October 25, 2021

Tracy Perry
Office of Pesticide Programs (OPP)
c/o Regulatory Public Docket Center (28221T),
U.S. Environmental Protection Agency (EPA)
1200 Pennsylvania Ave. NW
Washington, DC 20460–0001

Subject: Draft Biological Evaluations for the Neonicotinoid Insecticides Clothianidin, Imidacloprid, and Thiamethoxam [Docket EPA-HQ-OPP-2021-0575]

Dear Tracy Perry:

On behalf of the Bay Area Clean Water Agencies (BACWA), we thank you for the opportunity to comment on the Draft Biological Evaluations for the Neonicotinoid Insecticides Clothianidin, Imidacloprid, and Thiamethoxam. BACWA's members include 55 publicly owned wastewater treatment facilities and collection system agencies serving 7.1 million San Francisco Bay Area residents. We take our responsibilities for safeguarding receiving waters seriously. We are concerned that EPA did not evaluate indoor uses of neonicotinoids, which have a downstream path to publicly owned treatment works (POTWs). This has grave implications for our members, as pesticides in treated wastewater pose a threat to municipal climate adaptation plans.

Draft Biological Evaluations Lack Important Data on Indoor Use

BACWA was surprised and disappointed that despite detailed scientific evidence shared with EPA Office of Pesticide Programs (OPP) on multiple occasions since 2017 (attached), the neonicotinoid Draft Biological Evaluations do not include the indoor sources of neonicotinoids that are subsequently discharged to municipal wastewater systems, pass through POTWs, and result in discharges that pose ecological risks. Based on the scientific data, we conclude that pet treatments should be expected to cause widespread non-compliance with the Federal Clean Water Act. Because 100% of POTWs must comply with the Federal Clean Water Act 100% of the time, risk mitigation for the neonicotinoids is imperative.

We request that EPA and the Services lay out a specific plan that addresses the primary source of neonicotinoids in municipal wastewater – topically applied pet treatments (pet "spot-ons" and sprays). A first step would be to implement a program to eliminate unnecessary use of neonicotinoids in pet treatments and to minimize POTW discharge quantities.

In multiple enclosed scientific papers, we again share the scientific evidence (see Sandaria et al. 2017 and Sandaria et al. 2016, enclosed) around neonicotinoids in municipal wastewater, highlighting the concentrations in municipal wastewater effluent.

Pesticides in Treated Wastewater Pose a Threat to Municipal Climate Adaptation Plans

As the effects of climate change impact available water supplies, municipalities around the country must pursue other sources of drinking water, including indirect and direct potable reuse. Pesticides in wastewater effluent pose a serious challenge to the feasibility of potable reuse. Treated wastewater effluent continuously discharged into surface waters represents an ongoing source of contaminants recalcitrant to removal. Concentrations of at least half a dozen pesticides reported in undiluted POTW effluents exceed the USEPA OPP benchmarks for chronic[1] exposure to aquatic invertebrates (see Sutton et al. 2019, enclosed[2]). Many more would exceed these benchmarks when concentrated by a factor of 5 (or greater) in the wastewater stream generated as a byproduct of reverse osmosis to create water suitable for potable reuse.

Given the growing efforts toward potable use of wastewater effluents[3], ensuring that the presence of pesticides in this concentrated waste stream does not render such projects technologically or economically infeasible is in the nation's interest (see Moran & LaBella 2020, enclosed[4]). Pesticides in reverse osmosis concentrate will increase costs for public agencies—or entirely prevent potable reuse of wastewater effluent. The indoor pet uses of neonicotinoids such as imidacloprid could prevent a municipality from recycling water for indirect or direct potable use, impacting a source of water that is essential to municipal climate adaptation plans. Modifying uses of persistent mobile pesticides in ways that avoid sewer discharges may be the best—and perhaps only—means to allow society to access this future water supply.

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,

Lorien Fono, Ph.D., P.E.
Executive Director
Bay Area Clean Water Agencies

Enclosures:

A. Prior BACWA Comment Letter from May 4, 2020, which contains background, cost information, scientific information, and mitigation recommendations:

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

[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.

[3] US EPA Office of Water (2017). *Potable Reuse Compendium*.

[4] Moran, K. and M. LaBella (2020). "Will Pesticides Prevent Publicly-Owned Wastewater Treatment Plant Effluent from Becoming a Much- Needed Drinking Water Supply?" North America Society of Environmental Toxicology and Chemistry SciCon2 Conference (online).

B. Prior BACWA Comments from 2017 and 2018, which contain background, cost information, scientific information, and mitigation recommendations:
   1. Imidacloprid – Preliminary Aquatic Risk Assessment (July 24, 2017)
   2. Clothianidin – Preliminary Aquatic and Non-Pollinator Terrestrial Risk Assessment (April 21, 2018)
   3. Dinotefuran – Preliminary Ecological Risk Assessment (April 21, 2018)
   4. Thiamethoxam – Preliminary Aquatic and Non-Pollinator Terrestrial Risk Assessment (April 21, 2018)

C. Two scientific papers documenting the presence of neonicotinoid insecticides in POTW effluent:
   1. Sadaria, A.M. et al. 2017. Passage of Fiproles and Imidacloprid from Urban Pest Control Uses Through Wastewater Treatment Plants in Northern California. *Environmental Toxicology and Chemistry*. 36(6):1473-1482
   2. Sadaria A.M., Supowit S.D., Halden R.U. 2016. Mass balance assessment for six neonicotinoid insecticides during conventional wastewater and wetland treatment: Nationwide reconnaissance in United States wastewater. *Environ Sci Technol* 50:6199–6206

D. Sutton, R., Xie, Y., Moran, K., & Teerlink, J. (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.

E. Moran, K. and M. LaBella (2020). "Will Pesticides Prevent Publicly-Owned Wastewater Treatment Plant Effluent from Becoming a Much-Needed Drinking Water Supply?" North America Society of Environmental Toxicology and Chemistry SciCon2 Conference (online).

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May 4, 2020

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Jonathan Williams
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c/o Regulatory Public Docket Center (28221T),
U.S. Environmental Protection Agency (EPA)
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Subject: Proposed Interim Registration Review Decisions for the Neonicotinoid Insecticides Acetamiprid, Clothianidin, Dinotefuran, Imidacloprid, and Thiamethoxam [Dockets EPA–HQ–OPP–2012–0329, EPA–HQ–OPP–2011–0865, EPA–HQ–OPP–2011–0920, EPA–HQ–OPP–2008–0844, EPA–HQ–OPP–2011–0581]

Dear Mr. Khan and Mr. Williams:

On behalf of the Bay Area Clean Water Agencies (BACWA), we thank you for the opportunity to comment on the Proposed Interim Registration Review Decisions (PIDs) for the neonicotinoid insecticides Acetamiprid, Clothianidin, Dinotefuran, Imidacloprid, and Thiamethoxam. BACWA's members include 55 publicly owned wastewater treatment facilities ("POTWs") and collection system agencies serving 7.1 million San Francisco Bay Area residents. We take our responsibilities for safeguarding receiving waters seriously.

BACWA was surprised and disappointed that despite the detailed scientific evidence shared with OPP, EPA's PIDs do not even mention the scientific fact that neonicotinoid insecticides are discharged to municipal wastewater systems, pass through POTWs, and result in discharges that pose ecological risks. Based on these data, we have substantial reason to believe that pet treatments and a few other indoor uses of neonicotinoid insecticides will cause widespread non-compliance with the Federal Clean Water Act. Because 100% of POTWs must comply with the Federal Clean Water Act 100% of the time, risk mitigation for neonicotinoids is imperative.

We request EPA please lay out a specific plan to address POTW discharges associated with ordinary use of neonicotinoid insecticides that addresses the primary sources of neonicotinoids in municipal wastewater. We suggest two mitigation approaches, which are further detailed later in this letter:

- Topically applied companion animal treatments ("Pet Spot-Ons") – using the soon to be completed updated efficacy testing guidelines, implement a program to eliminate unnecessary use of neonicotinoids and to minimize POTW discharge quantities.
- Product label improvements, including several that parallel those proposed for pyrethroid insecticides

We have detailed below our recommendations. Rather than repeat the scientific basis for these requests, we have attached our 2017 and 2018 comment letters on the Preliminary Aquatic Risk Assessments and the two most important scientific papers documenting the presence of neonicotinoid insecticides in POTW effluent.[1]

Summary Background

Every day, BACWA members' Publicly Owned Treatment Works (POTWs) treat millions of gallons of pesticide-containing wastewater that is then discharged to fresh or salt water 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 there is a lack of mixing at certain times due to thermal or saline stratification.

As detailed in our prior correspondence (see our July 2017 and April 2018 letters, enclosed), BACWA is especially interested in neonicotinoid insecticides due to their high aquatic toxicity and ability to pass through POTWs and appear in our effluent. Even the most sophisticated wastewater treatment plants cannot fully remove neonicotinoid insecticides (see enclosed papers).[2] In almost every US state – including California – state law precludes any local regulation of pesticide sales or use. As municipal wastewater treatment facilities have no local option to control use of pesticides consumer products, it is essential to us that EPA implement mitigation measures ensuring that impacts to the beneficial uses of the receiving water are prevented. This is not just a California issue – the Clean Water Act toxicity standards that drive our interest in neonicotinoid insecticides affect POTWs across the entire nation.

Effluent toxicity is regulated throughout the US. It is Federal law – the US Clean Water Act – that requires that surface waters cannot be toxic to aquatic life and requires the establishment of effluent limitations as necessary to achieve this standard. When addressing neonicotinoids and other currently used pesticides, California water regulators must implement the Federal Clean Water Act toxicity standard. As EPA has acknowledged in other settings (e.g., see EPA's Pyrethroids Ecological Risk Mitigation Proposal [Docket ID # EPA-HQ-OPP-2008-0331-0096]), failure to meet this nationwide standard imposes burdensome costs on POTWs.

BACWA Requests That EPA Provide a Schedule and a Specific Plan to Address POTW Discharge Ecological Risks from Pet Spot-Ons

As documented by the scientific data previously shared with OPP, pet spot-on treatments are the primary source of neonicotinoid insecticides in municipal wastewater. Given the burdensome compliance costs faced by US POTWs for Federal Clean Water Act toxicity standard compliance

[1]Sadaria, A.M. et al. 2017. Passage of Fiproles and Imidacloprid from Urban Pest Control Uses Through Wastewater Treatment Plants in Northern California. *Environmental Toxicology and Chemistry*. 36(6):1473-1482; Sadaria A.M., Supowit S.D., Halden R.U. 2016. Mass balance assessment for six neonicotinoid insecticides during conventional wastewater and wetland treatment: Nationwide reconnaissance in United States wastewater. *Environ Sci Technol* 50:6199–6206.

[2] *Ibid*.

when pesticides are present in effluent above toxicity thresholds,[3] action to minimize pet flea control use of neonicotinoid insecticides is essential. BACWA requests that that EPA provide a plan and schedule to address POTW discharge ecological risks from pet spot-on products. We request that the plan have the specific, stated goals of eliminating unnecessary use of neonicotinoid insecticides and to minimize POTW discharge quantities.

According to its responses to public comments on the pyrethroids ecological risk assessment, EPA is "working with the HCPA [Household and Commercial Products Association] Pet Care Products Task Force to quantify household exposures from pet product uses and is also working to develop new Proposed Guidelines for Efficacy Testing of Topically Applied Pesticides Used Against Certain Ectoparasitic Pests on Pets." According to EPA's ecological risk mitigation proposal for the pyrethroids, this effort involves EPA's Scientific Advisory Panel. Information in Docket ID #EPA-HQ-OPP-2019-0161 indicates that the effort is close to fruition. Importantly, publicly available information does not specify a linkage between the Proposed Guidelines and ecological risks posed by the post-application transfer of pet flea control chemicals to municipal wastewater treatment plants.

We request that EPA develop a plan to address POTW discharge ecological risks from pet spot-on products that includes the following elements:

(1) A schedule for completion of the Proposed Guidelines
(2) A requirement for testing of all neonicotinoid-containing pet spot-on products in accordance with the final version of the Proposed Guidelines, conducted with multiple application quantities, to determine the minimum necessary application quantity (by pet size).
(3) A requirement for products to be relabeled or reformulated such that applications do not use excess active ingredient (i.e., more than necessary to control pests).

BACWA Requests Label Clarifications Like those EPA Proposed for Pyrethroids – Pictograms, Stewardship Statement, and Indoor/Outdoor Use Specification

BACWA requests that EPA require neonicotinoid products to carry the same product stewardship label elements that are proposed for the pyrethroid insecticides. We list below the ones that are our highest priorities.

(1) Drain discharge prohibition pictogram. A graphic on product packages showing an image of an "X" – or better the "do not" symbol "⃠" – over images of both indoor and outdoor drains. An example of such a schematic graphic for an indoor drain is to the right (courtesy of Dublin San Ramon Services District).

Example Indoor Drain Pictogram

We have extensive experience with regard to graphically communicating "do not discharge" to various audiences and have found the graphic approach to be very effective, if the graphic is properly designed. We request that EPA please select clear, schematic graphics that are very obvious as to what is prohibited. We would be pleased to work with EPA, our national association NACWA, and

[3] Please see the see EPA's Pyrethroids Ecological Risk Mitigation Proposal [Docket ID # EPA-HQ-OPP-2008-0331-0096] and NACWA, BACWA, and California Water Board correspondence for details.

registrants toward selecting an appropriate graphic.

(2) Stewardship statements prohibiting discharge to any drain. The following statements, which are proposed to be included on pyrethroids products, would also be appropriate for neonicotinoid insecticide products:

Storage and disposal label section:

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

Advisory statements:

"Do not allow to enter indoor or outdoor drains"
"No permita la entrada a desagües internos o externos."

(3) Specific statement as to whether particular products are allowed to be used indoors only, outdoors only, or both indoors and outdoors. This will assist with identification of products that may be discharged to the sewer system.

To ensure that these label elements completely and effectively address products that may be discharged "down-the-drain" into municipal wastewater collection systems, we request that EPA:

1. Identify a specific graphic and require the same graphic be used on all products.
2. Establish minimum size for the graphic, to ensure that it is legible, i.e., no smaller than 1.5 square centimeters unless this size is greater than 10% of the size of the label.
3. Establish a list of products that must include the graphic and stewardship language to specify that these are required on:
    a. All products that are packaged in a form that could be discharged into a drain (i.e., anything other than an impregnated material like a collar or fly strip).
    b. All categories of products. At a minimum, the graphic should be placed on all products labeled use in non-agricultural settings. We would prefer that the graphic be required on all products, as even agricultural and mosquito abatement products are often mixed in facilities with sinks and floor drains.

BACWA Requests Modification of Pet Washing Label Language on Spot-On Pet Products

BACWA requests that EPA require removal of all label language on pet spot-on products that encourages washing and water exposure of treated pets. Label statements such as "waterproof" should be removed. All labels should dissuade owners from washing their pets for at least 2 weeks after treatment. Please see our prior letter (attached) which provides the scientific basis for this request.

Examples of products with this language: U.S. EPA Registration Numbers 11556-117, -122, -118, -119, -120, -116, 11556-132, -134, -133, -135

Example label statements that should be deleted:

Advantage is waterproof and remains effective following a shampoo treatment, swimming or after exposure to rain or sunlight.

K9 Advantix® is waterproof and remains effective following a shampoo treatment, swimming or after exposure to rain or sunlight.

BACWA Requests Expanding Prohibition of Treatment of Washable Items

Currently, bed linens are the only washable item that neonicotinoids are prohibited to be used on (e.g., US EPA clothianidin products with registration numbers 1021-2793, 1021- 2780, 1021-2788, 1021-2776, 1021-2780). Some labels actually encourage use on washable items such as pet bedding and curtains. Neonicotinoid insecticides, which are highly water soluble, will enter the sewer collection system when washable items are laundered.

BACWA requests that EPA expand this existing bed linen treatment prohibition to explicitly prohibit use on any washable item, by adding the bolded text to the labels:

*"Infested bed linens **and washable items** should not be treated."*

BACWA Requests POTW Notification Requirement for Wastewater Collection System Applications

Wastewater collection systems are commonly managed separately from wastewater treatment plants, and it is not uncommon for multiple municipal and private wastewater collection systems to flow to a single, separately owned and operated wastewater treatment facility. Treatment plant operators may not be aware of chemicals being applied in the upstream collection system. Collection system operators may not be aware of the cost and compliance implications of their selection of insecticides. To bridge this gap, BACWA requests that EPA add label language on the small number of neonicotinoid insecticide products that may be applied in wastewater collection systems to require downstream POTW notification prior to initiating use of the product.

Examples of products registered for these uses

a. Imidacloprid: US EPA Registration Numbers 72155-70, 73079-10, 73079-14)
b. Clothianidin: US EPA Registration Numbers 432-1531 and 1021-2796

If notification to downstream wastewater treatment facilities is required, wastewater treatment operations staff can work with collection system staff to ensure that applications do not contribute to effluent compliance challenges (e.g., toxicity test failures). Specifically, we request that EPA require the following language be placed on all products labeled for application in wastewater collection systems (including manholes):

"Applicators must notify downstream wastewater treatment facilities prior to the first application of this product on manholes or in the wastewater collection system."

Conclusion

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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Executive Director
Bay Area Clean Water Agencies

Enclosures:

A. Prior BACWA Comments, which contain background, cost information, scientific information, and mitigation recommendations:
   1. Imidacloprid – Preliminary Aquatic Risk Assessment (July 24, 2017)
   2. Clothianidin – Preliminary Aquatic and Non-Pollinator Terrestrial Risk Assessment (April 21, 2018)
   3. Dinotefuran – Preliminary Ecological Risk Assessment (April 21, 2018)
   4. Thiamethoxam – Preliminary Aquatic and Non-Pollinator Terrestrial Risk Assessment (April 21, 2018)

B. Two most important scientific papers documenting the presence of neonicotinoid insecticides in POTW effluent:
   1. Sadaria, A.M. et al. 2017. Passage of Fiproles and Imidacloprid from Urban Pest Control Uses Through Wastewater Treatment Plants in Northern California. *Environmental Toxicology and Chemistry*. 36(6):1473-1482
   2. Sadaria A.M., Supowit S.D., Halden R.U. 2016. Mass balance assessment for six neonicotinoid insecticides during conventional wastewater and wetland treatment: Nationwide reconnaissance in United States wastewater. *Environ Sci Technol* 50:6199–6206

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Kelly D. Moran, Urban Pesticides Pollution Prevention Partnership
BACWA Executive Board
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July 24, 2017

Mr. Ricardo Jones
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1200 Pennsylvania Ave., NW.
Washington, DC 20460–0001

Subject: Imidacloprid – Preliminary Aquatic Risk Assessment (EPA-HQ-OPP-2008-0844)

Dear Mr. Jones:

On behalf of the Bay Area Clean Water Agencies (BACWA), we thank you for the opportunity to comment on the Preliminary Aquatic Risk Assessment (PARA) for imidacloprid. BACWA's members include 55 publicly owned wastewater treatment facilities ("POTWs") and collection system agencies serving 7.1 million San Francisco Bay Area residents. We take our responsibilities for safeguarding receiving waters seriously. BACWA is especially interested in pesticides that are used in manners that have transport pathways to the sanitary sewer, as even the most sophisticated wastewater treatment plants cannot fully remove complex chemicals like pesticides.

Every day, BACWA members treat millions of gallons of wastewater that is then discharged to fresh or salt water bodies, including local creeks and rivers, bays, and the Pacific Ocean. These waterways provide crucial habitat to a wide array of aquatic species and waterfowl. 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 there is a lack of mixing at certain times due to thermal or saline stratification.

BACWA has a strong interest in imidacloprid due to its high aquatic toxicity and proven ability to pass through POTWs and appear in our effluent. The primary purpose of this letter is to request that the ecological risk assessment be expanded to include an evaluation of sewer discharges from pet flea control products and other indoor imidacloprid uses. A recent study involving several of our member agencies suggests that pet flea control products are the primary source of imidacloprid discharges to municipal wastewater treatment plants.

BACWA appreciates that OPP has started to conduct evaluation of risks associated with pesticide discharges to the sewer system ("down the drain" risk assessments). OPP's imidacloprid risk assessment did not include a down-the-drain assessment. Omitting evaluation of the sewer discharge environmental exposure pathway can prove costly for POTWs, as detailed below.

