, P. E.; Thelin, G. P.; Wolock, D. M. *The Quality of our Nation's Waters—Pesticides in the Nation's Streams and Ground Water, 1992-2001* 2006; p 172.
2. Lao, W. J.; Tsukada, D.; Greenstein, D. J.; Bay, S. M.; Maruya, K. A. Analysis, occurrence, and toxic potential of pyrethroids, and fipronil in sediments from an urban estuary *Environ. Toxicol. Chem.* **2010,** *29*, 843-851.
3. Ensminger, M.; Budd, R.; Kelley, K.; Goh, K. Pesticide occurrence and aquatic benchmark exceedances in urban surface waters and sediments in three urban areas of California, USA, 2008–2011. *Environ. Monit. Assess.* **2013**, 1-14.
4. Stone, W. W.; Gilliom, R. J.; Ryberg, K. R. Pesticides in U.S. streams and rivers: Occurrence and trends during 1992-2011. *Environ. Sci. Technol.* **2014,** *48*, 11025-11030.
5. Hladik, M.; Kolpin, D. W. First national-scale reconnaissance of neonicotinoid insecticides in streams across the USA. *Environ. Chem.* **2015,** *13*, 12-20.
6. Luo, Y.; Deng, X.; Xie, Y.; Singhasemanon, N.; Goh, K. S., Improved Modeling Approaches for Pesticide Registration Evaluation for Surface Water Protection in California. In *Pesticides in Surface Water: Monitoring, Modeling, Risk Assessment, and Management*, K.S. Goh, J. G., Y. Luo, D.F. Young, Ed. American Chemical Society Symposium Series, vol. 1308, in press, 2018.
7. Deng, X.; Wang, D.; Wagner, S.; Goh, K. S., Surface Water Monitoring for Pesticides in Agricultural Areas of California. In *Pesticides in Surface Water: Monitoring, Modeling, Risk Assessment, and Management*, K.S. Goh, J. G., Y. Luo, D.F. Young, Ed. American Chemical Society Symposium Series, vol. 1308, in press, 2018.
8. Domagalski, J.; Nowell, L., Daily Models of Agricultural Chemical Concentrations and Loads in Rivers Draining the Central Valley, California, to the San Francisco Bay-Delta Estuary: Before and During an Extended

Drought. In *Pesticides in Surface Water: Monitoring, Modeling, Risk Assessment, and Management*, K.S. Goh, J. G., Y. Luo, D.F. Young, Ed. American Chemical Society Symposium Series, vol. 1308, in press, 2018.

9. Weston, D. P.; Ramil, H. L.; Lydy, M. J. Pyrethroid insecticides in municipal wastewater. *Environ. Toxicol. Chem.* **2013,** *32*, 2460-2468.
10. Markle, J. C.; van Buuren, B. H.; Moran, K. D.; Barefoot, A. C. *Pyrethroid pesticides in municipal wastewater: A baseline survey of publicly owned treatment works facilities in California in 2013*; Pyrethroid Working Group: 2014.
11. Sadaria, A. M.; Sutton, R.; Moran, K. D.; Teerlink, J.; Brown, J. V.; Halden, R. U. Passage of fiproles and imidacloprid from urban pest control uses through wastewater treatment plants in northern California, USA. *Environ. Toxicol. Chem.* **2017,** *36*, 1473-1482.
12. Brooks, B. W.; Riley, T. M.; Taylor, R. D. Water Quality of Effluent-dominated Ecosystems: Ecotoxicological, Hydrological, and Management Considerations. *Hydrobiologia* **2006,** *556*, 365-379.
13. Shamim, M.; Meléndez, J.; Sappington, K.; Ruhman, M., Conducting Ecological Risk Assessments of Urban Pesticide Uses. In *Describing the Behavior and Effects of Pesticides in Urban and Agricultural Settings*, American Chemical Society: 2014; Vol. 1168, pp 207-274.
14. CVRWQCB (Central Valley Regional Water Quality Control Board). *Proposed Amendments to the Water Quality Control Plan for the Sacramento River and San Joaquin River Basins for the Control of Pyrethroid Pesticides Discharges, Final Staff Report*; Rancho Cordova, CA, 2017.
15. Merel, S.; Snyder, S. A. Critical assessment of the ubiquitous occurrence and fate of the insect repellent *N,N*-diethyl-*m*-toluamide in water. *Environ. Int.* **2016,** *96*, 98-117.
16. Halos, L.; Beugnet, F.; Cardoso, L.; Farkas, R.; Franc, M.; Guillot, J.; Pfister, K.; Wall, R. Flea control failure? Myths and realities. *Trends Parasitol.* **2014,** *30*, 228-233.
17. Siak, M.; Burrows, M. Flea control in cats: new concepts and the current armoury. *J. Feline Med. Surg.* **2013,** *15*, 31-40.
18. DPR (California Department of Pesticide Regulation). *California Product/Label Database Queries & Lists.*; Sacramento, CA, 2018.
19. Teerlink, J.; Hernandez, J.; Budd, R. Fipronil washoff to municipal wastewater from dogs treated with spot-on products. *Sci. Total Environ.* **2017,** *599-600*, 960-966.
20. Jennings, K. A.; Canerdy, T. D.; Keller, R. J.; Atieh, B. H.; Doss, R. B.; Gupta, R. C. Human exposure to fipronil from dogs treated with frontline. *Vet. Hum. Toxicol.* **2002,** *44*, 301-303.