In almost every US state – including California – state law precludes any local regulation of pesticide sales or use. As we have no local option to control use of pesticides consumer products, it is essential to us that OPP's Registration Review adequately evaluates potential impacts to wastewater quality, and results in mitigation measures ensuring that impacts to the beneficial uses of the receiving water are *prevented*.

For these reasons, it is of utmost importance to BACWA that pet flea control products and all other imidacloprid-containing products with pathways to the sewer be carefully and thoroughly evaluated.

In addition to commenting on the preliminary aquatic risk assessment, we are also taking this opportunity to provide input on mitigation strategies for U.S. EPA to discuss with imidacloprid registrants. We are providing this input at this time because mitigation measures are essential and we understand that the next opportunity for public comment will be after such discussions and after U.S. EPA has prepared its proposed decision.

Thank you for this opportunity to present our input on each of these topics.

Background – Pesticide Discharges to the Sewer Can Be Costly

Pesticide discharges to the sewer system can prove costly for POTWs, due to the potential for pesticides to cause or contribute to wastewater treatment process interference, NPDES Permit compliance issues, impacts to receiving waters, recycled water quality and/or biosolids reuse, in addition to exposing POTWs to the potential for third party lawsuits under the Clean Water Act (CWA).

Of particular concern is the ability of a specific pesticide to exceed effluent toxicity limits. One universal water quality standard in the U.S., which stems directly from the Federal Clean Water Act (CWA), is that surface waters cannot be toxic to aquatic life. NPDES permits require POTWs to demonstrate that they meet this standard by evaluating toxicity using U.S. EPA standard methods (set forth in 40 CFR Part 136). To evaluate toxicity, every POTW must (1) conduct toxicity screening tests with a range of species, (2) select the most sensitive species, and (3) perform routine monitoring (typically monthly or quarterly). These monitoring data are used to determine whether the discharger has a *reasonable potential* to cause or contribute to toxicity in the receiving water. If it does, the CWA requires that numeric effluent limits be imposed, otherwise POTWs may be given numeric effluent triggers for further action. In the event that routine monitoring *does exceed* a toxicity limit or trigger, the POTW must perform accelerated monitoring (e.g., monthly); and if there is still evidence of consistent toxicity, the discharger must do a Toxicity Reduction Evaluation (TRE) to get back into compliance. The TRE requires dischargers to evaluate options to optimize their treatment plants and conduct a Toxicity Identification Evaluation (TIE), the cost of which can vary from $10,000 to well over $100,000 depending on complexity and persistence of the toxicant. The goal of the TIE is to identify the substance or combination of substances causing the observed toxicity. If a POTW's effluent is toxic because of a pesticide, it may not have any practical means to comply with CWA-mandated toxicity permit limits.

Once identified, the cost to treat or remove the toxicity causing compound(s) can vary dramatically. Often, there are few ways for a discharger to mitigate the problem other than extremely costly treatment plant upgrades. Upgrading treatment plants is often ineffective for

organic chemicals like pesticides that appear at sub microgram per liter concentrations, largely because sewage is a complex mixture of natural organic compounds. Regardless of this, the discharger must comply with its CWA permit limits. If a discharger violates a toxicity limit, it can be subject to significant penalties (in California up to $10/gallon or $10,000 per day).

In addition, when surface water bodies become impaired by pesticides, wastewater facilities may be subject to additional requirements established as part of Total Maximum Daily Loads (TMDLs) set for the water bodies by U.S. EPA and state water quality regulatory agencies. A number of pesticide-related TMDLs have been adopted or are in preparation in California. The cost to wastewater facilities and other dischargers to comply with TMDLs can be up to millions of dollars per water body per pollutant. This process will continue as long as pesticides are approved for uses that result in water quality impacts; it is therefore imperative that U.S. EPA conducts a Registration Review focusing on water quality impacts and for U.S. EPA to take action to ensure that any impacts are prevented or fully mitigated.

Background - Imidacloprid in POTW Influent and Effluent

As summarized below and detailed in attached scientific papers, imidacloprid is frequently detected in POTW influent and effluent. Available data suggest that typical municipal wastewater treatment processes do not reduce imidacloprid concentrations, i.e., that imidacloprid passes through POTWs. Concentrations reported in undiluted POTW effluents exceed the aquatic invertebrates chronic toxicity endpoints used in the PARA, as illustrated in Figure 1.

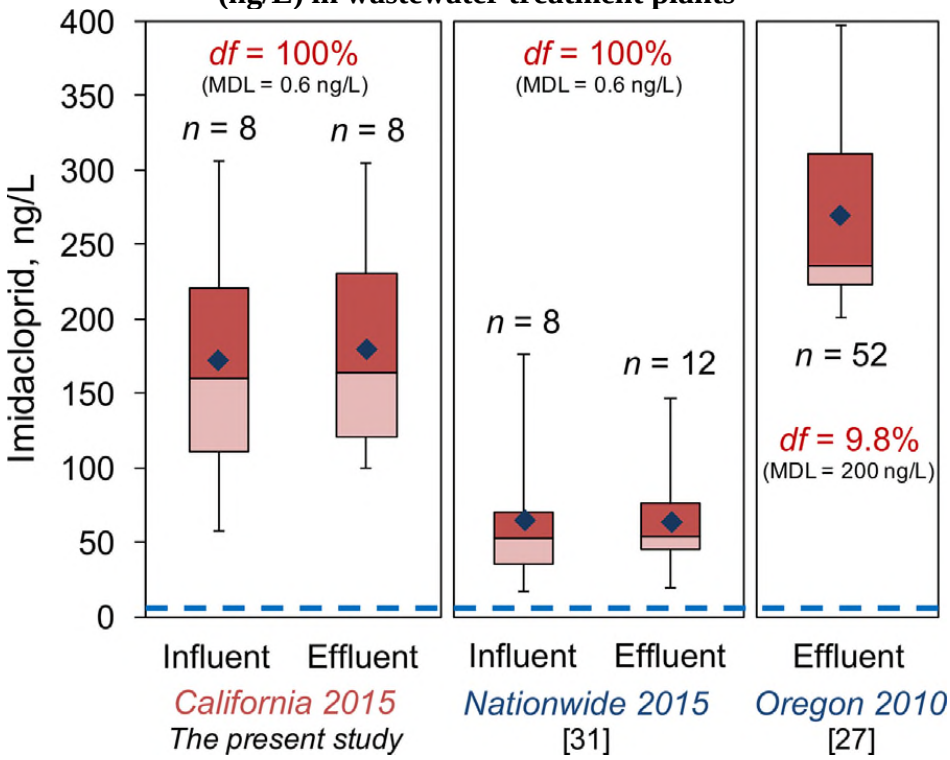
Recent scientific studies have measured imidacloprid in POTW influent and effluent, and have examined sources, per-capita loadings, and the reasons that it appears to pass through POTW treatment processes. We enclose three key papers:

- A recent study conducted by the San Francisco Bay Regional Monitoring Program in collaboration with California Department of Pesticide Regulation and Arizona State University (Sadaria et al. 2017; enclosed) measured imidacloprid and fipronil, as well as its degradates, in the influent and effluent of eight urban California POTWs. The results indicated that fipronil, its degradates, and imidacloprid were ubiquitous in the influent sewage and final treated effluent of all eight participating POTWs, and suggested that pet flea control products may be the primary source of both chemicals in wastewater. Pet washing is likely a major discharge pathway for pet flea control products (Teerlink et al. 2017; enclosed). Based on data from Bigelow Dyk et al (2012; enclosed) characterizing topical flea control active ingredient transfer to owners' hands and per capita pet population data, study authors found that owner hand washing could potentially explain the entire influent load of POTWs sampled in their study, suggesting that indirect transfer is also likely to be a discharge pathway.

- Elsewhere in the US, Sadaria et al (2016; enclosed) reported that imidacloprid was detected in 100% of influent and effluent samples from 12 US POTWs. POTWs had similar influent and effluent concentrations (ranging from 18.5 ng/L to 146.4 ng/L). This study included wintertime samples in cold climates, when pet flea pressure is minimal – such samples likely had minimal contributions from pet flea control products (source: personal communication with author).

- In 2010, Hope et al. measured imidacloprid in effluents from 52 Oregon WWTPs. This study (which is enclosed) found a lower detection frequency (9.8%), perhaps due to its relatively high quantification limit (200 ng/L) as compared to the more recent studies above, which had reporting limits <1 ng/L. In this study, effluents with detectable imidacloprid had levels in the range of 202 ng/L to 387 ng/L.

Figure 1. (from Sadaria et. al. 2017) Summary of detected concentrations of imidacloprid (ng/L) in wastewater treatment plants



Note: Dashed blue horizontal line indicates European Union freshwater predicted no-effect concentration value (close to the chronic aquatic invertebrate toxicity endpoint value used in the PARA). df = detection frequency; MDL = method detection limit. "Nationwide 2015" data from Sadaria et al. 2016; "Oregon 2010" data from Hope et al. 2010.

The higher concentrations reported in northern California POTWs likely reflect real differences between these communities and those monitored in the nationwide study. The northern California study was conducted during a severe drought that triggered water use restrictions throughout the study area and significant reductions in POTW influent flows. Its September timing coincides with what may be the peak pet flea control season in the study area. According to Sadaria et al 2017:

> "Higher overall concentrations and detection frequencies in effluent from northern California may reflect regional, seasonal, and/or climate-related differences from other sampled facilities, such as lower dilution caused by drought-related water use reductions, presence of pests during all seasons because of the mild coastal climate, and pesticide use responding to regional pest pressures (e.g., high flea populations in California coastal areas)."

BACWA requests that U.S. EPA imidacloprid modeling and mitigation approaches account for these factors. Please see BACWA's comments on the Preliminary Ecological Risk Assessment

for the Pyrethroid Insecticides (enclosed), where we detailed potential approaches for addressing these factors within U.S. EPA's current POTW model.

California Department of Pesticide Regulation (CDPR) is in the process of completing a collection system ("sewershed") study with the City of Palo Alto's Regional Water Quality Control Plant. Preliminary results from the pet-grooming site provide evidence that pet washing is a pathway for imidacloprid discharges to sewer systems (See http://www.cdpr.ca.gov/docs/emon/surfwtr/presentations/presentation_130_targeted.pdf). We encourage OPP to obtain the final results of this study, which should be available in 2017.

1) BACWA requests that the PARA be expanded to include an evaluation of sewer discharges from pet flea control treatments and other indoor imidacloprid uses

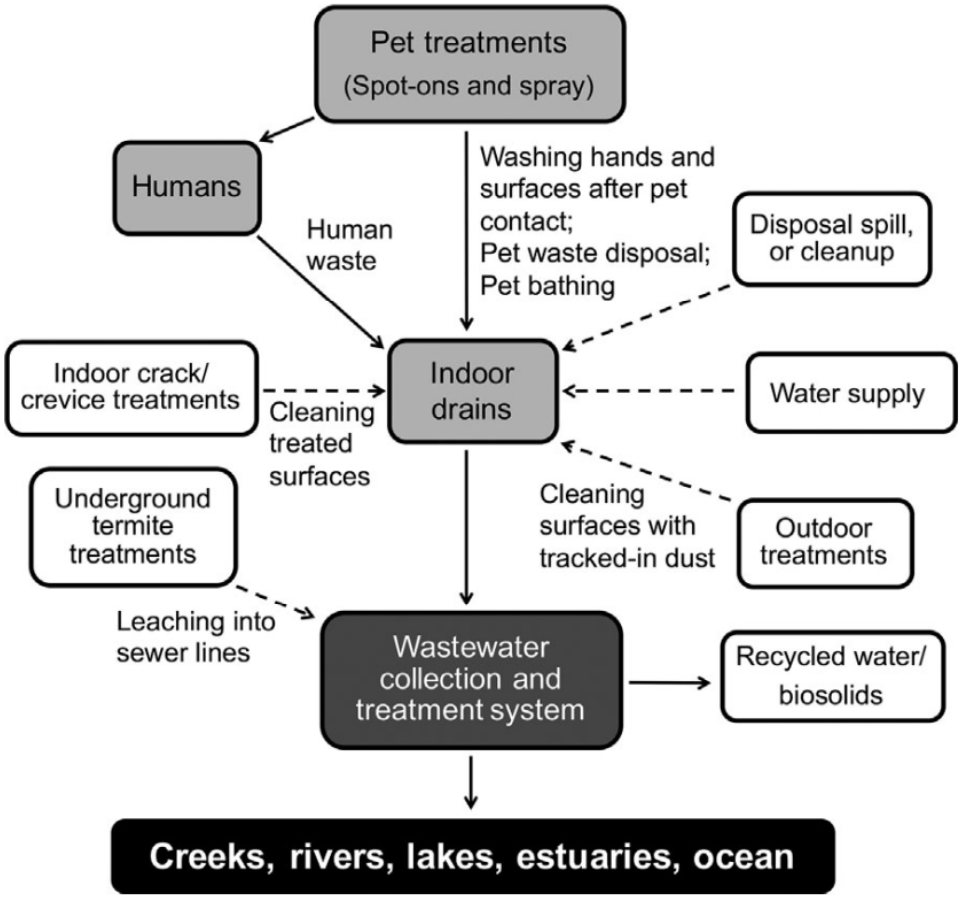
BACWA is concerned that risks associated with indoor imidacloprid use were not examined in the PARA and respectfully asks the U.S. EPA to include this analysis (a "down the drain" risk assessment) in the revised assessment. U.S. EPA has POTW predictive modeling tools to suitable for conducting this assessment and has conducted similar assessments for many other pesticides.

We request that U.S. EPA specifically analyze sewer discharge sources such as:

- Pet flea control products (including spot-ons and collars)
- Indoor treatments (such as crack/crevice, sprays for ant and roaches, bedbug treatments, houseplant treatments, etc.)
- Direct use of imidacloprid inside sewers and manholes

Based on product labels and information in the literature, Sadaria et al 2017 developed a detailed conceptual model linking imidacloprid use patterns (such as the sources listed above) and the transport pathways by which imidacloprid reaches the wastewater collection system. Due to its myriad of uses, imidacloprid has many pathways by which it can be transported, as shown in Figure 2.

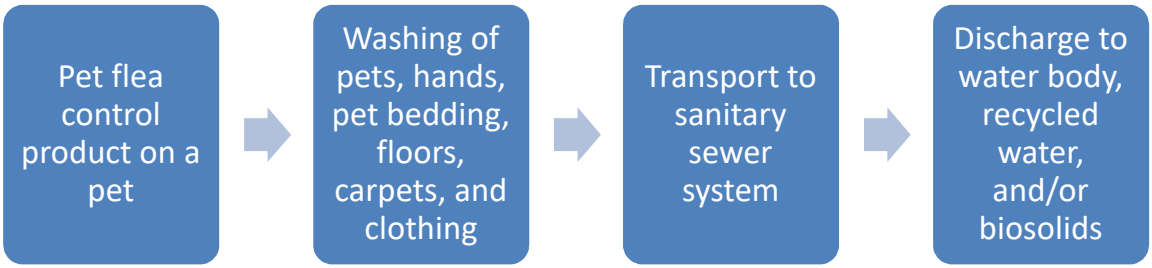
Figure 2. (from Sadaria et. al. 2017)
Conceptual Model of Sources of Imidacloprid in Municipal Wastewater



Note: Dashed lines denote pathways believed to be relatively small in the present study. Uses without a clear pathway (e.g., containerized baits) and with unlikely pathways (e.g., air transport and deposition) are excluded from the figure.

As explained in Appendix 1, pet flea control products contribute to POTW influent pesticides loads. Pet flea control chemicals are transported within a home to an indoor drain that flows to a POTW via the pathways illustrated in Figure 3.

Figure 3. Imidacloprid Pathway: From Pet to Wastewater Discharge



Scientific studies described above and those detailed in Appendix 1 examined the pathways that transport active ingredients from pet flea control products to the sewer system, both directly (through dog washing) and indirectly (such as after transfer onto human hands or socks that are

subsequently washed). Based on the data from these studies and pet population data, it is clear that pet flea control products are significant sources of pesticides to POTWs that should be accounted for in the PARA.

2) BACWA Requests that U.S. EPA Pursue Risk Mitigation for Imidacloprid

Because imidacloprid concentrations reported in undiluted POTW effluents exceed the aquatic invertebrates chronic toxicity endpoints used in the PARA, we expect that the "down-the-drain" risk assessment will likely conclude that risk mitigation is warranted to reduce POTW imidacloprid discharges. Because 100% of POTWs must comply with the Federal Clean Water Act 100% of the time, whenever U.S. EPA identifies significant risks from pesticides discharged to POTWs, BACWA believes that a robust exploration of risk mitigation is imperative.

In response to the finding that pet flea control products are major sources of pesticides to POTWs, BACWA completed an assessment of pet flea control alternatives. This assessment, which is summarized in Appendix 2, identified multiple practical, effective, non-pesticide alternatives.

In light of these findings, BACWA requests that OPP conduct its risk-benefit evaluation for pet flea control products as a group (i.e. considering pyrethroids and fipronil, which are also undergoing Registration Review) and in the context of the broad range of available non-pesticide alternatives, including FDA-approved oral medications and mechanical controls (e.g., vacuuming, washing of pet bedding).

While we agree that pet flea and tick control has societal benefits, our review of control options detailed in Appendix 2 identified plentiful alternatives that are far less environmentally problematic than imidacloprid. For example, the new generation of FDA-approved orals seems to be more convenient, equally or more effective, and well accepted by pet owners and veterinarians. Mechanical controls (vacuuming, washing of pet bedding) offer lower cost and greater long-term control as these are the sole option that addresses all life cycle stages of fleas. Finally, we emphasize that we do <u>not</u> believe that fipronil or pyrethroids are good alternatives to imidacloprid.

BACWA suggests that U.S. EPA consider the following additional risk mitigation strategies for indoor imidacloprid products:

- Determine the minimum application rate necessary to achieve pest control. This would eliminate unnecessary overuse and minimize POTW discharge quantities.
- Consider adding wastewater-protective use restrictions to product labels—such as forbidding use of imidacloprid directly in sewers and dissuading pet owners from washing their pets for two weeks after applying treatments. (See Appendix 3 for details)

Thank you for the opportunity to provide this feedback regarding both the risk assessment and subsequent mitigation strategies. We ask that OPP evaluate imidacloprid discharges to POTWs and fully explore mitigation options, particularly for pet flea control products. BACWA requests that U.S. EPA coordinate with CDPR (which has extensive relevant information and expertise), veterinarians, and registrants; bring in the latest scientific information – including CDPR scientific studies and modeling that are currently underway; and develop mitigation strategies for

imidacloprid. If you have any questions, please contact BACWA's Project Managers:

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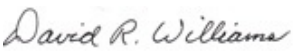
Respectfully Submitted,



David R. Williams
Executive Director
Bay Area Clean Water Agencies

Enclosures:

1. Sadaria, A.M. et al. 2017. Passage of Fiproles and Imidacloprid from Urban Pest Control Uses Through Wastewater Treatment Plants in Northern California. *Environmental Toxicology and Chemistry*. 36 (6), 1473-1482.
2. Sadaria A.M., Supowit SD, Halden RU. 2016. Mass balance assessment for six neonicotinoid insecticides during conventional wastewater and wetland treatment: Nationwide reconnaissance in United States wastewater. Environ Sci Technol 50:6199–6206.
3. Hope BK, Pillsbury L, Boling B. 2012. A statewide survey in Oregon (USA) of trace metals and organic chemicals in municipal effluent. Sci Total Environ 417–418:263–272.
4. Bigelow Dyk, M. et al. (2012). Fate and distribution of fipronil on companion animals and in their indoor residences following spot-on flea treatments, *Journal of Environmental Science and Health, Part B: Pesticides, Food Contaminants, and Agricultural Wastes*, 47(10): 913-924
5. Halos, L. et al. 2014. Flea Control Failure? Myths and Realities. *Trends in Parasitology*, 30:5 228-233.
6. Blagburn, B., and Dryden, M., Biology, Treatment, and Control of Flea and Tick Infestations, *Vet Clin Small Anim*, 2009, Vol 39, pp 1173-1200.
7. Litchfield et al., Safety Evaluation of Permethrin and Indoxacarb in Dogs Topically Exposed to Activyl® Tick Plus, *J Veterinar Sci Technology* 2015, 6:2.
8. Teerlink, J., J Hernandez, R Budd. 2017. Fipronil washoff to municipal wastewater from dogs treated with spot-on products. Sci Total Environ 599-600: 960-966.
9. Craig, M.S., Gupta, R.C., Candery, T.D., Britton, D.A. Human Exposure to Imidacloprid with Dogs Treated with Advantage ™. 2005. Toxicology Mechanisms and Methods, 15: 287–291.
10. Bay Area Clean Water Agencies (BACWA). July 7, 2017.Comment Letter on U.S. EPA Preliminary Ecological Risk Assessment for the Pyrethroid Insecticides.

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Appendix 1

On-Pet Flea Treatments: Evidence for the Pathway to the Sewer

Part I – Evidence for the Pathway to the Sewer

There is mounting evidence that pesticides from pet flea control products (spot-ons and collars) have exposure pathways to the sewer. The research summary below is organized first by the consumer use, followed by specific studies throughout a sewage collection system and at POTWs.

Pet Flea Control Products - Background

The pesticidal mode of action for imidacloprid collars and spot-ons is topical in nature, not systemic.[1] These topical treatments are designed to impact one or more stages of the flea cycle through direct contact with the pesticide (rather than an adult flea biting the pet and obtaining the pesticide systemically with the consumed blood). Imidacloprid is an adulticide—it targets adult fleas; but it has been shown to have a larvicidal effect.[2] Therefore, pesticides in topicals and collars are not meant to enter the pet's bloodstream but rather are meant to stay on the pet's fur in order to be effective.

Pet Flea Control Products – Sewer Discharge Pathways

Several scientific studies have examined the transport of active ingredients from pet flea control products onto surfaces, such as human hands, that are subsequently washed, completing a transfer pathway to the sewer system.

- *Spot-on-treatment to glove (hands) and dogs' blood pathway:* A 2005 study by Craig et al. demonstrated that a transferable residue of imidacloprid—from application of a spot-on treatment on the dogs' neck and back—can be detected for up to four weeks.[3] Residues were evident in the dogs' blood for up to 72 hours after application, which indicate that imidacloprid can have a systemic mode after topical application, but that is not the primary mode of action. This study reinforces the knowledge that imidacloprid affects fleas by persisting in the environment, rather than being continually emitted by the dogs' bodies. It also documented the levels of imidacloprid that persist on the dog after application: 254.16±25.49 ppm at the 24-hour mark to 0.08±0.02 ppm at the four week mark.

- *Spot-on treatment product to glove (hands) pathway:* A 2012 study by Bigelow Dyk et al. presents additional evidence of transport of pet flea control products onto human hands and through homes.[4] In the study, researchers monitored transfer of fipronil (from a

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[1] McTier, T., et al., Comparison of the activity of selamectin, fipronil, and imidacloprid against flea larvae (Ctenocephalides felis felis) in vitro, Veterinary Parasitology, Vol. 116, pp 45-50, 2003.
[2] Biology, Treatment, and Control of Flea and Tick Infestations, Blagburn, B., and Dryden, M., Vet Clin Small Anim, 2009, Vol 39, pp 1173-1200. (enclosed)
[3] Craig, M.S., Gupta, R.C., Candery, T.D., Britton, D.A. Human Exposure to Imidacloprid with Dogs Treated with Advantage ™. 2005. Toxicology Mechanisms and Methods, 15: 287–291. (enclosed)
[4] Bigelow Dyk, M., et al. (2012) Fate and distribution of fipronil on companion animals and in their indoor residences following spot-on flea treatments, Journal of Environmental Science and Health, Part B: Pesticides, Food

commercially available spot-on product) onto pet owners' hands and within their homes over a four-week period following spot treatment application. Participants used cotton gloves to pet their dog or cat for 2 minutes at a time at specific intervals after the application (24 hours, 1 week, 2 weeks, 3 weeks, and 4 weeks). Participants also wore cotton socks for 2 hours a night for 7 nights in a row, for four consecutive weeks following application. The gloves, socks, and brushed pet hair were subsequently analyzed for fipronil and its degradates. Bigelow Dyk and colleagues also incorporated a fluorescent dye into the spot treatment to provide photographic evidence of spot-on pesticide transfer. The photographic results shown in the paper illustrate the transfer from the application location to other areas of the pet's fur and onto the pet owners' hands.

- *Spot-on treatment product to glove (hands) pathway*: A 2015 study by Litchfield et al. evaluated the transfer of permethrin and indoxacarb from a topical pet flea control treatment to people's hands.[5] In the study, the topical treatment was applied to dogs that had not received a topical treatment for at least two months. To simulate human exposure to the pesticides, "Glove sampling included the wipe sampling technique, which consisted of petting the dog forward and back along its back and sides, while avoiding the application site, for five minutes while wearing a 100% cotton glove." The cotton glove samples were collected at days 0, 1, 2, 3, 7, 14, 21, 28, and 35. While the results showed that the largest mass of permethrin was transported within the first week, there continued to be measurable transfer to the gloves, even at day 35.

- *Pet collar to glove (hands) pathway*: One such study by Davis et al. quantified glove transfer of tetrachlorvinphos from pet collars.[6] We understand that the U.S. EPA team reviewing tetrachlorvinphos (EPA-HQ-OPP-2008-0316) has examined this paper and is planning to use the glove residue data following feedback from the U.S. EPA's Human Subjects Review Board.[7]

- *Human contact to human urine pathway*: A 2015 study of human urine from 295 human participants in China detected imidacloprid in 100% of rural participants and 95% of urban participants.[8] Urine from rural participants had an average level of 0.18 ng/mL while urine from urban participants had an average of 0.15 ng/mL. Although this study did not look specifically at pet flea control treatments, it did show that imidacloprid is commonly found in human urine, establishing another pathway to the sewer. In non-rural areas, based on the human exposures to pet flea control treatments documented in the papers summarized above, it is likely that one of the key sources of imidacloprid in human urine is from pet flea control products.

Contaminants, and Agricultural Wastes, **47**(10): 913-924

[5] Litchfield et al., "Safety Evaluation of Permethrin and Indoxacarb in Dogs Topically Exposed to Activyl® Tick Plus," J Veterinar Sci Technology 2015, 6:2 http://dx.doi.org/10.4172/2157-7579.1000218. (enclosed)

[6] Davis, M., et al. (2008). "Assessing Intermittent Pesticide Exposure From Flea Control Collars Containing the Organophosphorus Insecticide Tetrachlorvinphos," *J. of Exposure Science and Environ. Epidemiology* **18:**564-570.

[7] https://www.regulations.gov/document?D=EPA-HQ-OPP-2008-0316-0040

[8] Wang, L., Liu, T., Liu, F., Zhang, J., Wu, Y., and Sun, H. 2015. Occurrence and Profile Characteristics of the Pesticide Imidacloprid, Preservative Parabens, and Their Metabolites in Human Urine from Rural and Urban China. Environ. Sci. Technol. 2015, 49, 14633−14640.

Based on the data from these studies characterizing topical flea control active ingredient transfer to owners' hands[9] and per capita pet population data, owner hand washing as well as washing of clothing and mopping of floors could be a significant source of pesticides to POTWs.[10]

Evidence from Collection Systems

CDPR is in the process of completing a collection system ("sewershed") study within the City of Palo Alto's Regional Water Quality Control Plant.[11] The study involved twenty-four hour time weighted composite samples (influent, effluent, and ten sites in the collection system). Samples were collected from several discharge-specific sites with potential for relatively large mass flux of pesticides (i.e., discharges from pet grooming operation, pest control operator, and a laundromat). The samples were analyzed for a suite of pesticides, including imidacloprid. Preliminary results from the pet-grooming site provide evidence that pet washing is a pathway for imidacloprid discharges to sewer systems

We encourage OPP to obtain the final results of this study, which should be available within the timeframe of OPP's exploration of mitigation strategies for imidacloprid.

POTW Influent and Effluent

Lastly, further insights regarding transport of indoor flea control products to POTWs comes from a study of fipronil and imidacloprid at eight POTWs that was recently conducted by the San Francisco Bay Regional Monitoring Program in collaboration with BACWA, CDPR and Arizona State University.[12] The study monitored imidacloprid and fipronil, as well as its degradates, in the influent and effluent of eight urban California POTWs. The results indicated that fipronil, its degradates, and imidacloprid were ubiquitous in the influent sewage and final treated effluent of all eight participating POTWs, and – based on a detailed analysis of the sewer discharge sources of these two chemicals, which have relatively little indoor use other than pet flea control – provide compelling evidence that pet flea control products may be the primary source of both chemicals in wastewater. A copy of this paper is enclosed.

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[9] Bigelow Dyk, M., et al. (2012) Fate and distribution of fipronil on companion animals and in their indoor residences following spot-on flea treatments, Journal of Environmental Science and Health, Part B: Pesticides, Food Contaminants, and Agricultural Wastes, **47**(10): 913-924

[10] Sadaria, A.M., Sutton, R., Moran, K.D., Teerlink, J., Brown, J.V., Halden, R.U., 2017. Passage of fiproles and imidacloprid from urban pest control uses through wastewater treatment plants in northern California, USA. Environ. Toxicol. Chem. 36:6 1473-1482.

[11] See http://www.cdpr.ca.gov/docs/emon/surfwtr/presentations/presentation_130_targeted.pdf

[12] Sadaria, A.M., Sutton, R., Moran, K.D., Teerlink, J., Brown, J.V., Halden, R.U., 2017. Passage of fiproles and imidacloprid from urban pest control uses through wastewater treatment plants in northern California, USA. Environ. Toxicol. Chem. 36:6 1473-1482.

Appendix 2

Pet Flea Control Products: Alternatives Analysis

Alternatives and Mitigation

BACWA requests that U.S. EPA, in coordination with CDPR (which has extensive relevant information and expertise), veterinarians, and registrants, develop mitigation strategies for pet flea control products, including spot-ons and collars. Two specific topics are discussed below, as an effort to provide insight regarding mitigation options for flea control:

- Alternatives: oral medications and integrated pest management appear effective
- Optimization of application rates of pet flea control products

Alternatives: Integrated Pest Management and Oral Medications

Mechanical controls (e.g., vacuuming) appear to be key to avoiding a flea infestation in a home. Further, since the previous registration, there is now an opportunity provided by non-imidacloprid/non-pyrethroid oral treatments that have come on the market in recent years (available for both dogs and cats) that could avoid the on-pet use of not only imidacloprid, but also alternatives that are problematic from the water quality perspective (e.g., fipronil, pyrethroids, and indoxacarb).

The fleas found on a pet are estimated to represent only 1-5% of the flea cycle in a home; the other 95% are found as eggs, larvae, pupae, and adult fleas throughout the home and surrounding environment.[13] It takes about 18 days for a flea egg to grow into an adult flea, but in cool weather immature fleas can lay dormant in a pupal cocoon for up to 1 year. Adult fleas can live on a pet for 30 to 40 days. Fleas lay 20 to 50 eggs each day; consequently flea problems in residential settings can get out of control quickly.

Therefore, to avoid repeat infestations, one must address all stages of this flea cycle including flea eggs, larvae and pupae.[14] One way to do so is via non-pesticide mechanical controls, including frequent indoor vacuuming, washing of pet bedding, and use of a pet flea comb.[15] In particular, vacuuming needs to be both thorough and frequent. It should include the pet sleeping area, floors, furniture and all upholstered or carpeted surfaces, including under cushions, furniture and in other hard to reach places. Regarding frequency, it turns out that during the pupal stage, the flea is encased in a shell that is not penetrated by pesticides. The act of vacuuming can speed up the process. Specific guidance from one study notes the following:

> *"The vibration also stimulates adult fleas to emerge from their cocoons so that they can be collected in the vacuum machine. Therefore, frequent vacuuming, during a flea infestation, can reduce the overall flea burden in the home. It should be ensured that vacuum bags are disposed of properly, to prevent recolonization of the home with flea stages previously removed by vacuuming."* [16]

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[13] Halos, L., et al. (2014). Flea Control Failure? Myths and Realities. Trends in Parasitology, 30:5 228-233.
[14] Ibid, 228-233.(enclosed)
[15] American Veterinary Medical Association (2009). External Parasites.
[16] "Biology, Treatment, and Control of Flea and Tick Infestations," Blagburn, B., and Dryden, M., Vet Clin Small Anim, 2009, Vol 39, pp 1173-1200. (enclosed)

Although spot-on pet flea control products currently dominate the pet flea control market, new oral medications have recently become available. The table on the following page summarizes the current state of available oral medications for pets. The new pills, which are registered by U.S. FDA rather than U.S. EPA, appear to eliminate aquatic (and human) exposure pathways and should be equally or more convenient for pet owners, once they have obtained a prescription from a veterinarian. The involvement of the veterinarian has the added benefit of providing pet-specific guidance on flea control approach and safe dosage. Some studies indicate that oral medications may be more effective than topical spot treatments possibly because there is less reliance on proper application by the owner.[17]

[17] "Flea blood feeding patterns in cats treated with oral nitenpyram and the topical insecticides imidacloprid, fipronil and selamectin," McCoy, c., et al., Veterinary Parasitology, Vol. 156, pp 293-301, 2008.

List of Currently Available Oral Pet Treatments for Fleas (Alphabetical)

Active Ingredient	Example Product Names and Manufacturers	Dogs, Cats or Both?	Flea, Tick, Both	Dose Schedule	Adulticide?	Insect Growth Regulator?	Chemical Family	Year Registered
Afoxolaner	Nexgard (Merial)	Dogs only	Both	1 month	X	No	Isoxazoline[18]	2013
Fluralaner	Bravecto (Merck)	Dogs only	Both	2-3 months	X	No	Isoxazoline	2014
Lufenuron	Program (Novartis) and Sentinel (that also includes a heartworm pharma)	Both	Flea eggs, as well as hookworms, roundworms	1 month	No	X	Benzoylurea	1995 (for dogs)
Nitenpyram	Capstar (Novartis), Capguard (Sentry)	Both	Flea	A few hours only (meant for immediate infestation control)	X	No	Neonicotinoid	2000
Sarolaner	Simparica (Zoetis, a subsidiary of Pfizer)	Dogs only	Both	1 month	X	No	Isoxazoline	2016
Spinosad	Comfortis and Trifexis (Elanco)	Both	Flea	1 month	X	No	Spinosyn, macrocyclic lactone	2007 (approx)

[18] Flea products from the isoxazoline chemical family are new to the marketplace; therefore pet health insights are largely limited to the studies conducted by the manufacturers and the packaging text required by the FDA. There appears to be no published information about health and safety beyond the manufacturer guidance in the MSDS. Due to the application method (pill), human exposure is likely small, though no data are available to verify this assumption.

Optimization of Application Rates of Pet Flea Control Products

Another consideration for pet flea control products is that of application rate. Given that these household and pet flea control products have a transport pathway to the sewer, it would be of great interest to understand whether manufacturers have optimized the amounts applied. While spot-ons and collars do come in different sizes based on pet weight, it is unclear whether that optimization was based solely on pet health or whether that is also the minimum dosage for effective insecticidal activity.

Appendix 3

Suggested Imidacloprid Product Label Improvements

In this attachment, BACWA respectfully submits suggested concepts and goals for upgrades to the existing imidacloprid labels. Our suggestions come from our expertise as environmental scientists and engineers. As we are not pest control experts, we are not intending to provide specific label language, and recognize that these suggestions should be vetted by pesticide regulators and users.

To clarify some of our suggestions, we have included sections of current labels in boxes below.

1. Pet treatments: (U.S. EPA Registration Numbers 11556-117, -122, -118, -119, -120, -116, 11556-132, -134, -133, -135, etc.)

Examples of Current Label Language (excerpts)

> Advantage is waterproof and remains effective following a shampoo treatment, swimming or after exposure to rain or sunlight.

> K9 Advantix® is waterproof and remains effective following a shampoo treatment, swimming or after exposure to rain or sunlight.

Suggested change: Remove all label language that encourages washing and water exposure of treated pets. Label statements such as "waterproof" should be removed. All labels should dissuade owners from washing their pets for at least 2 weeks after treatment.

2. Sewer and manhole treatments: (U.S. EPA Registration Numbers 72155-70, 73079-10, 73079-14)

Example of Current Label Language (excerpt)

WHERE TO USE	• Kitchens - Cupboards, Dishwashers*, Garbage Cans, Refrigerators*, Stoves*. • Bathrooms - Bathtubs*, Garbage Cans • Laundry Rooms - Drains, Laundry Tubs*, Washing Machines* • Basements, Garages, Outdoor Areas - Drains, Garbage Cans, Laundry Tubs*, Manholes, Pipe Collars, Sewers, Washing Machines*, Water Pipes* • General - Cabinets, Closets, Counters, Cracks, Crevices, Shelving, Sinks * Do not apply bait inside these items. Locate behind or under item.

Suggested change: disallow all usage inside sewers, storm drains, or inside manholes.

3. Houseplant treatments: (U.S. EPA Registration Number 53883- 217)

Example of Current Label Language (excerpt)

FOR RESIDENTIAL USE ONLY

- Kills birch leaf miner
- Highly effective, Lasting protection
- No spraying…no mess
- Promotes strong roots and beautiful blooms
- For use in potted plants
- Long lasting, effective protection
- Protects plants from damage by Aphids, Scale, Whiteflies and other listed insects
- Even new growth is protected against insects for up to 8 weeks.
- For containerized plants
- Protects plants from damaging insects for up to 2 months

APPLICATION INSTRUCTIONS

For best results, apply IMI 0.22 G Plant Granules evenly, cultivate lightly, and water thoroughly. For containerized plants, apply the appropriate amount of granules evenly to the top of the soil. Mix the granules thoroughly into the top layer of the soil making sure not to damage the upper roots. Water in thoroughly. To help assure that the roots can absorb the insecticide, do not water too heavily for the first 10 days. Work granules into top 1 to 2 inches of soil. For flower beds, sprinkle granules evenly over the bed.

Suggested changes: add statement discouraging over-watering and forbidding discharge of water from treated houseplants in indoor sinks or baths, or anywhere that would allow water to runoff from the houseplant into the drain.

April 21, 2018

Thomas Harty
Office of Pesticide Programs (OPP)
Regulatory Public Docket Center (28221T)
U.S. Environmental Protection Agency (EPA)
1200 Pennsylvania Ave., NW.
Washington, DC 20460–0001

Subject: Clothianidin – Preliminary Aquatic and Non-Pollinator Terrestrial Risk Assessment (EPA–HQ–OPP–2011–0865)

Dear Mr. Harty:

On behalf of the Bay Area Clean Water Agencies (BACWA), we thank you for the opportunity to comment on the Preliminary Aquatic and Non-Pollinator Terrestrial Risk Assessment (RA) for clothianidin. BACWA's members include 55 publicly owned wastewater treatment facilities ("POTWs") and collection system agencies serving 7.1 million San Francisco Bay Area residents. We take our responsibilities for safeguarding receiving waters seriously. BACWA is especially interested in pesticides that are used in manners that have transport pathways to the sanitary sewer, as even the most sophisticated wastewater treatment plants cannot fully remove complex chemicals like pesticides.

Every day, BACWA members treat millions of gallons of wastewater that is then discharged to fresh or salt water bodies, including local creeks and rivers, bays, and the Pacific Ocean. These waterways provide crucial habitat to a wide array of aquatic species and waterfowl. 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 there is a lack of mixing at certain times due to thermal or saline stratification.

BACWA has a strong interest in clothianidin (a neonicotinoid insecticide) due to its toxicity to aquatic invertebrates and proven ability to pass through POTWs and appear in our effluent. Clothianidin is found in multiple types of consumer products – including bed bug products and cockroach products– that have transport pathways to the sanitary sewer. Even the most sophisticated wastewater treatment plants cannot fully remove neonicotinoids. The primary purposes of this letter are to request that the RA be expanded to include an evaluation of sewer discharges from indoor clothianidin uses and to share POTW monitoring data and aquatic toxicity data recently published in the scientific literature.

BACWA appreciates that OPP has started to conduct evaluation of risks associated with pesticide discharges to the sewer system ("down the drain" risk assessments). OPP's clothianidin risk assessment did not include a down-the-drain assessment. Omitting evaluation of the sewer discharge environmental exposure pathway can be harmful to the environment and prove costly for POTWs, as detailed below.