21. Craig, M. S.; Gupta, R. C.; Candery, T. D.; Britton, D. A. Human exposure to imidacloprid from dogs treated with Advantage. *Toxicol. Mech. Methods* **2005,** *15*, 287-291.
22. Gupta, R. C.; Masthay, M. B.; Canerdy, T. D.; Acosta, T. M.; Provost, R. J.; Britton, D. M.; Atieh, B. H.; Keller, R. J. Human exposure to selamectin from dogs treated with Revolution: Methodological consideration for selamectin isolation. *Toxicol. Mech. Methods* **2005,** *15*, 317-321.
23. Bigelow Dyk, M.; Liu, Y.; Chen, Z.; Vega, H.; Krieger, R. I. Fate and distribution of fipronil on companion animals and in their indoor residences following spot-on flea treatments. *J. Environ. Sci. Health, Part B* **2012,** *47*, 913-924.
24. Driver, J. H.; Ross, J. H.; Guerino, F.; Wrzesinski, C. Measurement of the temporal transferability of indoxacarb to cotton gloves from spot-on treated dogs. *J. Toxicol. Environ. Health, Part A* **2014,** *77*, 696-704.
25. Case, K. M.; Vega, N. M.; Gupta, R. C.; Lasher, M. A.; Canerdy, T. D. Safety evaluation of Parastar Plus in dogs and assessment of transferable residue of fipronil and cyphenothrin from dogs to humans. *Front. Vet. Sci* **2016,** *3*, 89.
26. Jacobs, D. E.; Hutchinson, M. J.; Stanneck, D.; Mencke, N. Accumulation and persistence of flea larvicidal activity in the immediate environment of cats treated with imidacloprid. *Med. Vet. Entomol.* **2001,** *15*, 342-345.
27. Colt, J. S.; Lubin, J.; Camann, D.; Davis, S.; Cerhan, J.; Severson, R. K.; Cozen, W.; Hartge, P. Comparison of pesticide levels in carpet dust and self-reported pest treatment practices in four US sites. *J. Expo. Anal. Environ. Epidemiol.* **2004,** *14*, 74-83.
28. Obendorf, S. K.; Lemley, A. T.; Hedge, A.; Kline, A. A.; Tan, K.; Dokuchayeva, T. Distribution of pesticide residues within homes in central New York State. *Arch. Environ. Contam. Toxicol.* **2006,** *50*, 31-44.
29. Mahler, B. J.; Van Metre, P. C.; Wilson, J. T.; Musgrove, M.; Zaugg, S. D.; Burkhardt, M. R. Fipronil and its degradates in indoor and outdoor dust. *Environ. Sci. Technol.* **2009,** *43*, 5665-5670.
30. Moschet, C.; Anumol, T.; Lew, B. M.; Bennett, D. H.; Young, T. M. Household dust as a repository of chemical accumulation: New insights from a comprehensive high-resolution mass spectrometric study. *Environ. Sci. Technol.* **2018,** *52*, 2878-2887.
31. Simcox, N. J., Fenske, R.A., Wolz, S.A., Lee, I.C., and Kalman, D.A. Pesticides in household dust and soil: Exposure pathways for children of agricultural families. *Environ. Health Perspect.* **1995,** *103*, 1126-1134.
32. Fenske, R. A.; Lu, C.; Negrete, M.; Galvin, K. Breaking the take home pesticide exposure pathway for agricultural families: Workplace predictors of residential contamination. *Am. J. Ind. Med.* **2013,** *56*, 1063-1071.
33. Deziel, N. C.; Friesen, M. C.; Hoppin, J. A.; Hines, C. J.; Thomas, K.; Freeman, L. E. A review of nonoccupational pathways for pesticide