In almost every US state – including California – state law precludes any local regulation of pesticide sales or use. As we have no local option to control use of pesticides consumer products, it is essential to us that OPP's Registration Review adequately evaluates potential impacts to wastewater quality, and results in mitigation measures ensuring that impacts to the beneficial uses of the receiving water are *prevented*.

For these reasons, it is of utmost importance to BACWA that all clothianidin-containing products with pathways to the sewer be carefully and thoroughly evaluated.

In addition to commenting on the RA, we are also taking this opportunity to provide input on possible mitigation strategies for EPA to discuss with clothianidin registrants. We are providing this input at this time because mitigation measures may be necessary and we understand that the next opportunity for public comment will be after such discussions and after EPA has prepared its proposed decision.

Thank you for this opportunity to present our input on each of these topics.

Background – Pesticide discharges to the sewer can harm the environment and be costly

Pesticide discharges to the sewer system can prove costly for POTWs, due to the potential for pesticides to cause or contribute to wastewater treatment process interference, NPDES permit compliance issues, adverse impacts to receiving waters, degradation of recycled water quality and/or ability to reuse biosolids, in addition to exposing POTWs to the potential for third party lawsuits under the Federal Clean Water Act (CWA).

Of particular concern is the ability of a specific pesticide to cause exceedance of a POTW's effluent toxicity limits. One universal water quality standard in the U.S., which stems directly from the CWA, is that surface waters cannot be toxic to aquatic life. NPDES permits require POTWs to demonstrate that they meet this standard by evaluating acute and chronic toxicity using EPA standard methods (set forth in 40 CFR Part 136). To evaluate toxicity, every POTW must (1) conduct toxicity screening tests with a range of species, (2) select the most sensitive species, and (3) perform routine monitoring (typically monthly or quarterly). These monitoring data are used to determine whether the discharger has a *reasonable potential* to cause or contribute to toxicity in the receiving water. If it does, the CWA requires that numeric effluent limits be imposed, otherwise POTWs may be given numeric effluent triggers for further action. In the event that routine monitoring *does exceed* a toxicity limit or trigger, the POTW must perform accelerated monitoring (e.g., monthly); and if there is still evidence of consistent toxicity, the discharger must do a Toxicity Reduction Evaluation (TRE) to get back into compliance. The TRE requires dischargers to evaluate options to optimize their treatment plants and conduct a Toxicity Identification Evaluation (TIE), the cost of which can vary from $10,000 to well over $100,000 depending on complexity and persistence of the toxicant. The goal of the TIE is to identify the substance or combination of substances causing the observed toxicity. If a POTW's effluent is toxic because of a pesticide, it may not have any practical means to comply with CWA-mandated toxicity permit limits.

Once identified, the cost to treat or remove the toxicity causing compound(s) can vary dramatically. Often, there are few ways for a discharger to mitigate the problem other than extremely costly treatment plant upgrades. Upgrading treatment plants is often ineffective for organic chemicals like pesticides that appear at sub microgram per liter concentrations, largely

because sewage is a complex mixture of natural organic compounds. Regardless of this, the discharger must comply with its CWA permit limits. If a discharger violates a toxicity limit, it can be subject to significant penalties (in California up to $10/gallon or $10,000 per day).

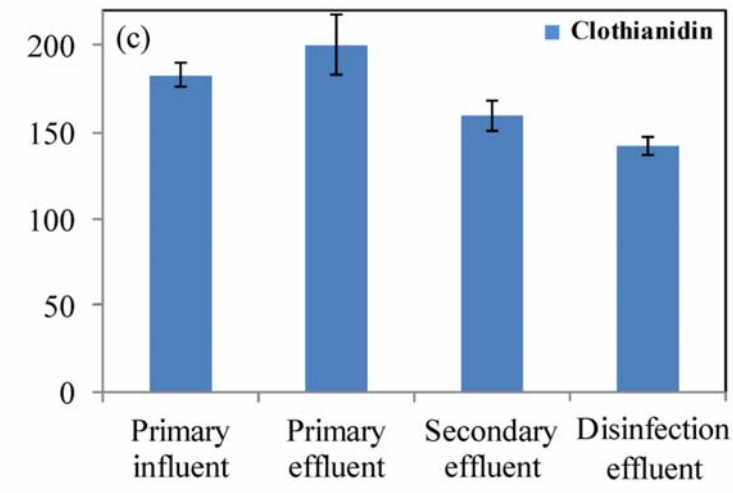
In addition, when surface water bodies become impaired by pesticides, wastewater facilities may be subject to additional requirements established as part of Total Maximum Daily Loads (TMDLs) set for the water bodies by EPA and state water quality regulatory agencies. A number of pesticide-related TMDLs have been adopted or are in preparation in California. The cost to wastewater facilities and other dischargers to comply with TMDLs can be up to millions of dollars per water body per pollutant. This process will continue as long as pesticides are approved for uses that result in water quality impacts; it is therefore imperative that EPA conducts a Registration Review focusing on water quality impacts and for EPA to take action to ensure that any impacts are prevented or fully mitigated.

Clothianidin in POTW Influent and Effluent

As it is still a relatively new insecticide, clothianidin is not commonly measured by POTWs. The sole published monitoring study, by Sadaria et al (2016; enclosed) reported that clothianidin was detected in 33% of influent and effluent samples from 13 US POTWs. At one POTW that was examined in detail over multiple days, effluent concentrations (70.2 ± 121.8 ng/L) were highly variable but often exceeded the chronic toxicity reference value (50 ng/L, LOAEC for *Chironomus dilutus*) used in the RA.

Sadaria et. al. noted that secondary treatment did not remove clothianidin, that there was "no discernible removal by processes including microbial degradation, hydrolysis, and oxidation in the aeration basin". Figure 1 shows the mass balance of clothianidin over five days occurring at one of the tested wastewater treatment plants. The study also noted that clothianidin was not oxidized (removed) during the chlorine disinfection treatment process and an insignificant amount (less than one percent by mass) accumulates in biosolids ("sludge").

Figure 1. (from Sadaria et. al. 2016) Total mass of clothianidin in wastewater unit operation flows over a 5-day period.



Note: Whiskers represent maximum and minimum values from two experimental replicates.

While this single study is too limited to characterize clothianidin concentrations in POTW effluent, it demonstrates the presence of clothianidin in wastewater, its capacity to pass through treatment processes and to occur in effluent at concentrations of interest from the ecological perspective.

BACWA requests that the RA be expanded to include an evaluation of sewer discharges from indoor use of clothianidin

BACWA is concerned that risks associated with indoor clothianidin use were not examined in the RA and respectfully asks the EPA to include this analysis (a "down-the-drain" risk assessment) in the revised assessment. We request that U.S. EPA specifically analyze sewer discharges associated with indoor treatments (such as bedbug treatments, cockroach treatments, etc.) and specifically evaluate direct use of clothianidin inside sewers and floor drains. EPA has POTW predictive modeling tools to suitable for conducting this assessment and has conducted similar assessments for many other pesticides.

BACWA requests that EPA include the latest aquatic toxicity data, particularly that for chronic toxicity

The EPA noted that there are significant data gaps with regards to acute and chronic toxicity data on clothianidin's effect on invertebrates. BACWA would like to respectfully submit the following recently published studies that were not included in the RA, which report acute aquatic toxicity at concentrations lower than the data used in the RA:

- Maloney, et. al. (2017) measured acute toxicity of clothianidin to *C. dilutus*..
- Raby, et.al. (2018) measured acute toxicity of clothianidin to 21 different aquatic invertebrates.
- Miles, et.al. (2017) measured the acute toxicity of clothianidin on eight aquatic species.

While these papers provide additional acute toxicity data, BACWA requests that EPA seek to obtain chronic toxicity data to incorporate into the findings in the proposed decision in order to ensure that any associated mitigation measures are sufficient to prevent POTW effluent toxicity. Chronic toxicity data are recommended for two reasons:

1) POTWs continuously discharge to surface waters.
2) Use of acute toxicity data and the common default assumption that the acute-to-chronic toxicity ratio is 10 might significantly underestimate chronic toxicity given that some neonicotinoids are known to have chronic toxicity values that are more than 300-fold lower than the lowest acute toxicity value.[1]

BACWA requests that EPA consider risk mitigation for clothianidin

Because clothianidin concentrations reported in undiluted POTW effluents sometimes exceeded the aquatic freshwater invertebrates chronic toxicity endpoint used in the RA, we expect that the "down-the-drain" risk assessment may conclude that risk mitigation is warranted to reduce POTW clothianidin discharges. Because 100% of POTWs must comply with the Federal Clean

[1] Roessink, I et al. (2013). *Environmental Toxicology and Chemistry* V.32, No. 5, pp. 1096–1100.

Water Act 100% of the time, whenever EPA identifies significant risks from pesticides discharged to POTWs, BACWA believes that a robust exploration of risk mitigation is imperative.

BACWA suggests that EPA consider the following risk mitigation strategies for indoor clothianidin products:

- Determine the minimum application rate necessary to achieve pest control for indoor uses. This would eliminate unnecessary overuse and minimize POTW discharge quantities.
- Eliminate the usage of clothianidin in floor drains and sewers. It is currently allowed in the following labels: 432-1531 and 1021-2796.
- Prohibit the use of clothianidin on anything that is washable. Currently, bed linens are the only washable item that it is prohibited to be used on: (1021-2793, 1021-2780, 1021- 2788, 1021-2776, 1021- 2780). Expand to explicitly prohibit use on any washable item, by adding the bolded text to the labels: "Infested bed linens ***and washable items*** should not be treated." The current labels actually encourage use on washable items such as pet bedding and curtains. It is possible that this is causing pulses of clothianidin to enter the sewer collection system when these washable items are laundered, given the relatively high water solubility of clothianidin.

Thank you for the opportunity to provide this feedback regarding both the risk assessment and subsequent mitigation strategies. We ask that OPP evaluate clothianidin discharges to POTWs and the subsequent potential impacts to effluent quality and explore mitigation options. BACWA requests that EPA coordinate with the California Department of Pesticide Regulation (CDPR) (which has extensive relevant information and expertise), and registrants; and bring in the latest scientific information – including CDPR scientific studies and modeling that are currently underway.

If you have any questions, please contact BACWA's Project Managers:

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Respectfully Submitted,

David R. Williams

David R. Williams

Executive Director
Bay Area Clean Water Agencies

Enclosures:

1. Sadaria A.M., Supowit SD, Halden RU. 2016. Mass balance assessment for six neonicotinoid insecticides during conventional wastewater and wetland treatment: Nationwide reconnaissance in United States wastewater. Environ Sci Technol 50:6199–6206.

2. Miles, J.C., et.al. 2017. Effects of clothianidin on aquatic communities: Evaluating the impacts of lethal and sublethal exposure to neonicotinoids. PLoS ONE 12(3): e0174171. https://doi.org/10.1371/journal.pone.0174171
3. Maloney, E.M. et.al. 2017. Cumulative Toxicity of Neonicotnoid Insecticide Mixtures to Chironomus Dilutus under Acute Exposure Scenarios. Environmental Toxicology and Chemistry. 36 (11), 3091–3101.
4. Raby, M., Nowierski, M., Perlov, D., Zhao, X., Hao, C., Poirier, D.G., Sibley, P.K., 2018. Acute Toxicity of Six Neonicotinoid Insecticides to Freshwater Invertebrates. Environ. Toxicol. Chem.

cc: Yu-Ting Guilaran, Director, Pesticide Re-Evaluation Division
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Paul Hann, California State Water Resources Control Board
Dawit Tadesse, California State Water Resources Control Board
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Tom Mumley, California Regional Water Quality Control Board, San Francisco Bay Region
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James Parrish, California Regional Water Quality Control Board, SF Bay Region
Jennifer Teerlink, California Department of Pesticide Regulation
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Cynthia Finley, Director, Regulatory Affairs, National Association of Clean Water Agencies
Kelly D. Moran, Urban Pesticides Pollution Prevention Partnership
BACWA Executive Board
BACWA Pesticides Workgroup

April 21, 2018

Steven Snyderman
Office of Pesticide Programs (OPP)
Regulatory Public Docket Center (28221T)
U.S. Environmental Protection Agency (EPA)
1200 Pennsylvania Ave., NW
Washington, DC 20460–0001

Subject: Dinotefuran – Preliminary Ecological Risk Assessment (EPA-HQ-OPP-2011-0920)

Dear Mr. Snyderman:

On behalf of the Bay Area Clean Water Agencies (BACWA), we thank you for the opportunity to comment on the Preliminary Ecological Risk Assessment (ERA) for dinotefuran. BACWA's members include 55 publicly owned wastewater treatment facilities ("POTWs") and collection system agencies serving 7.1 million San Francisco Bay Area residents. We take our responsibilities for safeguarding receiving waters seriously. BACWA is especially interested in pesticides that are used in manners that have transport pathways to the sanitary sewer, as even the most sophisticated wastewater treatment plants cannot fully remove complex chemicals like pesticides.

Every day, BACWA members treat millions of gallons of wastewater that is then discharged to fresh or salt water bodies, including local creeks and rivers, bays, and the Pacific Ocean. These waterways provide crucial habitat to a wide array of aquatic species and waterfowl. 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 there is a lack of mixing at certain times due to thermal or saline stratification.

BACWA has a strong interest in dinotefuran due to the existence of indoor uses and the associated pathway to sanitary sewers and the ERA's conclusion of "*potential for direct adverse effects to aquatic invertebrates on an acute and chronic basis…*". The primary purpose of this letter is to request that (1) the ERA incorporate the latest available invertebrate toxicity data and (2) the ERA be expanded to include an evaluation of sewer discharges from pet flea control products and other indoor dinotefuran uses. Several studies, including a recent study involving several of our member agencies, suggest that pet flea control products have a direct pathway, via sewer collection systems, to municipal wastewater treatment plants.

BACWA appreciates that OPP has started to conduct evaluation of risks associated with pesticide discharges to the sewer system ("down the drain" risk assessments). OPP's dinotefuran risk assessment did not include a down-the-drain assessment. Omitting evaluation of the sewer discharge environmental exposure pathway can be harmful to the environment and prove costly for POTWs, as detailed below.

In almost every US state – including California – state law precludes any local regulation of pesticide sales or use. As we have no local option to control use of pesticides consumer products, it is essential to us that OPP's Registration Review adequately evaluates potential impacts to wastewater quality, and results in mitigation measures ensuring that impacts to the beneficial uses of the receiving water are *prevented*.

For these reasons, it is of utmost importance to BACWA that pet flea control products and all other dinotefuran -containing products with pathways to the sewer be carefully and thoroughly evaluated.

In addition to commenting on the preliminary ecological risk assessment, we are also taking this opportunity to provide input on possible mitigation strategies for EPA to discuss with dinotefuran registrants. We are providing this input at this time because mitigation measures may be necessary and we understand that the next opportunity for public comment will be after such discussions and after EPA has prepared its proposed decision.

Thank you for this opportunity to present our input on each of these topics.

Background – Pesticide discharges to the sewer can harm the environment and be costly

Pesticide discharges to the sewer system can prove costly for POTWs, due to the potential for pesticides to cause or contribute to wastewater treatment process interference, NPDES permit compliance issues, adverse impacts to receiving waters, degradation of recycled water quality and/or ability to reuse biosolids, in addition to exposing POTWs to the potential for third party lawsuits under the Federal Clean Water Act (CWA).

Of particular concern is the ability of a specific pesticide to cause exceedance of a POTW's effluent toxicity limits. One universal water quality standard in the U.S., which stems directly from the CWA, is that surface waters cannot be toxic to aquatic life. NPDES permits require POTWs to demonstrate that they meet this standard by evaluating acute and chronic toxicity using EPA standard methods (set forth in 40 CFR Part 136). To evaluate toxicity, every POTW must (1) conduct toxicity screening tests with a range of species, (2) select the most sensitive species, and (3) perform routine monitoring (typically monthly or quarterly). These monitoring data are used to determine whether the discharger has a *reasonable potential* to cause or contribute to toxicity in the receiving water. If it does, the CWA requires that numeric effluent limits be imposed, otherwise POTWs may be given numeric effluent triggers for further action. In the event that routine monitoring *does exceed* a toxicity limit or trigger, the POTW must perform accelerated monitoring (e.g., monthly); and if there is still evidence of consistent toxicity, the discharger must do a Toxicity Reduction Evaluation (TRE) to get back into compliance. The TRE requires dischargers to evaluate options to optimize their treatment plants and conduct a Toxicity Identification Evaluation (TIE), the cost of which can vary from $10,000 to well over $100,000 depending on complexity and persistence of the toxicant. The goal of the TIE is to identify the substance or combination of substances causing the observed toxicity. If a POTW's effluent is toxic because of a pesticide, it may not have any practical means to comply with CWA-mandated toxicity permit limits.

Once identified, the cost to treat or remove the toxicity causing compound(s) can vary dramatically. Often, there are few ways for a discharger to mitigate the problem other than

extremely costly treatment plant upgrades. Upgrading treatment plants is often ineffective for organic chemicals like pesticides that appear at sub microgram per liter concentrations, largely because sewage is a complex mixture of natural organic compounds. Regardless of this, the discharger must comply with its CWA permit limits. If a discharger violates a toxicity limit, it can be subject to significant penalties (in California up to $10/gallon or $10,000 per day).

In addition, when surface water bodies become impaired by pesticides, 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. A number of pesticide-related TMDLs have been adopted or are in preparation in California. The cost to wastewater facilities and other dischargers to comply with TMDLs can be up to millions of dollars per water body per pollutant. This process will continue as long as pesticides are approved for uses that result in water quality impacts; it is therefore imperative that EPA conducts a Registration Review focusing on water quality impacts and for EPA to take action to ensure that any impacts are prevented or fully mitigated.

BACWA requests that EPA include the latest aquatic toxicity data, particularly that for chronic toxicity

The OPP notes that there is limited open literature with regards to acute and chronic RQs for freshwater invertebrates, on pages 8-9 of the ERA:

> *"Acute: Acute RQs for freshwater invertebrates were not calculable because there were no quantitative endpoints available…there is potential acute risk to freshwater and estuarine/marine aquatic invertebrates.*
> *Chronic: Not able to calculate RQs because quantitative data are not available…recently submitted data on the midge indicating potential risk; and, 4) monitoring data suggesting potential risk."*

A 2018 study by Raby et al.[1] provides further insight into the acute toxicity of dinotefuran to freshwater invertebrates (attached). Raby et al. evaluated the acute toxicity of thirteen different insects including the following that are mentioned in the ERA: midge (Chironomus sp.), yellow fever mosquito (Aedes aegypti), and Caddisfly (Cheumatopsyche sp.). In the case of the midge, the toxicity value occurs at a lower concentration than the qualitative value noted in the ERA, which would place the midge in the "very highly toxic" category. The other thirteen freshwater invertebrates evaluated in the study give a more robust and quantitative look at the toxicity of dinotefuran than was available at the time of the ERA. The study also notes that:

> *"(n)eonicotinoids are acutely toxic to aquatic macroinvertebrates at concentrations that span six orders of magnitude…This wide range in sensitivity within and between groups highlights the need for testing across different aquatic invertebrate orders, including those outside the typical model species, to better understand the range of neonicotinoid toxicity and hence potential risks in aquatic ecosystems."*

While the Raby study provides additional acute toxicity data, BACWA requests that EPA seek to obtain chronic toxicity data to incorporate into the findings in the proposed decision in order to

[1] Raby, M., Nowierski, M., Perlov, D., Zhao, X., Hao, C., Poirier, D.G., Sibley, P.K., 2018. Acute Toxicity of Six Neonicotinoid Insecticides to Freshwater Invertebrates. Environ. Toxicol. Chem.

ensure that any associated mitigation measures are sufficient to prevent POTW effluent toxicity. Chronic toxicity data are recommended for two reasons:

1) POTWs continuously discharge to surface waters.
2) Use of acute toxicity data and the common default assumption that the acute-to-chronic toxicity ratio is 10 might significantly underestimate chronic toxicity given that some neonicotinoids are known to have chronic toxicity values that are more than 300-fold lower than the lowest acute toxicity value.[2]

BACWA requests that the ERA be expanded to include an evaluation of sewer discharges from pet flea control treatments and other indoor Dinotefuran uses

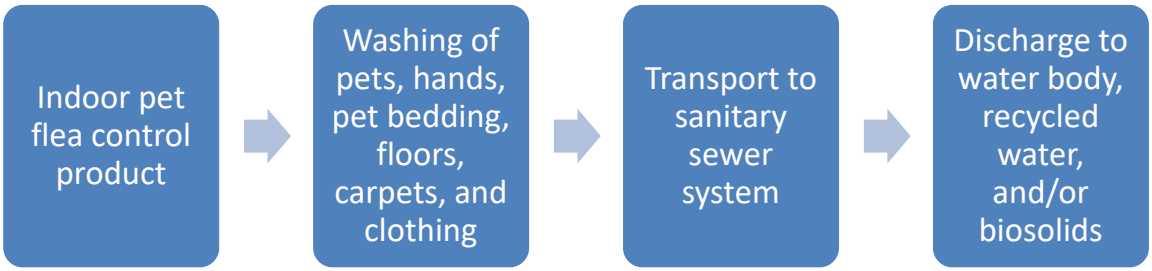
BACWA is concerned that risks associated with indoor dinotefuran use were not examined in the ERA and respectfully asks the EPA to include this analysis (a "down the drain" risk assessment) in the revised assessment. EPA has POTW predictive modeling tools which are suitable for conducting this assessment and has conducted similar assessments for many other pesticides.