exposure in women living in agricultural areas. *Environ. Health Perspect.* **2015,** *123*, 515-524.

34. Ueyama, J.; Harada, K. H.; Koizumi, A.; Sugiura, Y.; Kondo, T.; Saito, I.; Kamijima, M. Temporal levels of urinary neonicotinoid and dialkylphosphate concentrations in Japanese women between 1994 and 2011. *Environ. Sci. Technol.* **2015,** *49*, 14522-14528.
35. Klarich, K. L.; Pflug, N. C.; DeWald, E. M.; Hladik, M. L.; Kolpin, D. W.; Cwiertny, D. M.; LeFevre, G. H. Occurrence of neonicotinoid insecticides in finished drinking water and fate during drinking water treatment. *Environ. Sci. Technol. Lett.* **2017,** *4*, 168-173.
36. Glassmeyer, S. T.; Furlong, E. T.; Kolpin, D. W.; Batt, A. L.; Benson, R.; Boone, J. S.; Conerly, O.; Donohue, M. J.; King, D. N.; Kostich, M. S.; Mash, H. E.; Pfaller, S. L.; Schenck, K. M.; Simmons, J. E.; Varughese, E. A.; Vesper, S. J.; Villegas, E. N.; Wilson, V. S. Nationwide reconnaissance of contaminants of emerging concern in source and treated drinking waters of the United States. *Sci. Total Environ.* **2017,** *581-582*, 909-922.
37. Budd, R.; Ensminger, M.; Wang, D.; Goh, K. S. Monitoring Fipronil and Degradates in California Surface Waters, 2008–2013. *J. Environ. Qual.* **2015,** *44*, 1233-1240.
38. Vander Werf, R.; Aldana, A.; Teerlink, J.; Budd, R. *Retail Store Survey of Consumer-Use Indoor Pesticide Products, 2014*; California Department of Pesticide Regulation, Environmental Monitoring Branch: 2015.
39. Hope, B. K.; Pillsbury, L.; Boling, B. A state-wide survey in Oregon (USA) of trace metals and organic chemicals in municipal effluent. *Science of The Total Environment* **2012,** *417*, 263-272.
40. Sadaria, A. M.; Supowit, S. D.; Halden, R. U. Mass balance assessment for six neonicotinoid insecticides during conventional wastewater and wetland treatment: nationwide reconnaissance in United States wastewater. *Environmental science & technology* **2016,** *50*, 6199-6206.
41. Barber, L. B.; Keefe, S. H.; Brown, G. K.; Furlong, E. T.; Gray, J. L.; Kolpin, D. W.; Meyer, M. T.; Sandstrom, M. W.; Zaugg, S. D. Persistence and potential effects of complex organic contaminant mixtures in wastewater-impacted streams. *Environmental science & technology* **2013,** *47*, 2177-2188.
42. Barber, L. B.; Keefe, S. H.; Kolpin, D. W.; Schnoebelen, D. J.; Flynn, J. L.; Brown, G. K.; Furlong, E. T.; Glassmeyer, S. T.; Gray, J. L.; Meyer, M. T. *Lagrangian sampling of wastewater treatment plant effluent in Boulder Creek, Colorado, and Fourmile Creek, Iowa, during the summer of 2003 and spring of 2005--Hydrological and chemical data*; 2331-1258; US Geological Survey: 2011.
43. Fairbairn, D. J.; Arnold, W. A.; Barber, B. L.; Kaufenberg, E. F.; Koskinen, W. C.; Novak, P. J.; Rice, P. J.; Swackhamer, D. L. Contaminants of emerging concern: mass balance and comparison of wastewater effluent and