We request that EPA specifically analyze sewer discharge sources such as:

- Pet spot-ons and sprays
- Indoor treatment granules, aerosols, sprays and foggers for cockroaches, bedbugs, fleas, and ants

Further, as explained in Appendix 1, pet flea control products contribute to POTW influent pesticides loads. Pet flea control chemicals are transported within a home to an indoor drain that flows to a POTW via the pathways illustrated in Figure 1.

Figure 1. Dinotefuran Pathway: From Pet Treatments to Wastewater Discharge



Scientific studies detailed in Appendix 1 examined the pathways that transport active ingredients from pet flea control products to the sewer system, both directly (through dog washing) and indirectly (such as after transfer onto human hands, socks, or clothing that are subsequently washed).

Based on the data from these studies and pet population data, it is clear that pet flea control products are significant sources of pesticides to POTWs that should be accounted for in the ERA.

[2] Roessink, I et al. (2013). *Environmental Toxicology and Chemistry* V.32, No. 5, pp. 1096–1100.

Monitoring data for pet flea control chemicals in POTW influents and effluents show higher concentrations in northern California POTWs (Sadaria et al 2017).[3] These data likely reflect real differences between these communities and those monitored in the nationwide study. The Sadaria et al. 2017 northern California study was conducted during a severe drought that triggered water use restrictions throughout the study area and significant reductions in POTW influent flows. Its September timing coincides with what may be the peak pet flea control season in the study area. According to Sadaria et al 2017:

> "Higher overall concentrations and detection frequencies in effluent from northern California may reflect regional, seasonal, and/or climate-related differences from other sampled facilities, such as lower dilution caused by drought-related water use reductions, presence of pests during all seasons because of the mild coastal climate, and pesticide use responding to regional pest pressures (e.g., high flea populations in California coastal areas)."

BACWA requests that EPA dinotefuran modeling and mitigation approaches account for these factors. Please see Appendix 2 of BACWA's comments on the Preliminary Ecological Risk Assessment for the Pyrethroid Insecticides (enclosed), where we detail potential approaches for addressing these factors within EPA's current POTW model. BACWA has developed an approach for evaluating both acute and chronic toxicity of pet flea control treatments in the face of limited sales volume data, based on treatment frequency, per capita pet ownership, concentration of active ingredient, and estimated POTW removal efficiency (see BACWA's Revised Appendix 4 of the Comments on the Preliminary Ecological Risk Assessment for the Pyrethroid Insecticides, October 20, 2017, attached).

Information to support assessment of other indoor treatments may be found in OPP's Occupational Risk Exposure Assessment for dinotefuran (OREA),[4] which carefully documented the use rates for indoor treatments and described a range of personal protective equipment (PPE) from manufacturer labels. Since PPE (such as clothing and coveralls) would be expected to be laundered after use, it provides a pathway for dinotefuran to enter the sanitary sewer.

BACWA requests that EPA consider risk mitigation for dinotefuran

Given findings for other pet flea control products, the "down-the-drain" risk assessment for dinotefuran may conclude that risk mitigation is warranted to reduce POTW dinotefuran discharges and associated invertebrate toxicity. Because 100% of POTWs must comply with the Federal Clean Water Act 100% of the time, whenever EPA identifies significant risks from pesticides discharged to POTWs, BACWA believes that a robust exploration of risk mitigation is imperative.

In response to the finding that pet flea control products are major sources of pesticides to POTWs, BACWA completed an assessment of pet flea control alternatives. This assessment, which is summarized in Appendix 2, identified multiple practical, effective, non-pesticide

[3] Sadaria, A.M., Sutton, R., Moran, K.D., Teerlink, J., Brown, J.V., Halden, R.U., 2017. Passage of fiproles and imidacloprid from urban pest control uses through wastewater treatment plants in northern California, USA. Environ. Toxicol. Chem. 36:6 1473-1482.

[4] "Dinotefuran**.** Occupational and Residential Exposure Assessment for Registration Review." U.S. EPA, September 12, 2017

alternatives.

In light of these findings, BACWA requests that OPP conduct its risk-benefit evaluation for pet flea control products as a group (i.e. considering pyrethroids, imidacloprid, indoxacarb, and fipronil, which are also undergoing Registration Review) and in the context of the broad range of available non-pesticide alternatives, including FDA-approved oral medications and mechanical controls (e.g., vacuuming, washing of pet bedding).

While we agree that pet flea and tick control has societal benefits, our review of control options detailed in Appendix 2 identified many alternatives that are likely far less environmentally problematic than on-pet or indoor pesticide treatments. For example, the new generation of FDA-approved orals seems to be more convenient, equally or more effective, and well accepted by pet owners and veterinarians. Mechanical controls (vacuuming, washing of pet bedding) offer lower cost and greater long-term control, as these are the sole option that addresses all life cycle stages of fleas. Finally, we emphasize that we do not believe that fipronil, imidacloprid, indoxacarb, or pyrethroids are acceptable alternatives to dinotefuran.

BACWA suggests that EPA consider the following additional risk mitigation strategies for indoor dinotefuran products:

- Determine the minimum application rate necessary to achieve pest control for indoor uses like pet flea control. This would eliminate unnecessary overuse and minimize POTW discharge quantities.
- Consider adding wastewater-protective use restrictions to product labels—such as dissuading pet owners from washing their pets for two weeks after applying treatments.
- Consider alternative application methods. Indoor aerosols, sprays, and foggers disperse chemicals in a way that significantly increases the likelihood that the active ingredient would be transported to the sanitary sewer, such as through laundered PPE or the washing of floors. On the other hand, containerized gel baits are unlikely to be significant collection system sources.

Thank you for the opportunity to provide this feedback regarding both the risk assessment and subsequent mitigation strategies. We ask that OPP evaluate dinotefuran discharges to POTWs and the subsequent potential impacts to effluent toxicity, and explore mitigation options, particularly for pet flea control products. BACWA requests that EPA coordinate with the California Department of Pesticide Regulation (CDPR) (which has extensive relevant information and expertise), veterinarians, and registrants; and bring in the latest scientific information – including CDPR scientific studies and modeling that are currently underway.

If you have any questions, please contact BACWA's Project Managers:

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Respectfully Submitted,

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Enclosures:

1. Raby, M., Nowierski, M., Perlov, D., Zhao, X., Hao, C., Poirier, D.G., Sibley, P.K., 2018. Acute Toxicity of Six Neonicotinoid Insecticides to Freshwater Invertebrates. Environ. Toxicol. Chem.
2. Sadaria, A.M. et al. 2017. Passage of Fiproles and Imidacloprid from Urban Pest Control Uses Through Wastewater Treatment Plants in Northern California. *Environmental Toxicology and Chemistry*. 36 (6), 1473-1482.
3. Bigelow Dyk, M. et al. (2012). Fate and distribution of fipronil on companion animals and in their indoor residences following spot-on flea treatments, *Journal of Environmental Science and Health, Part B: Pesticides, Food Contaminants, and Agricultural Wastes*, 47(10): 913-924
4. Halos, L. et al. 2014. Flea Control Failure? Myths and Realities. *Trends in Parasitology*, 30:5 228-233.
5. Blagburn, B., and Dryden, M., Biology, Treatment, and Control of Flea and Tick Infestations, *Vet Clin Small Anim,* 2009, Vol 39, pp 1173-1200.
6. Litchfield et al., Safety Evaluation of Permethrin and Indoxacarb in Dogs Topically Exposed to Activyl® Tick Plus, *J Veterinar Sci Technology* 2015, 6:2.
7. Teerlink, J., J. Hernandez, R Budd. 2017. Fipronil washoff to municipal wastewater from dogs treated with spot-on products. Sci Total Environ 599-600: 960-966.
8. Bay Area Clean Water Agencies (BACWA). July 7, 2017. Appendix 2 - Comment Letter on EPA Preliminary Ecological Risk Assessment for the Pyrethroid Insecticides.
9. BACWA. October 20, 2017. Revised Appendix 4 – Comment Letter on the Preliminary Ecological Risk Assessment for the Pyrethroid Insecticides.

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Appendix 1

Pet Flea Treatments:
Evidence for the Pathway to the Sewer

Part I – Evidence for the Pathway to the Sewer

There is mounting evidence that pesticides from on-pet flea control products (spot-ons and collars) and indoor foggers and sprays have exposure pathways to the sewer. The research summary below is organized first by the consumer use, followed by specific studies throughout a sewage collection system and at POTWs.

Topical Pet Flea Control Products - Background

Pet topical treatments are designed to impact one or more stages of the flea cycle through direct contact with the pesticide (rather than an adult flea biting the pet and obtaining the pesticide systemically with the consumed blood). Therefore, pesticides in topicals are not meant to enter the pet's bloodstream but rather are meant to stay on the pet's fur in order to be effective.

Pet Washing Discharge Pathway

Pet washing is likely a major discharge pathway for pet flea control products. A study by California Department of Pesticide Regulation (CDPR) (Teerlink et al. 2017; enclosed)[5] measured the washoff of fipronil spot-on products when bathing treated dogs. Fipronil was detected in all samples – even those collected 28 days post-application. According to the authors of the study:

> "Results confirm a direct pathway of pesticides to municipal wastewater through the use of spot-on products on dogs and subsequent bathing by either professional groomers or by pet owners in the home. Comparisons of mass loading calculated using California sales data and recent wastewater monitoring results suggest fipronil-containing spot-on products are a potentially important source of fipronil to wastewater treatment systems in California. This study highlights the potential for other active ingredients (i.e., bifenthrin, permethrin, etofenprox, imidacloprid) contained in spot-on and other pet products (i.e., shampoos, sprays) to enter wastewater catchments through bathing activities, posing a potential risk to the aquatic organisms downstream of wastewater discharge."[6]

Indirect Sewer Discharge Pathways

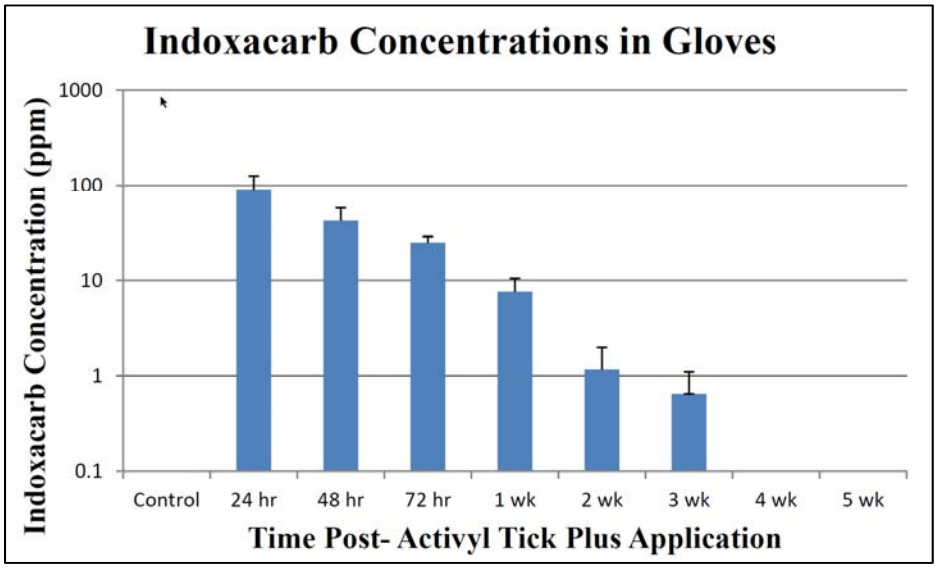
Several scientific studies have examined the transport of active ingredients from pet flea control products onto surfaces, such as human hands, that are subsequently washed, completing a transfer pathway to the sewer system.

- *Spot-on treatment product to glove (hands) pathway*: A 2015 study by Litchfield et al. evaluated the transfer of permethrin and indoxacarb from a topical pet flea control

[5] Teerlink, J., J Hernandez, R Budd. 2017. Fipronil washoff to municipal wastewater from dogs treated with spot-on products. Sci Total Environ 599-600: 960-966.
[6] Teerlink, J., J Hernandez, R Budd. 2017. Fipronil washoff to municipal wastewater from dogs treated with spot-on products. Sci Total Environ 599-600: 960-966.

treatment to people's hands.[7] In the study, the topical treatment was applied to dogs that had not received a topical treatment for at least two months. To simulate human exposure to the pesticides, "Glove sampling included the wipe sampling technique, which consisted of petting the dog forward and back along its back and sides, while avoiding the application site, for five minutes while wearing a 100% cotton glove." The cotton glove samples were collected at days 0, 1, 2, 3, 7, 14, 21, 28, and 35. While the results showed that the largest mass of indoxacarb was transported within the first week, there continued to be measurable transfer to the gloves, even at day 21. The study did not measure indoxacarb degradates, which likely formed during the study period.

Figure 2. (from Litchfield et. al. 2015) Indoxacarb concentrations in gloves after petting dogs who had application of indoxacarb ("Activyl Tick Plus") spot-on flea control (µg/L)



- *Spot-on treatment product to glove (hands) pathway:* A 2012 study by Bigelow Dyk et al. presents additional evidence of transport of a pet flea control products onto human hands and through homes.[8] In the study, researchers monitored transfer of fipronil (from a commercially available spot-on product) onto pet owners' hands and within their homes over a four-week period following spot treatment application. Participants used cotton gloves to pet their dog or cat for 2 minutes at a time at specific intervals after the application (24 hours, 1 week, 2 weeks, 3 weeks, and 4 weeks). Participants also wore cotton socks for 2 hours a night for 7 nights in a row, for four consecutive weeks following application. The gloves, socks, and brushed pet hair were subsequently analyzed for fipronil and its degradates. Bigelow Dyk and colleagues also incorporated a fluorescent dye into the spot treatment to provide photographic evidence of spot-on pesticide transfer. The photographic results shown in the paper illustrate the transfer from

[7] Litchfield et al., "Safety Evaluation of Permethrin and Indoxacarb in Dogs Topically Exposed to Activyl® Tick Plus," J Veterinar Sci Technology 2015, 6:2 http://dx.doi.org/10.4172/2157-7579.1000218. (enclosed)
[8] Bigelow Dyk, M., et al. (2012) Fate and distribution of fipronil on companion animals and in their indoor residences following spot-on flea treatments, Journal of Environmental Science and Health, Part B: Pesticides, Food Contaminants, and Agricultural Wastes, **47**(10): 913-924

the application location to other areas of the pet's fur and onto the pet owners' hands.

- *In-house fogger and spray pathway*: A UC Riverside study from 2010 sought to better understand the human health consequences of indoor insecticidal treatments, comparing a fogger, a perimeter spray, and both crack-and-crevice sprays, and spot sprays.[9] Researchers selected registered commercial products and applied per label instructions in rooms of unoccupied homes. They then evaluated the deposition of active ingredients, which included permethrin, chlorpyrifos, cyfluthrin, cypermethrin, and deltamethrin. They found that:

  > *"Each application type produced a surface residue, but the residues differed sharply in deposition and distribution. Relative to the general distribution of residue following fogger applications, perimeter, crack-and-crevice, and spot applications resulted in less total chemical residue and limited distribution to within 0–40 cm of the wall."*
  >
  > *"…fogger applications differ from all other methods of application that rely on directed sprays examined in this paper. This supports our proposal that deposition and spatial distribution are principally determined by the type of pesticide application (i.e. fogger vs. crack-and-crevice) and the actions of the applicator (i.e. heavy vs. light applications)."*

  In 1990, the California Department of Food and Agriculture published a dermal contact study presenting findings regarding the transfer of residue to people and their clothing following a chlorpyrifos/allethrin fogger treatment in carpeted rooms.[10] The rooms were all located in a new hotel so as to eliminate background pesticide residue and to provide repeatability from room to room. The foggers were set up per label instructions and were activated for two hours followed by ventilation of the room. Male and female participants later conducted a standardized exercise routine in specific locations in the room. Shirts, tights, gloves and socks were subsequently collected for analysis. Both allethrin and chlorpyrifos were detected in all exposed samples exceeding the minimum detection limits. Had these garments been placed in the laundry, this would have resulted in discharge to the sewer. Similarly, when the volunteer participants showered, the residue on their heads and other bare skin transferred to the sewer.

Based on the data from these studies characterizing topical flea control active ingredient transfer to owners' hands and the transfer of fogger active ingredients to room occupants, it appears that washing of hands, clothing, carpets and floors could be significant sources of pesticides to POTWs.

<u>Evidence from Collection Systems</u>

[9] Keenan, James J., John H. Ross, Vincent Sell, Helen M. Vega, Robert I. Krieger, "Deposition and spatial distribution of insecticides following fogger, perimeter sprays, spot sprays, and crack-and-crevice applications for treatment and control of indoor pests," Regulatory Toxicology and Pharmacology 58 (2010) 189–195.

[10] Ross, J., T. Thongsinthusak, H.R. Fong, S. Margetich, R. Krieger, California Department of Food and Agriculture, "Measuring Potential Dermal Transfer of Surface Pesticide Residue Generated from Indoor Fogger Use: An Interim Report," Chemosphere, Vol.20, Nos.3/4, pp 349-360, 1990.

CDPR is in the process of completing a collection system ("sewershed") study within the City of Palo Alto's Regional Water Quality Control Plant.[11] The study involved twenty-four hour time weighted composite samples (influent, effluent, and ten sites in the collection system). Samples were collected from several discharge-specific sites with potential for relatively large mass flux of pesticides (i.e., discharges from pet grooming operation, pest control operator, and a laundromat). The samples were analyzed for a suite of pesticides. Preliminary results from the pet-grooming site provide evidence that pet washing is a pathway for pesticide discharges to sewer systems.

We encourage OPP to obtain the final results of this study, which should be available within the timeframe of OPP's exploration of mitigation strategies for dinotefuran.

POTW Influent and Effluent

Lastly, further insights regarding transport of indoor flea control products to POTWs comes from a study of fipronil and imidacloprid at eight POTWs that was recently conducted by the San Francisco Bay Regional Monitoring Program in collaboration with BACWA, CDPR and Arizona State University.[12] The study monitored imidacloprid and fipronil, as well as its degradates, in the influent and effluent of eight urban California POTWs. The results indicated that fipronil, its degradates, and imidacloprid were ubiquitous in the influent sewage and final treated effluent of all eight participating POTWs, and – based on a detailed analysis of the sewer discharge sources of these two chemicals, which have relatively little indoor use other than pet flea control – provide compelling evidence that pet flea control products may be the primary source of both chemicals in wastewater.

[11] See http://www.cdpr.ca.gov/docs/emon/surfwtr/presentations/presentation_130_targeted.pdf

[12] Sadaria, A.M., Sutton, R., Moran, K.D., Teerlink, J., Brown, J.V., Halden, R.U., 2017. Passage of fiproles and imidacloprid from urban pest control uses through wastewater treatment plants in northern California, USA. Environ. Toxicol. Chem. 36:6 1473-1482.