upstream sources in a mixed-use watershed. *Environmental science & technology* **2015,** *50*, 36-45.
44. Mohapatra, S.; Huang, C.-H.; Mukherji, S.; Padhye, L. P. Occurrence and fate of pharmaceuticals in WWTPs in India and comparison with a similar study in the United States. *Chemosphere* **2016,** *159*, 526-535.
45. Teerlink, J.; Hering, A. S.; Higgins, C. P.; Drewes, J. E. Variability of trace organic chemical concentrations in raw wastewater at three distinct sewershed scales. *Water Research* **2012,** *46*, 3261-3271.
46. Vatovec, C.; Phillips, P.; Van Wagoner, E.; Scott, T.-M.; Furlong, E. Investigating dynamic sources of pharmaceuticals: Demographic and seasonal use are more important than down-the-drain disposal in wastewater effluent in a University City setting. *Science of The Total Environment* **2016,** *572*, 906-914.
47. Kolpin, D. W.; Thurman, E. M.; Lee, E. A.; Meyer, M. T.; Furlong, E. T.; Glassmeyer, S. T. Urban contributions of glyphosate and its degradate AMPA to streams in the United States. *Science of The Total Environment* **2006,** *354*, 191-197.
48. Weston, D. P.; Ramil, H. L.; Lydy, M. J. Pyrethroid insecticides in municipal wastewater. *Environmental Toxicology and Chemistry* **2013,** *32*, 2460-2468.
49. Parry, E.; Lesmeister, S.; Teh, S.; Young, T. M. Characteristics of suspended solids affect bifenthrin toxicity to the calanoid copepods *Eurytemora affinis* and *Pseudodiaptomus forbesi*. *Environ. Toxicol. Chem.* **2015,** *34*, 2302-2309.
50. Weston, D. P.; Lydy, M. J. Urban and agricultural sources of pyrethroid insecticides to the Sacramento-San Joaquin Delta of California. *Environmental science & technology* **2010,** *44*, 1833-1840.
51. Snyder, S. A.; Wert, E. C.; Rexing, D. J.; Zegers, R. E.; Drury, D. D. Ozone oxidation of endocrine disruptors and pharmaceuticals in surface water and wastewater. *Ozone: Science and Engineering* **2006,** *28*, 445-460.
52. Glassmeyer, S. T.; Furlong, E. T.; Kolpin, D. W.; Cahill, J. D.; Zaugg, S. D.; Werner, S. L.; Meyer, M. T.; Kryak, D. D. Transport of chemical and microbial compounds from known wastewater discharges: potential for use as indicators of human fecal contamination. *Environmental science & technology* **2005,** *39*, 5157-5169.
53. Meador, J. P.; Yeh, A.; Young, G.; Gallagher, E. P. Contaminants of emerging concern in a large temperate estuary. *Environmental Pollution* **2016,** *213*, 254-267.
54. Nelson, E. D.; Do, H.; Lewis, R. S.; Carr, S. A. Diurnal variability of pharmaceutical, personal care product, estrogen and alkylphenol concentrations in effluent from a tertiary wastewater treatment facility. *Environmental science & technology* **2010,** *45*, 1228-1234.