Appendix 2

Pet Flea Control Products:
Alternatives Analysis

Alternatives and Mitigation

BACWA requests that EPA, in coordination with CDPR (which has extensive relevant information and expertise), veterinarians, and registrants, develop mitigation strategies for pet flea control products, including spot-ons and collars. Two specific topics are discussed below, as an effort to provide insight regarding mitigation options for flea control:

- Alternatives: oral medications and integrated pest management appear effective
- Optimization of application rates of pet flea control products

Alternatives: Integrated Pest Management and Oral Medications
Mechanical controls (e.g., vacuuming) appear to be key to avoiding a flea infestation in a home. Further, since the previous registration, there is now an opportunity provided by oral treatments that have come on the market in recent years (available for both dogs and cats) that could avoid the on-pet use of not only dinotefuran, but also alternatives that are problematic from the water quality perspective (e.g., fipronil, pyrethroids, indoxacarb, and imidacloprid).

The fleas found on a pet are estimated to represent only 1-5% of the flea cycle in a home; the other 95% are found as eggs, larvae, pupae, and adult fleas throughout the home and surrounding environment.[13] It takes about 18 days for a flea egg to grow into an adult flea, but in cool weather immature fleas can lay dormant in a pupal cocoon for up to 1 year. Adult fleas can live on a pet for 30 to 40 days. Fleas lay 20 to 50 eggs each day; consequently flea problems in residential settings can get out of control quickly.

Therefore, to avoid repeat infestations, one must address all stages of this flea cycle including flea eggs, larvae and pupae.[14] One way to do so is via non-pesticide mechanical controls, including frequent indoor vacuuming, washing of pet bedding, and use of a pet flea comb.[15] In particular, vacuuming needs to be both thorough and frequent. It should include the pet sleeping area, floors, furniture and all upholstered or carpeted surfaces, including under cushions, furniture and in other hard to reach places. Regarding frequency, it turns out that during the pupal stage, the flea is encased in a shell that is not penetrated by pesticides. The act of vacuuming can speed up the process. Specific guidance from one study notes the following:

> *"The vibration also stimulates adult fleas to emerge from their cocoons so that they can be collected in the vacuum machine. Therefore frequent vacuuming, during a flea infestation, can reduce the overall flea burden in the home. It should be ensured that vacuum bags are disposed of properly, to prevent recolonization of the home with flea stages previously removed by vacuuming."* [16]

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[13] Halos, L., et al. (2014). Flea Control Failure? Myths and Realities. Trends in Parasitology, 30:5 228-233.
[14] Ibid, 228-233.(enclosed)
[15] American Veterinary Medical Association (2009). External Parasites.
[16] "Biology, Treatment, and Control of Flea and Tick Infestations," Blagburn, B., and Dryden, M., Vet Clin Small Anim, 2009, Vol 39, pp 1173-1200. (enclosed)

Although spot-on pet flea control products currently dominate the pet flea control market, new oral medications have recently become available. The table on the following page summarizes the current state of available oral medications for pets. The new pills, which are registered by U.S. FDA rather than EPA, appear to eliminate aquatic (and human) exposure pathways and should be equally or more convenient for pet owners, once they have obtained a prescription from a veterinarian. The involvement of the veterinarian has the added benefit of providing pet-specific guidance on flea control approach and safe dosage. Some studies indicate that oral medications may be more effective than topical spot treatments possibly because there is less reliance on proper application by the owner.[17]

Optimization of Application Rates of Pet Flea Control Products

Another consideration for pet flea control products is that of application rate. Given that these household and pet flea control products have a transport pathway to the sewer, it would be of great interest to understand whether manufacturers have optimized the amounts applied. While spot-ons come in different doses based on pet weight, it is unclear whether that optimization was based solely on pet health or whether that is also the minimum dosage for effective insecticidal activity.

[17] "Flea blood feeding patterns in cats treated with oral nitenpyram and the topical insecticides imidacloprid, fipronil and selamectin," McCoy, c., et al., Veterinary Parasitology, Vol. 156, pp 293-301, 2008.

List of Currently Available Oral Pet Treatments for Fleas (Alphabetical)

Active Ingredient	Example Product Names and Manufacturers	Dogs, Cats or Both?	Flea, Tick, Both	Dose Schedule	Adulticide?	Insect Growth Regulator?	Chemical Family	Year Registered
Afoxolaner	Nexgard (Merial)	Dogs only	Both	1 month	X	No	Isoxazoline[18]	2013
Fluralaner	Bravecto (Merck)	Dogs only	Both	2-3 months	X	No	Isoxazoline	2014
Lufenuron	Program (Novartis) and Sentinel (that also includes a heartworm pharma)	Both	Flea eggs, as well as hookworms, roundworms	1 month	No	X	Benzoylurea	1995 (for dogs)
Nitenpyram	Capstar (Novartis), Capguard (Sentry)	Both	Flea	A few hours only (meant for immediate infestation control)	X	No	Neonicotinoid	2000
Sarolaner	Simparica (Zoetis, a subsidiary of Pfizer)	Dogs only	Both	1 month	X	No	Isoxazoline	2016
Spinosad	Comfortis and Trifexis (Elanco)	Both	Flea	1 month	X	No	Spinosyn, macrocyclic lactone	2007 (approx)

[18] Flea products from the isoxazoline chemical family are new to the marketplace; therefore pet health insights are largely limited to the studies conducted by the manufacturers and the packaging text required by the FDA. There appears to be no published information about health and safety beyond the manufacturer guidance in the MSDS. Due to the application method (pill), human exposure is likely small, though no data are available to verify this assumption.

April 21, 2018

Thomas Harty
Office of Pesticide Programs (OPP)
Regulatory Public Docket Center (28221T)
U.S. Environmental Protection Agency (EPA)
1200 Pennsylvania Ave., NW.
Washington, DC 20460–0001

Subject: Thiamethoxam – Preliminary Aquatic and Non-Pollinator Terrestrial Risk Assessment (EPA-HQ-OPP-2011-0581)

Dear Mr. Harty:

On behalf of the Bay Area Clean Water Agencies (BACWA), we thank you for the opportunity to comment on the Preliminary Aquatic and Non-Pollinator Terrestrial Risk Assessment (RA) for thiamethoxam. BACWA's members include 55 publicly owned wastewater treatment facilities ("POTWs") and collection system agencies serving 7.1 million San Francisco Bay Area residents. We take our responsibilities for safeguarding receiving waters seriously. BACWA is especially interested in pesticides that are used in manners that have transport pathways to the sanitary sewer, as even the most sophisticated wastewater treatment plants cannot fully remove complex chemicals like pesticides.

Every day, BACWA members treat millions of gallons of wastewater that is then discharged to fresh or salt water bodies, including local creeks and rivers, bays, and the Pacific Ocean. These waterways provide crucial habitat to a wide array of aquatic species and waterfowl. 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 there is a lack of mixing at certain times due to thermal or saline stratification.

BACWA has a strong interest in thiamethoxam (a neonicotinoid insecticide) due to its toxicity to aquatic invertebrates and proven ability to pass through POTWs and appear in our effluent. Thiamethoxam is found in multiple types of consumer products – including cockroach, ant, and termite products– that have transport pathways to the sanitary sewer. Even the most sophisticated wastewater treatment plants cannot fully remove neonicotinoids. The primary purposes of this letter are to request that the RA be expanded to include an evaluation of sewer discharges from indoor thiamethoxam uses and to share POTW monitoring data and aquatic toxicity data recently published in the scientific literature.

BACWA appreciates that OPP has started to conduct evaluation of risks associated with pesticide discharges to the sewer system ("down the drain" risk assessments). OPP's thiamethoxam risk assessment did not include a down-the-drain assessment. Omitting evaluation of the sewer discharge environmental exposure pathway can be harmful to the environment and prove costly for POTWs, as detailed below.

In almost every US state – including California – state law precludes any local regulation of pesticide sales or use. As we have no local option to control use of pesticides consumer products, it is essential to us that OPP's Registration Review adequately evaluates potential impacts to wastewater quality, and results in mitigation measures ensuring that impacts to the beneficial uses of the receiving water are *prevented*.

For these reasons, it is of utmost importance to BACWA that all thiamethoxam-containing products with pathways to the sewer be carefully and thoroughly evaluated.

Thank you for this opportunity to present our input on each of these topics.

Background – Pesticide discharges to the sewer can harm the environment and be costly

Pesticide discharges to the sewer system can prove costly for POTWs, due to the potential for pesticides to cause or contribute to wastewater treatment process interference, NPDES permit compliance issues, adverse impacts to receiving waters, degradation of recycled water quality and/or ability to reuse biosolids, in addition to exposing POTWs to the potential for third party lawsuits under the Federal Clean Water Act (CWA).

Of particular concern is the ability of a specific pesticide to cause exceedance of a POTW's effluent toxicity limits. One universal water quality standard in the U.S., which stems directly from the CWA, is that surface waters cannot be toxic to aquatic life. NPDES permits require POTWs to demonstrate that they meet this standard by evaluating acute and chronic toxicity using EPA standard methods (set forth in 40 CFR Part 136). To evaluate toxicity, every POTW must (1) conduct toxicity screening tests with a range of species, (2) select the most sensitive species, and (3) perform routine monitoring (typically monthly or quarterly). These monitoring data are used to determine whether the discharger has a *reasonable potential* to cause or contribute to toxicity in the receiving water. If it does, the CWA requires that numeric effluent limits be imposed, otherwise POTWs may be given numeric effluent triggers for further action. In the event that routine monitoring *does exceed* a toxicity limit or trigger, the POTW must perform accelerated monitoring (e.g., monthly); and if there is still evidence of consistent toxicity, the discharger must do a Toxicity Reduction Evaluation (TRE) to get back into compliance. The TRE requires dischargers to evaluate options to optimize their treatment plants and conduct a Toxicity Identification Evaluation (TIE), the cost of which can vary from $10,000 to well over $100,000 depending on complexity and persistence of the toxicant. The goal of the TIE is to identify the substance or combination of substances causing the observed toxicity. If a POTW's effluent is toxic because of a pesticide, it may not have any practical means to comply with CWA-mandated toxicity permit limits.

Once identified, the cost to treat or remove the toxicity causing compound(s) can vary dramatically. Often, there are few ways for a discharger to mitigate the problem other than extremely costly treatment plant upgrades. Upgrading treatment plants is often ineffective for organic chemicals like pesticides that appear at sub microgram per liter concentrations, largely because sewage is a complex mixture of natural organic compounds. Regardless of this, the discharger must comply with its CWA permit limits. If a discharger violates a toxicity limit, it can be subject to significant penalties (in California up to $10/gallon or $10,000 per day).

In addition, when surface water bodies become impaired by pesticides, 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. A number of pesticide-related TMDLs have been adopted or are in preparation in California. The cost to wastewater facilities and other dischargers to comply with TMDLs can be up to millions of dollars per water body per pollutant. This process will continue as long as pesticides are approved for uses that result in water quality impacts; it is therefore imperative that EPA conducts a Registration Review focusing on water quality impacts and for EPA to take action to ensure that any impacts are prevented or fully mitigated.

Thiamethoxam in POTW Influent and Effluent

As it is still a relatively new insecticide, thiamethoxam is not commonly measured by POTWs. The sole published monitoring study, by Sadaria et al (2016; enclosed) reported that thiamethoxam was not detected in influent and effluent samples from 13 US POTWs. This may be due to the low presence of thiamethoxam in the marketplace at the time the data was collected (2014-2015). The monitoring data for other neonicotinoids with similar uses suggest that as the use of thiamethoxam increases, it could be discharged to POTWs and pass through them into aquatic ecosystems.

BACWA requests that the RA be expanded to include an evaluation of sewer discharges from indoor use of thiamethoxam

BACWA is concerned that risks associated with indoor thiamethoxam use were not examined in the RA and respectfully asks the EPA to include this analysis (a "down-the-drain" risk assessment) in the revised assessment. We request that U.S. EPA specifically analyze sewer discharges associated with indoor treatments (such as cockroach, ant and termite treatments). EPA has POTW predictive modeling tools suitable for conducting this assessment and has conducted similar assessments for many other pesticides.

BACWA requests that EPA include the latest aquatic toxicity data, particularly that for chronic toxicity

The EPA noted that there are significant data gaps with regards to acute and chronic toxicity data on thiamethoxam's effect on invertebrates. BACWA would like to respectfully submit the following recently published studies that were not included in the RA:

- Maloney, et. al. (2017) measured acute toxicity of thiamethoxam to *C. dilutus*.
- Raby, et.al. (2018) measured acute toxicity of thiamethoxam to 21 different aquatic invertebrates.

While these papers provide additional acute toxicity data, BACWA requests that EPA seek to obtain chronic toxicity data to incorporate into the findings in the proposed decision in order to ensure that any associated mitigation measures are sufficient to prevent POTW effluent toxicity. Chronic toxicity data are recommended for two reasons:

1) POTWs continuously discharge to surface waters.
2) Use of acute toxicity data and the common default assumption that the acute-to-chronic toxicity ratio is 10 might significantly underestimate chronic toxicity given that some neonicotinoids are known to have chronic toxicity values that are more than 300-fold

lower than the lowest acute toxicity value.[1]

Thank you for the opportunity to provide this feedback regarding the risk assessment. We ask that OPP evaluate thiamethoxam discharges to POTWs and the subsequent potential impacts to effluent quality and explore mitigation options as appropriate. BACWA requests that EPA coordinate with the California Department of Pesticide Regulation (CDPR) (which has extensive relevant information and expertise), and registrants; and bring in the latest scientific information – including CDPR scientific studies and modeling that are currently underway.

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Respectfully Submitted,

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

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

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

INTRODUCTION

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

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

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

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

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

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

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

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

MATERIALS AND METHODS

Standards and reagents

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

Sample collection

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

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

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

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

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

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

Extraction of influent solid and biosolids samples.

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

Extraction of wastewater samples

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

Chromatography separation and MS/MS

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

Quality assurance and quality control

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

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

Method performance

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

RESULTS AND DISCUSSION

Detection of fipronil and its degradates in wastewater treatment streams

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

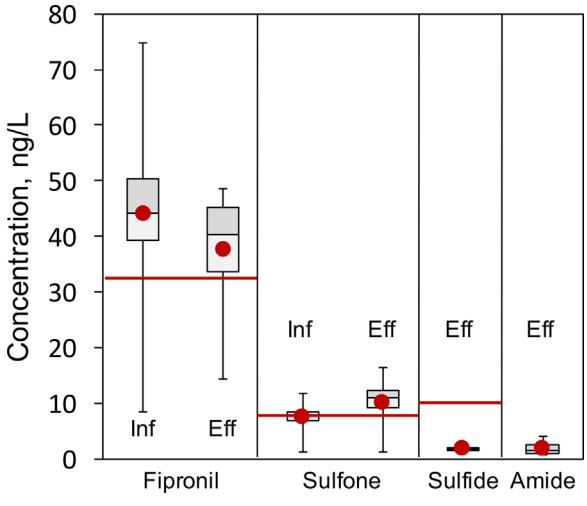

Figure 1. Detected concentrations of fipronil and its degradates (ng/L) in the dissolved phase from 8 wastewater treatment plants in northern California. Red horizontal lines indicate published chronic toxicity values for *Chironomus dilutus*, a freshwater invertebrate [15]. Inf = influent; Eff = effluent.

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

Distribution of fipronil and its degradates in wastewater

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

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

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

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

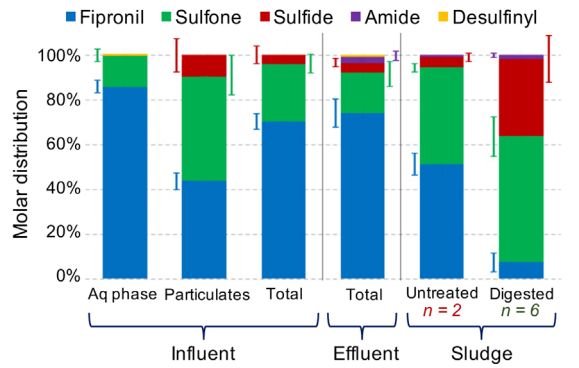

Figure 2. Molar distribution of fipronil and its degradates in treatment streams of 8 wastewater treatment plants. Error bars indicate standard deviation or min/max values when only 2 measurements were available (i.e., for untreated sludge).

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

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

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

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

Accumulation of fipronil and its degradates in solids

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

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

Detection of imidacloprid in wastewater treatment streams

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

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

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

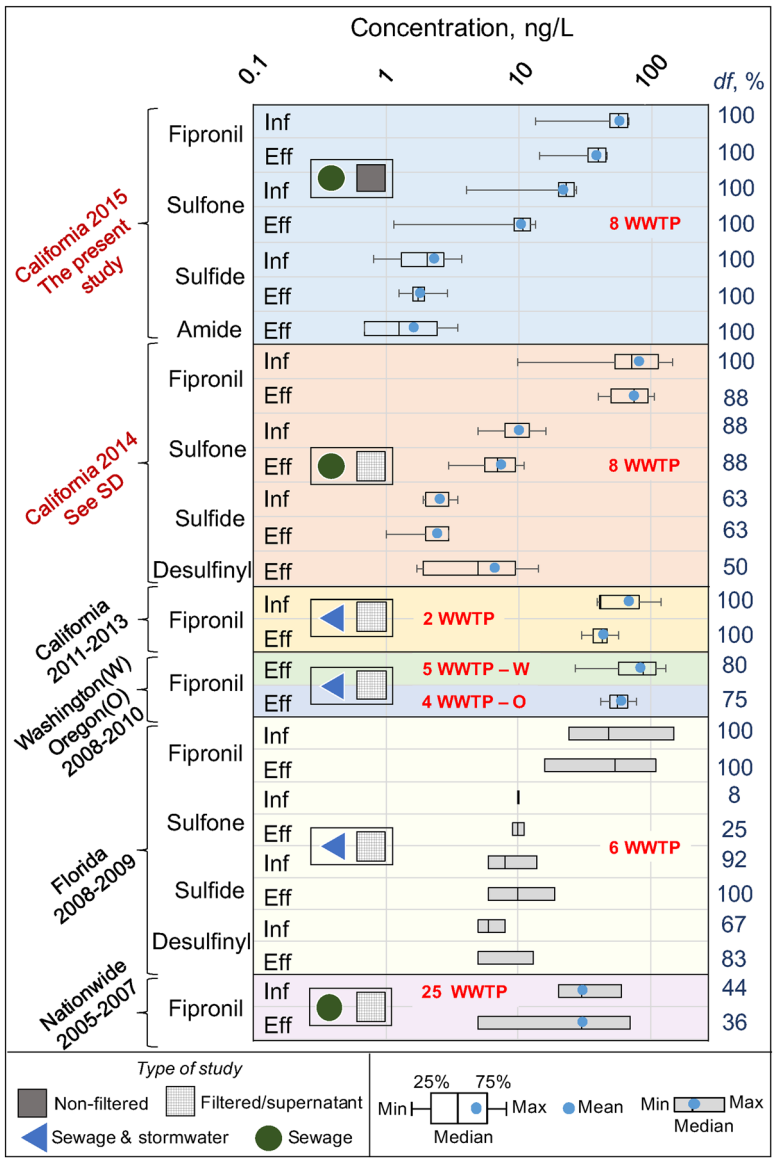

Figure 3. Concentrations of fipronil and its degradates in wastewater samples from 8 California wastewater treatment plants (present study) contrasted with data from past studies [15,22–24]. Years correspond to sampling period. df = detection frequency of compound in process flow; inf = influent; eff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

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

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

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

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

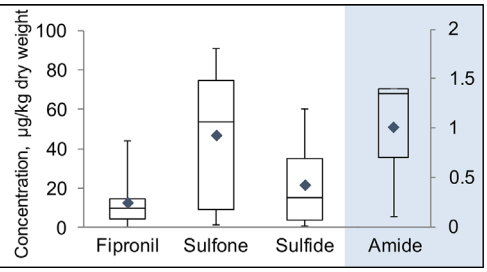

Figure 4. Concentrations of fipronil and its degradates detected in sludge samples obtained from 8 wastewater treatment plants in northern California in 2015. Highlighted in red italics are facilities not performing anaerobic treatment. In the plot, amide concentrations (highlighted blue) correspond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

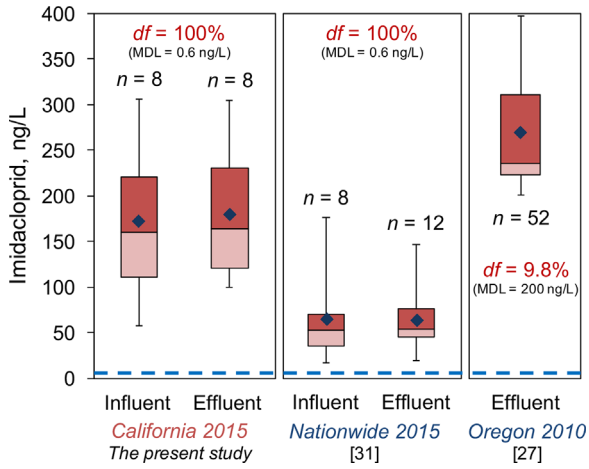

Figure 5. Detected concentrations of imidacloprid (ng/L) in 8 wastewater treatment plants in northern California and summary of data from previous studies [27,31]. Dashed blue horizontal line indicates European Union freshwater predicted no-effect concentration value [17]. df = detection frequency; MDL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

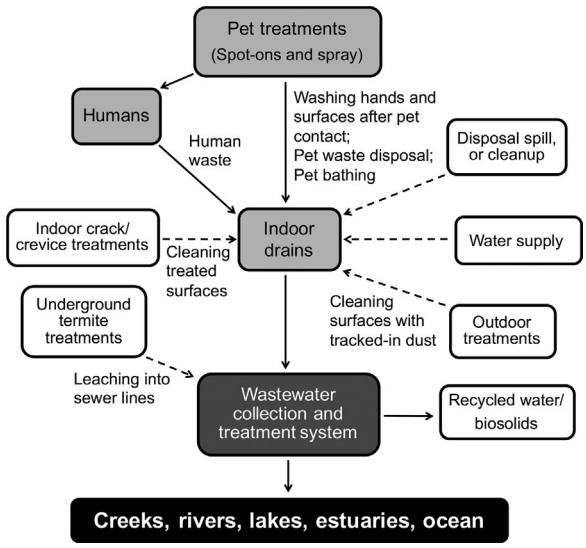

Figure 6. Conceptual model for sources of fipronil and imidacloprid in municipal wastewater. Dashed lines denote pathways believed to be relatively small in the present study. Uses without a clear pathway (e.g., containerized baits) and with unlikely pathways (e.g., air transport and deposition) [50]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

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

Fipronil and imidacloprid sources

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

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

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

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

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

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

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

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

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

Environmental implications

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

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

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

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

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

CONCLUSIONS

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

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

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

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Supporting Information

Passage of Fiproles and Imidacloprid from Urban Pest Control Uses Through Wastewater Treatment Plants in Northern California

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Summary

This supporting information contains 10 pages, including 9 tables and 1 figure.

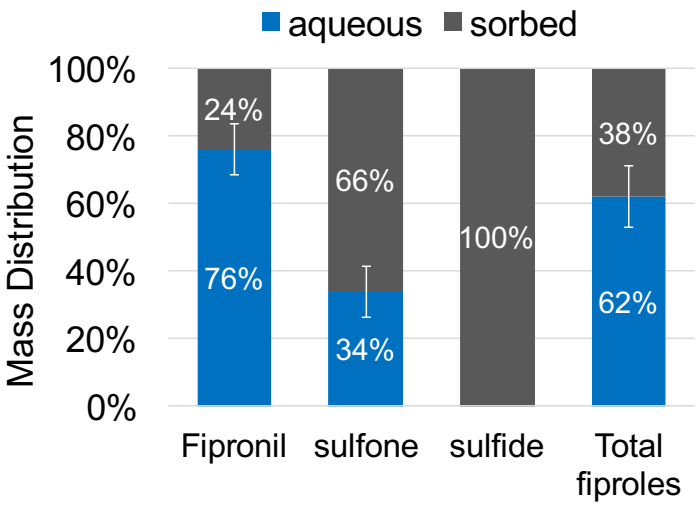

Figure S1. Relative distribution of the mass of imidacloprid, fipronil and major degradates between the dissolved and sorbed state (suspended solids) of wastewater influent samples (n=8). Error bars represent standard deviation among 8 samples.

Data Statistics

A paired two tailed t-test was performed ($\alpha = 0.05$) to compare influent and effluent concentration. Differences were determined at the $p < 0.05$ significance level. Shapiro-Wilk test was performed to assess the normality of the data.

For comparison of all fipronil related compounds in aqueous phase influent and effluent at all eight WWTPs, p value for Shapiro-Wilk test was 0.17, and p value for a paired two tailed t-test was 0.95.

For comparison of imidacloprid concentration in influent and effluent at seven WWTPs, p value for Shapiro-Wilk test was 0.18, and p value for a paired two tailed t-test was 0.49.

Instrument Selection for the Analysis of Fipronil and Its Degradates

Fipronil and degradates – sulfone, sulfide and amide showed higher sensitivity on LC-MS/MS, and desulfinyl on GC-MS/MS. Considering isotope dilution method was used, matrix effects were not a considerable concern. Therefore, analytes were analyzed with separate instruments to achieve the best result.

Table S1. Mass Spectrometric Parameters for the Detection of Analytes and Isotope-Labeled Surrogate Standards

analyte	Q_1 (m/z)	Q_3 (m/z)	Q_3'(m/z)	DP (V)	CE(V)	EP (V)	CXP (V)
imidacloprid	256	175.1	209.2	50	30	10	8
fipronil	434.9	329.9	250.0	-70	-10	-24	-5
-sulfone	450.8	281.8	414.7	-70	-10	-40	-4
-sulfide	418.7	382.8	262.1	-75	-10	-18	-5
-amide	386.7	350.8	281.9	-70	-10	-40	-9
-desulfinyl	384.9	305.8	254.7	-110	-6	-28	-15
internal standards							
imidacloprid-d_4	260.1	213.1	179.2	76	25	6	14
fipronil ($^{13}C_2{}^{15}N_2$)	438.8	333.8	254	-65	-10	-24	-13
-sulfone ($^{13}C_4{}^{15}N_2$)	456.8	420.5	287.6	-75	-10	-24	-15

Table S2. Method detection limit in different matrices and Octanol-Water Partition Coefficient (K_{OW})

analyte	MDL		Log K_{OW}
	wastewater	solids	
	ng/L	ng/g	
Imidacloprid	0.6	1.1	- 0.41
Fipronil	0.1	0.1	4.00
sulfide	0.2	0.1	4.42
sulfone	0.1	0.1	4.82
amide	0.3	0.1	5.43
desulfinyl	0.8	0.2	4.22

Table S3. Total detected concentrations of fipronil and its degradates in influent and effluent samples obtained from 8 wastewater treatment plants in northern California in 2015 (ng/L).

WWTP	Fipronil		sulfone		sulfide		amide		desulfinyl	
	inf	eff	inf	eff	inf	eff	inf	eff	inf	eff
SFTP	13.3	14.3	4.1	1.1	2.5	1.3	<0.3	0.6	<0.8	<0.8
PARP	59.2	31.2	21.1	10.4	1.5	1.7	<0.3	2.5	<0.8	<0.8
SJSC	54.5	42.9	26.6	16.3	2.0	1.8	<0.3	1.1	<0.8	<0.8
SLWP	45.3	36.6	24.0	12.3	0.8	1.6	<0.3	1.4	<0.8	<0.8
SMWP	82.2	48.3	31.2	12.7	3.4	2.5	<0.3	0.7	<0.8	<0.8
EBMUD	61.7	44.3	22.1	7.6	2.1	1.5	<0.3	<0.3	<0.8	<0.8
FSSD	49.6	34.4	16.7	11.4	0.9	1.9	<0.3	4.1	<0.8	<0.8
CCSD	88.1	48.6	28.2	9.8	5.2	2.0	<0.3	2.4	1.0	1.2

Table S4. Aqueous and sorbed phase concentration of fipronil and its degradates in influent samples obtained from 8 wastewater treatment plants in northern California in 2015.

WWTP	Fipronil		sulfone		sulfide	
	aqueous phase, ng/L	sorbed phase, ng/g	aqueous phase, ng/L	sorbed phase, ng/g	aqueous phase, ng/L	sorbed phase, ng/g
SFTP	8.6	4.7	1.1	3.0	< 0.2	2.5
PARP	47.0	37.9	7.8	41.4	< 0.2	4.5
SJSC	42.1	41.6	7.3	58.2	< 0.2	6.3
SLWP	30.9	27.9	7.9	31.3	< 0.2	1.6
SMWP	60.9	51.7	10.3	50.7	< 0.2	8.3
EBMUD	45.5	47.6	5.4	49.1	< 0.2	6.1
FSSD	42.7	28.9	7.7	38.3	< 0.2	3.6
CCSD	74.9	42.3	11.9	52.2	< 0.2	16.6

Table S5. Molar distribution of fipronil and its degradates in treatment streams of 8 WWTPs in northern California in 2015.

	influent - particulates				
WWTP	Fipronil	sulfone	sulfide	amide	desulfinyl
SFTP	46%	28%	26%	0%	0%
PARP	46%	48%	6%	0%	0%
SJSC	40%	54%	6%	0%	0%
SLWP	47%	51%	3%	0%	0%
SMWP	47%	45%	8%	0%	0%
EBMUD	47%	47%	6%	0%	0%
FSSD	42%	53%	5%	0%	0%
CCSD	38%	46%	16%	0%	0%
	influent - dissolved phase				
WWTP	Fipronil	sulfone	sulfide	amide	desulfinyl
SFTP	89%	11%	0%	0%	0%
PARP	86%	14%	0%	0%	0%
SJSC	86%	14%	0%	0%	0%
SLWP	80%	20%	0%	0%	0%
SMWP	86%	14%	0%	0%	0%
EBMUD	90%	10%	0%	0%	0%
FSSD	85%	15%	0%	0%	0%
CCSD	86%	13%	0%	0%	1%
	influent - total				
WWTP	Fipronil	sulfone	sulfide	amide	desulfinyl
SFTP	67%	20%	13%	0%	0%
PARP	73%	25%	2%	0%	0%
SJSC	67%	30%	3%	0%	0%
SLWP	65%	33%	1%	0%	0%
SMWP	71%	26%	3%	0%	0%
EBMUD	72%	25%	3%	0%	0%
FSSD	74%	24%	1%	0%	0%
CCSD	73%	23%	4%	0%	1%
	effluent - total				
WWTP	Fipronil	sulfone	sulfide	amide	desulfinyl
SFTP	83%	6%	8%	3%	0%
PARP	69%	22%	4%	5%	0%
SJSC	70%	25%	3%	2%	0%
SLWP	71%	23%	3%	3%	0%
SMWP	76%	19%	4%	1%	0%
EBMUD	83%	14%	3%	0%	0%
FSSD	67%	21%	4%	8%	0%
CCSD	76%	15%	3%	4%	2%

	sludge				
WWTP	Fipronil	sulfone	sulfide	amide	desulfinyl
SFTP	5%	42%	50%	3%	0%
PARP	55%	42%	3%	0%	0%
SJSC	4%	62%	32%	3%	0%
SLWP	7%	65%	27%	1%	0%
SMWP	12%	58%	29%	1%	0%
EBMUD	4%	50%	45%	1%	0%
FSSD	13%	61%	25%	1%	0%
CCSD	48%	44%	6%	1%	0%

Sample Collection and Analysis, 2014

Influent and effluent fipronil samples were 24-hr composites collected by the respective WWTP in fall 2014. Composites were transferred to 1 L amber glass containers. Neither disinfectant nor preservative (Kathon CG/ICP) was added to the samples. Samples were refrigerated below 4^{o} C and shipped overnight to the California Department of Fish and Wildlife's Water Pollution Control Laboratory (WPCL; Rancho Cordova, CA, USA) within 7 days of collection.

The WWTP influent and effluent samples were analyzed for fipronil, fipronil desulfinyl, fipronil sulfide, fipronil sulfone, fipronil amide, and fipronil desulfinyl amide using WPCL Method LC-007. A 500 mL aliquot was pre-filtered using Whatman #5 filter paper, 2.5 µm particle retention. The aliquot was then passed then through a pre-conditioned solid phase extraction cartridge (6 cc Waters Oasis HLB cartridge). The sample was eluted with methanol and 0.1% formic acid, evaporated under nitrogen, and brought up to a final volume of 2 mL with methanol. The extract was then filtered into a vial using a 13mm syringe filter with 0.45 µm PTFE membrane. The analysis was performed on an Agilent 1200 series LC system with a G6410A QQQ Mass Spectrometer with electrospray ionization in negative polarity. A Phenomenex, Kinetex XB-C18, 2.1 x 100 mm, 2.6 µm column was used.

This method has limitations compared to that used for samples collected in 2015 and discussed in the main text, including the lack of isotopically labeled standards. Recoveries determined on matrix spikes were within 35% of expected values, with the exception of fipronil desulfinyl amide (56%). Recoveries determined on blank spikes were within 20% of expected

values. However, field replicates, especially for influent, varied as much as two-fold, suggesting these measurements are semi-quantitative. The method detection limit (MDL) was 0.5 ng/L for all analytes. Two of the six analytes, fipronil amide and fipronil desulfinyl amide, were not detected in samples from all eight WWTPs.

Table S6. Detected concentrations (ng/L) of fipronil and its degradates in influent and effluent samples obtained from 8 wastewater treatment plants in northern California in 2014. Fipronil amide and fipronil desulfinyl amide were not detected above the method detection limit (0.05 ng/L). See *Sample Collection and Analysis, 2014*, below, for further information.

	Fipronil		sulfone		sulfide		desulfinyl	
WWTP	inf	eff	inf	eff	inf	eff	inf	eff
SFTP	10	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
PARP	70	50	8	3	<0.5	<0.5	<0.5	<0.5
SJSC	125	107	8	5	2	1	<0.5	<0.5
SLWP	111	50	8	10	<0.5	3	<0.5	<0.5
SMWP	45	98	5	9	1.9	3	<0.5	1.7
EBMUD	56	75	12	6	3.5	<0.5	5.5	2
FSSD	71	40	12	7	2	2	<0.5	8
CCSD	146	93	16	11	3	3	3	14

Table S7. Detected concentrations of imidacloprid in influent and effluent samples obtained from 8 wastewater treatment plants in northern California in 2015.

WWTP	Imidacloprid, ng/L	
	influent	effluent
SFTP	58.1	177.6
PARP	109.4	100.1
SJSC	206.9	264.9
SLWP	261.4	219.9
SMWP	171.8	150.8
EBMUD	306.1	305.2
FSSD	110.5	83.8
CCSD	149.5	127.4

Table S8. WWTP service area drinking water suppliers and their water supply characteristics.

WWTP	WWTP Service Area Drinking Water Supplier(s)	Are there agricultural, urban runoff or wastewater influences on water supply?
SFTP	San Francisco Public Utilities Commission (SFPUC)	No. SFTP and SMWP receive water from a pipeline coming from the Hetch Hetchy Reservoir and Alameda County watersheds. The SFPUC water supply is free of wastewater discharges and virtually unaffected by urban or agricultural runoff.[1]
SMWP	SFPUC	
SLWP	East Bay Municipal Utilities District (EBMUD)	Very Limited. Typically supplied almost entirely by sources with little or no urban or agricultural use in the watershed. However, during summer 2015, a limited amount of water was sourced from the Sacramento River at Freeport,[2] which is influenced by upstream agricultural and urban runoff as well as wastewater discharges.[3] USGS monitored the Sacramento River twice monthly for two years near the intake and only detected fipronil and imidacloprid during a single large winter storm event, with RLs of 4.9 ng/L (imidacloprid) and 2.9 ng/L (fipronil), 1.8 (fipronil sulfide), 3.5 (fipronil sulfone), 1.6 ng/L (desulfinyl fipronil).[4]
EBMUD	EBMUD	
PARP	SFPUC (≈75%), Santa Clara Valley Water District (SCVWD) (<20%); local groundwater (<10%)	Very Limited. Non-SFPUC water supplies may show limited influence of agricultural and urban runoff and wastewater.
SJSC	SFPUC, SCVWD, local groundwater, San Jose Water Company reservoir	Very Limited. Non-SFPUC water supplies may show limited influence of agricultural and urban runoff and wastewater.
FSSD	Solano Water Project (Lake Berryessa), State Water Project/North Bay Aqueduct; local groundwater (limited use)	Yes. Lake Berryessa has very limited urban or agricultural activity in its watershed. The State Water Project / North Bay Aqueduct water supply is the San Joaquin / Sacramento River Delta, which is influenced by upstream agricultural and urban runoff and wastewater discharges.[5]
CCSD	EBMUD (>50%), Contra Costa Water District (CCWD)	Yes. The CCWD water supply is the San Joaquin/Sacramento River Delta, which is influenced

		by upstream agricultural and urban runoff and wastewater discharges.[5]

[1] San Francisco Public Utilities Commission (SFPUC) 2008. *San Francisco Water Quality Protection Plan*.
[2] EBMUD Water Operations Department (2015). Water Supply Briefing. May.
[3] Starr Consulting (2015). Sacramento River Watershed Sanitary Survey 2015 Update Report. December.
[4] Orlando, J.L., McWayne, Megan, Sanders, Corey, and Hladik, Michelle, 2014, Dissolved pesticide concentrations entering the Sacramento–San Joaquin Delta from the Sacramento and San Joaquin Rivers, California, 2012–13: U.S. Geological Survey Data Series 876, 28 p., *http://dx.doi.org/10.3133/ds876*.
[5] CALFED Bay-Delta Program (2005). Delta Region Drinking Water Quality Management Plan. June.

Table S9. *Chironomus dilutus* - hazard quotient (HQ) of the influent and effluent aqueous wastewater streams. HQ calculation does not consider degradates amide and desulfinyl.

$$HQ_{Stream} = \frac{C_{fipronil}}{33} + \frac{C_{sulfone}}{8} + \frac{C_{sulfide}}{10}$$

WWTP	HQ *effluent* / HQ *influent*
SFTP	1.8
PARP	1.0
SJSC	1.6
SLWP	1.5
SMWP	1.1
EBMUD	1.2
FSSD	1.2
CCSD	0.8

Kathon CG/ICP

In this study 600 mg/L of Kathon CG/ICP (purchased from Sigma-Aldrich Corp., St. Louis, MO, USA) preservative was added to wastewater to disinfect the samples. During method development, potential for interference of Kathon CG/ICP with detection was tested in deionized water, synthetic wastewater (made of peat moss) and wastewater. Results showed that Kathon CG/ICP did not interfere with the LC-MS/MS and GC-MS/MS measurement of insecticides.

Comparison of Gel Product Fipronil Content to Influent Load

The highest concentration (0.05%) fipronil crack and crevice gel products was identified from the California Department of Pesticide Regulation database of registered pesticide products [1]. This product is packaged in "professional-sized" 33 g applicator units that, at 0.05% fipronil by weight, each contain 0.0165 g fipronil. At the seven community-serving WWTPs, daily influent fipronil loads measured were 0.7 g (SLWP) to 19.9 g (SJSC) fipronil, the equivalent of the fipronil content of 40 to 1,200 tubes of this gel product.

Estimated Influent Load per Fipronil-Treated Dog

Per capita dog ownership was estimated to be 0.24 dog / person on the basis of the July 1 2015 US population of 321 million [2] and total US dog ownership of 77.8 million [3]. An estimated 75% of pet owners use flea/tick treatment products [4]. Fipronil's market share among these products was roughly estimated at 30% based on product registration data [1], a retail shelf survey [5] and interviews of northern California dog owners. On this basis, an estimated 22% of all dogs receive fipronil treatments, which translates to 0.055 fipronil-treated dogs / person. The median daily per capita fipronil influent load (17 μg/person*day) divided by 0.055 fipronil-treated dogs / person generates an estimated daily fipronil load for per fipronil-treated dog of 300 μg.

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1. CDPR (California Department of Pesticide Regulation) 2016. California Product/Label Database Queries & Lists.
2. US Census Bureau. 2016. American Fact Finder. Monthly Population Estimates for the United States: April 1, 2010 to December 1, 2016. July 1 2015 Population Estimate, US resident population.
3. American Pet Products Association (APPA). 2015. 2015-2016 APPA National Pet Owners Survey. 660 p.
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5. Vander Werf R, Aldana A, Teerlink J, Budd, R. 2015. Retail Store Survey of Consumer-Use Indoor Pesticide Products, 2014.