55. Heidler, J.; Halden, R. U. Fate of organohalogens in US wastewater treatment plants and estimated chemical releases to soils nationwide from biosolids recycling. *J. Environ. Monit.* **2009,** *11*, 2207-2215.
56. McMahen, R. L.; Strynar, M. J.; McMillan, L.; DeRose, E.; Lindstrom, A. B. Comparison of fipronil sources in North Carolina surface water and identification of a novel fipronil transformation product in recycled wastewater. *Science of The Total Environment* **2016,** *569*, 880-887.
57. USEPA (United States Environmental Protection Agency) Office of Pesticide Programs Aquatic Life Benchmarks. http://www.epa.gov/oppefed1/ecorisk_ders/aquatic_life_benchmark.htm (7/1/18),
58. Singhasemanon, N.; Nordmark, C.; Barry, T. *Diazinon and Chlorpyrifos in the Central Contra Costa Sanitary District Sewer System, Summer 1996*; California Department of Pesticide Regulation: 1998.
59. USEPA (United States Environmental Protection Agency). *Interim Reregistration Eligibility Decision for Diazinon, Case No. 0238*; Washington, DC, 2002.
60. USEPA (United States Environmental Protection Agency). *Interim Reregistration Eligibility Decision for Chlorpyrifos, Case No. 0100*; Washington, DC, 2006.
61. USEPA (United States Environmental Protection Agency). *Occurrence of Contaminants of Emerging Concern in Wastewater from Nine Publicly Operated Treatment Works*; EPA-821-R-09-009; Washington, DC, 2009.
62. McMahen, R. L.; Strynar, M. J.; Dagnino, S.; Herr, D. W.; Moser, V. C.; Garantziotis, S.; Andersen, E. M.; Freeborn, D. L.; McMillan, L.; Lindstrom, A. B. Identification of fipronil metabolites by time-of-flight mass spectrometry for application in a human exposure study. *Environ. Int.* **2015,** *78*, 16-23.
63. Schreder, E. D.; La Guardia, M. J. Flame retardant transfers from U.S. households (dust and laundry wastewater) to the aquatic environment. *Environ. Sci. Technol.* **2014,** *48*, 11575-11583.
64. BACWA (Bay Area Clean Water Agencies). *Comment Letter: Imidacloprid - Preliminary Aquatic Risk Assessment (EPA-HQ-OPP-2008-0844)*; BACWA: Oakland, CA, 2017.
65. BACWA (Bay Area Clean Water Agencies). *Comment Letter: Dinotefuran - Preliminary Ecological Risk Assessment (EPA-HQ-OPP-2011-0920)*; BACWA: Oakland, CA, 2018.
66. Boix, C.; Ibáñez, M.; Bagnati, R.; Zuccato, E.; Sancho, J. V.; Hernández, F.; Castiglioni, S. High resolution mass spectrometry to investigate omeprazole and venlafaxine metabolites in wastewater. *J. Hazard. Mater.* **2016,** *302*, 332-340.

67. Margot, J.; Rossi, L.; Barry, D. A.; Holliger, C. A review of the fate of micropollutants in wastewater treatment plants. *Wiley Interdiscipl. Rev. Water* **2015,** *2*, 457-487.
68. Parry, E.; Young, T. M. Distribution of pyrethroid insecticides in secondary wastewater effluent *Environ. Toxicol. Chem.* **2013,** *32*, 2686-2694.
69. DPR (California Department of Pesticide Regulation). *Comment Letter: U.S. Environmental Protection Agency Ecological Risk Assessment and Registration Review Of Pyrethroids And Pyrethrins (Bifenthrin, Cyfluthrins (& Beta), Cypermethrin (Alpha & Zeta), Cyphenothrin, D-Phenothrin, Deltamethrin, Esfenvalerate, Etofenprox, Fenopropathrin, Flumethrin, Gamma-Cyhalothrin, Imiprothrin, Lambda-Cyhalothrin, Momfluorothrin, Permethrin, Prallethrin, Pyrethrins, Tau-Fluvalinate, Tefluthrin, Tetramethrin (Docket Identification Numbers: EPA-HQ-OPP-2010-0384, EPA-HQ-OPP-2010--0684, EPA-HQ-OPP-2012-0167, EPA-HQ-OPP-2009-0842, EPA-HQ-OPP-2011-0539, EPA-HQ-OPP-2009-0637, EPA-HQ-OPP-2009-0301, EPA-HQ-OPP-2007-0804, EPA-HQ-OPP2010-0422, EPA-HQ-OPP-2016-0031, EPA-HQ-OPP-2010-0479, EPA-HQ-OPP-2011-0692, EPA-HQ-OPP-2010-0480, EPA-HQ-OPP-2015-0752, EPA-HQ-OPP-2011-0039, EPA-HQOPP-2011-1009, EPA-HQ-2011-0885, EPA-HQ-OPP-2010-0915, EPA-HQ-OPP-2012-0501, EPA-HQ-OPP-2011-0907)*; DPR Environmental Monitoring Branch: 2017.

Figure – See Attachment

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