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Mass Balance Assessment for Six Neonicotinoid Insecticides During Conventional Wastewater and Wetland Treatment: Nationwide Reconnaissance in United States Wastewater

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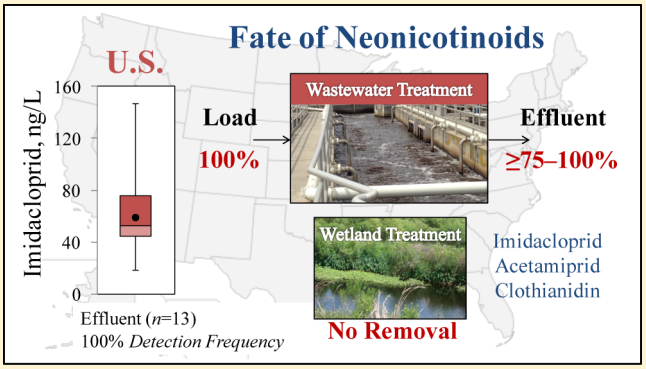
Supporting Information

ABSTRACT: Occurrence and removal of six high-production high-volume neonicotinoids was investigated in 13 conventional wastewater treatment plants (WWTPs) and one engineered wetland. Flow-weighted daily composites were analyzed by isotope dilution liquid chromatography tandem mass spectrometry, revealing the occurrence of imidacloprid, acetamiprid, and clothianidin at ng/L concentrations in WWTP influent (60.5 ± 40.0; 2.9 ± 1.9; 149.7 ± 289.5, respectively) and effluent (58.5 ± 29.1; 2.3 ± 1.4; 70.2 ± 121.8, respectively). A mass balance showed insignificant removal of imidacloprid (p = 0.09, CI = 95%) and limited removal of the sum of acetamiprid and its degradate, acetamiprid-N-desmethyl (18 ± 4%, p = 0.01, CI = 95%). Clothianidin was found only intermittently, whereas thiamethoxam, thiacloprid, and dinotefuran were never detected. In the wetland, no removal of imidacloprid or acetamiprid was observed. Extrapolation of data from 13 WWTPs to the nation as a whole suggests annual discharges on the order of 1000−3400 kg/y of imidacloprid contained in treated effluent to surface waters nationwide. This first mass balance and first United States nationwide wastewater reconnaissance identified imidacloprid, acetamiprid, and clothianidin as recalcitrant sewage constituents that persist through wastewater treatment to enter water bodies at significant loadings, potentially harmful to sensitive aquatic invertebrates.



INTRODUCTION

Neonicotinoids are the world's most widely used insecticides, with global production valued at US$2.5 billion and registrations in more than 120 countries for commercial use on more than 140 crops.[1] These insecticides are used for control of aphids, whiteflies, planthoppers, lepidoptera, and some coleopteran and other pests, where they function as powerful neurotoxins.[1−3]

In December, 2013, the European Commission introduced a two year moratorium on clothianidin, imidacloprid, and thiamethoxam, following reports by the European Food Safety Authority (EFSA) of these substances posing an "acute risk" to honeybees essential to farming and natural ecosystem.[4] Temporal and expired restrictions allow for potential current and future uses of neonicotinoids in these settings. Adverse effects from widespread use of neonicotinoids have been reported recently for many nontarget organisms like phloem-feeding insects,[5] pollinators and bees,[6] and aquatic invertebrates.[7] Median lethal dose values (LD_{50}) of neonicotinoids for bees vary from 5 to 70 ng/bee.[8] Sublethal doses have been shown to cause ATP synthesis inhibition,[9] resulting in weakening of foraging success, memory and learning, damage to the central nervous system,[6] and increased susceptibility to diseases.[10] A recent review based on 214 toxicity tests of 48 species suggested that average individual environmental concentrations of greater than 35 ng/L may severely affect sensitive aquatic invertebrates populations.[7] Another study indicated that aquatic macrofauna populations dropped sharply at concentrations between 13 and 67 ng/L.[11] Insectivorous birds are also susceptible to exposure through the food chain.[12] A study in The Netherlands observed a decline in the insectivorous bird population after the introduction of imidacloprid, the highest production volume insecticide in the world; imidacloprid concentrations of greater than 20 ng/L correlated with 3.5% average annual declines in bird populations.[13] Imidacloprid is moderately toxic to fish communities;[14] oxidative stress and DNA damage have been reported in zebrafish.[15] Furthermore, co-occurrence of multiple neonicotinoids is known to impart synergistic toxic effects.[16]

During the past decades global contamination with neonicotinoids has been observed in surface waters, many of which receiving treated effluent from wastewater treatment plants. In a nationwide assessment of United States streams, at least one neonicotinoid was detected in 53% of the samples analyzed (n = 38).[17] In California, imidacloprid was detected in 89%

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of surface water samples collected from agricultural regions (n = 75) in which 19% of the samples exceeded concentrations of 1.05 μg/L, the chronic invertebrate Aquatic Life Benchmark value established by the United States Environmental Protection Agency (USEPA).[18] In Canadian wetlands of the central-eastern region of Saskatchewan, neonicotinoids were detected frequently in 2012−2013 (48%; n = 440) at a total average concentration of 51.8 ng/L, with higher detection frequencies being observed in spring and higher mean concentrations in summer.[19] In several rivers around Sydney, Australia, the average total neonicotinoid concentration was 118 ng/L; imidacloprid was the most common neonicotinoid, detected in 93% of samples (n = 15).[20] Clothianidin was detected with a detection frequency of 46.6% in groundwater and surface water samples (n = 58) collected in Germany.[21]

Wastewater constitutes a potential source of neonicotinoids in the environment that has not received much attention yet. Neonicotinoids are widely used in nonindustrial agricultural applications such as pet flea treatment, horticulture, and household pest control products. Thus, these usages may contribute to neonicotinoid loadings detectable in sewage. A few studies have detected imidacloprid in wastewater, showing that treated effluent can inadvertently contribute to neonicotinoid discharge into receiving water bodies. Indeed, a nationwide assessment of United States streams showed a positive correlation between neonicotinoid occurrence and urban land usage but not with agricultural use.[17] In Oregon, effluent samples from 52 wastewater treatment plants (WWTPs) analyzed for imidacloprid showed detections in 9.8% samples (n = 102), with an average concentration of 270 ng/L.[22] In Spain, imidacloprid was detected in wastewater influent and effluent samples at concentrations ranging from 1.4−165.7 ng/L (59.4%; n = 32).[23] In another related Spanish study, imidacloprid was detected in river water receiving WWTP effluent at a maximum concentration of 19.2 ng/L, identifying sewage treatment facilities as a source of neonicotinoids in the environment.[24] In Beijing, China, imidacloprid was detected in WWTP influent and effluent at concentrations of 45−100 and 45−106 ng/L, respectively, with no further information being provided on the removal rate.[25]

With wastewater representing a likely source of neonicotinoids in the United States aquatic freshwater environment, the goal of the present study was to conduct a first mass balance assessing the fate of six neonicotinoids (listed in order of decreasing global annual turnover: imidacloprid, thiamethoxam, clothianidin, acetamiprid, thiacloprid, and dinotefuran[1]) during conventional wastewater treatment and wetland treatment and to obtain through a nationwide reconnaissance a first national emission estimate by monitoring additional treatment facilities from across the United States.

MATERIALS AND METHODS

Chemicals and Reagents. Organic solvent of high performance liquid chromatography (HPLC) grade and formic acid of American Chemical Society (ACS) grade (98%) were purchased from Sigma-Aldrich Corp., St. Louis, MO, U.S.A. Ultrapure LC-MS grade water was purchased from Thermo Fisher Scientific, Waltham, MA, U.S.A. Analytical standards for six neonicotinoids, an acetamiprid degradate, and deuterated labeled standards for imidacloprid (imidacloprid-d_4), acetamiprid (acetamiprid-d_3), and clothianidin (clothianidin-d_3) were obtained from Sigma-Aldrich Corp., St. Louis, MO, U.S.A. (CAS numbers provided in Table S1). Stock solutions of analytical standards (1 ppb to 10 ppm) and their mixtures were prepared in acetonitrile and stored at −20 °C.

Sample Collection. Sampling for this mass balance assessment was conducted at two levels. One plant and wetland were studied in great detail to obtain general information on the fate of neonicotinoids, and then additional plants were sampled to see whether the information obtained is more broadly applicable to treatment facilities in the United States. In early December 2014 for a period of five consecutive days (Thursday through Monday), a large activated sludge sewage treatment plant with an engineered wetland downstream was sampled extensively. The plant is located in the southwestern region of the United States and designed to serve a population of up to 2.5 million with design capacity of 870 million L/d (MLD), receiving sewage comprised of 94% domestic wastewater and 6% industrial wastewater. The treatment facility produces Class B+ reclaimed water discharged into a river and Class B sludge used for land application. The highest-flow treatment train was selected for detailed studies on plant performance. Unit processes performed at the WWTP include screening, grit removal, primary sedimentation, activated sludge biological treatment, secondary clarification, disinfection treatment by chlorination, thickening of primary sludge, waste-activated sludge by centrifugation, anaerobic sludge digestion, and dewatering of digested sludge by centrifugation. Primary sludge and waste activated sludge are digested at 35 °C, with an average solids retention time of 21 days. Effluents from a total of five parallel treatment trains are combined, and a portion of this total flow is directed into an engineered wetland located immediately downstream and featuring a hydraulic retention time (HRT) of about 4.7 days, an average water depth of about 1.5 m, total suspended solids (TSS) concentrations in wetland influent and effluent of 10−15 mg/L, and average wastewater flow received and discharged around 280 and 250 MLD, respectively. Average values of carbonaceous biochemical oxygen demand (cBOD) for plant influent and wetland effluent were 288 ± 23 and 7 ± 1 mg/L, respectively, demonstrating cBOD removal of approximately 98%. Average TSS values in plant influent and wetland effluent were 437 ± 160 and 14 ± 3 mg/L, respectively, achieving TSS removal of 96 ± 1%.

The treatment train selected for sampling received wastewater at a flow rate averaging 230 MLD. Seven portable automated samplers (6712 full-size portable sampler, Teledyne Isco, Lincoln, NE, U.S.A.) were programmed based on three-week average hourly daily flow rate data to collect 2.5 L of flow-weighted composite samples of primary influent, primary effluent, secondary effluent, waste activated sludge, disinfection basin effluent, wetland influent, and wetland effluent over a period of 24 h for 5 consecutive days. Detailed information on the sample programming and flow diagram of WWTP (Figure S1) is provided in the Supporting Information (SI). Samples were collected in precleaned (acetone washed and heated at 500 °C for 5 h) amber 2.5 L wide-mouth glass bottles. Grab samples of primary sludge and dewatered sludge were collected in precleaned amber 1 L glass bottles and amber 40 mL volatile organic analysis (VOA) glass vials, respectively.

After collection, samples were placed into coolers and shipped to the laboratory, where 600 mg/L of Kathon CG-ICP preservative and 80−100 mg/L of sodium thiosulfate were added to disinfect and dechlorinate the samples and to prevent biological and chemical degradation of analytes to take place during storage (see SI for additional information). Then, 500 mL of aliquots of water were fortified with 200 ng of the deuterated surrogate standards to account for losses during storage, extraction, and analysis. Solid samples were dried and fortified with labeled standards to a nominal concentration

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of 400 ng/g (dry weight solids). All samples were stored at 4 °C prior to processing.

For the expanded nationwide reconnaissance, 12 additional United States WWTPs voluntarily collected 24 h flow-adjusted samples that were provided to the study team in the year of 2015 as a composited sample. The WWTPs, who requested anonymity as a prerequisite of study participation, are located in different regions of the country as described in the Discussion section. Typically, only one composite each was provided of raw influent and treated effluent collected simultaneously on a random workday. Four facilities provided effluent only; three facilities performed tertiary treatment by filtration, three facilities performed UV disinfection instead of chlorination; all other facilities performed conventional treatment (secondary treatment followed by chlorine disinfection). Samples were stored at −20 °C prior to processing.

Sample Preparation and Analysis. *Extraction of Water Samples.* An automatic solid-phase extraction instrument (Dionex AutoTrace 280, Thermo Scientific, Waltham, MA, U.S.A.) was used to concentrate and elute analytes from water samples from the sorbent bed for analysis. Following screening of extraction efficiency of a combination of sorbents and sample volumes, reverse phase functionalized polymeric styrene divinylbenzene sorbent (Strata X and XL, 500 mg/3 mL, Phenomenex, Torrance, CA, U.S.A.) was selected and loaded with 500 mL of wastewater sample. Before loading, cartridges were conditioned with 3 mL of methanol, followed by 3 mL of water. Then, 500 mL of wastewater samples spiked with 200 ng of the deuterated surrogate standards were loaded onto the cartridges at a flow rate of 2 mL/min, washed with water, and dried with nitrogen gas for 5 min. Two consecutive elutions were performed, each with 4 mL of a mixture (95:5, v/v) of methanol and formic acid. Equal volumes of serial eluates were combined, evaporated, and reconstituted to half the volume of water and methanol solution (80:20, v/v) in 0.1% formic acid for LC-MS analysis. Waste activated sludge and primary sludge samples featuring a TSS content of approximately 2% and 6%, respectively were spun in a centrifuge at 7500*g* for 10 min. Resultant supernatants were extracted as described above for water samples, whereas the solids separated from the samples were extracted separately as described below.

Extraction of Solid Samples. Solid samples were dried under nitrogen using an evaporator (Reacti-Therm TS-18821, Thermo Scientific, Waltham, MA, U.S.A.). One gram aliquots of solids samples (dry weight) spiked with 400 ng of the deuterated surrogate standards were transferred into 40 mL VOA vials, extracted with 10 mL acetone, placed on a shaker for 24 h, and sonicated for 1 h. Extracts were spun in a centrifuge at 3000*g* for 5 min, and the supernatants were transferred into new vials. The solids were extracted a second time with acetone, vortexed for a minute, and centrifuged, and the supernatants were combined with the first extracts. After two extractions in sequence, the resultant acetone extracts were dried under a stream of nitrogen, and analytes were reconstituted in 6 mL of hexane, following which the resultant extract was cleaned up by solid phase extraction (similar to USEPA Method 3620C) with a sorbent bed featuring a blend of magnesium oxide and silica gel (Sep-Pak Vac Florisil Cartridge 6 cc containing 1 g of sorbent, Waters Corporation, Milford, MA, U.S.A.). Before loading, the sorbent was conditioned successively with 6 mL of dichloromethane (DCM), 6 mL of acetone, and 6 mL of hexane. Extracts in hexane were loaded onto the cartridges, the resin bed washed with 6 mL of hexane, and analytes eluted subsequently with 4 mL of DCM and 4 mL of acetone. Aliquots of 1 mL of each serial extract (acetone and DCM) were transferred and combined into 2 mL LC analysis vials, dried under a gentle stream of nitrogen, and reconstituted with 1 mL of a solution of water, methanol, and formic acid (80/20/0.1, v/v/v) for analysis.

Liquid Chromatography Separation and Tandem Mass Spectrometry Analysis. Separation was carried out using a Shimadzu Ultra Performance Liquid Chromatography (UPLC) system, equipped with the SIL-20AC autosampler and 20-AD solvent delivery system (Shimadzu Scientific Instruments, Inc., Columbia, MD, U.S.A.). Simultaneous chromatographic separation of the six neonicotinoids plus one degradate was performed by reverse phase liquid chromatography using a 4.6 mm × 150 mm C_8 column (XBridge, Waters Corporation Milford, MA, U.S.A.) with 3.5 μm bridged ethylene hybrid (BEH) particles. A binary gradient with 0.1% formic acid in water and methanol at a total flow rate of 0.5 mL/min was applied. The injection volume was 100 μL, and the mobile phase consisted of 20% organic with an initial 1 min ramp of 10% solvent content increased per min, followed by a 6 min ramp of 10.8% per min to 95% organic, where it was held for 3.5 min, for a total run time of 14 min. Identification and quantitation were performed using an API 4000 tandem mass spectrometer (ABSciex, Framingham, MA, U.S.A.) in positive electrospray (ESI+) mode by monitoring the first and second most abundant ion transitions for quantification and confirmation, respectively. Mass spectrometry was performed at a source heating temperature of 700 °C, ion spray voltage of 4500 V, curtain gas (nitrogen) pressure of 50 psi, nebulizer gas pressure of 90 psi, heater gas pressure of 75 psi, and dwell time of 70 ms. Analyst software, version 1.5 (ABSciex, Framingham, MA, U.S.A.) was used for LC-MS/MS system control and data analysis. Information on calibration curves, method validation, quality assurance, and quality control can be found in the SI.

Mass Balance Calculations. An analyte mass balance was performed for the full-scale wastewater treatment train over a period of 5 consecutive days (to account for the hydraulic residence time), combining primary, activated sludge, and disinfection treatment, using the following equation:

$$\dot{m}_{\text{transformed}} = \sum Q_{\text{inf}} \times C_{\text{inf}} - \sum Q_{\text{eff}} \times C_{\text{eff}} - \sum M_{\text{DWS}} \times C_{\text{DWS}} \quad (1)$$

where, $\dot{m}_{\text{transformed}}$ = mass input of neonicotinoids lost to transformation or unaccounted for (g/day), Q_{inf} = flow rate of influent to primary clarifier (L/day), C_{inf} = concentration of neonicotinoids in influent entering primary clarifier (g/L), Q_{eff} = flow rate of effluent after chlorine disinfection (L/day), C_{eff} = concentration of neonicotinoids in effluent leaving treatment plant (g/L), M_{DWS} = mass of dewatered sludge produced (kg/day), and C_{DWS} = concentration of neonicotinoids in dewatered sludge (g/kg).

Individual mass balance for primary treatment, activated sludge treatment, disinfection treatment, and constructed wetland were calculated similarly (see SI). A paired two tailed *t*-test was performed ($\alpha = 0.05$) to compare mean daily masses between treatment streams. Differences were determined at the $p < 0.05$ significance level.

Determination of Sludge Water Partitioning Coefficient (Distribution Coefficient, K_D). To determine the sorption affinity of analytes onto sludge particulates, a partitioning study was conducted.[26] Ten milliliters of aliquots of water having 1, 10, and 100 ppm of all six neonicotinoids was

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added to 1 g of dewatered sludge, and after 10 days of shaking in the dark at 22 °C, water and solids were analyzed to establish the partitioning behavior. Sludge was inactivated prior to shaking by addition of 600 mg Kathon CG/ICP and 300 mg of sodium azide to prevent any possible biotransformation. To determine K_D values, the sorbed concentration was plotted against bulk concentration remaining after sorption, and eq 2 was used:

$$K_D = \frac{C_S}{C_D} \quad (2)$$

where K_D = distribution coefficient, L/kg dry weight; C_S = sorbed concentration on the solid particulates, mg/kg dry weight of dewatered solids; C_D = bulk concentration remaining after sorption, mg/L.

RESULTS AND DISCUSSION

Method Performance. The tandem mass spectrometry method developed for this study targeted six neonicotinoids and one degradate simultaneously at part-per-trillion levels by monitoring two ion transitions via multiple reaction monitoring (MRM). Mass spectrometry parameters optimized for detection are summarized in Table S2 of the SI.

Limits of detection of analytes in different matrices are shown in Table 1 (see SI for information on data analysis and reporting methods). To ensure the quality and validity of results, each analysis batch of environmental samples contained a field blank, method blank, and check samples. No false positive values suggesting postsample collection contamination were detected during the analysis of all samples. Values of relative percent deviation (RPD) were in an acceptable range for imidacloprid (25 ± 17%), acetamiprid (20 ± 17%), acetamiprid-*N*-desmethyl (28 ± 22%), and clothianidin (18 ± 22%), as summarized in Table S3.

Occurrence and Fate of Neonicotinoids in the Wastewater Treatment Process. Over the sampling period of 5 consecutive days (Thursday through Monday) with 3 workweek days and 2 weekend days, consistent loading with imidacloprid (45−55 ng/L; 100% DF) and acetamiprid (3−5 ng/L; 100% DF), and erratic loading of clothianidin (<1−666 ng/L; 80% DF) was observed (Table 1). Also detected was acetamiprid-*N*-desmethyl (1−2 ng/L; 100% DF), a degradate of acetamiprid formed here as a result of activated sludge treatment. Neonicotinoids not detected in process streams included thiacloprid, thiamethoxam, and dinotefuran, with their corresponding method detection limits summarized in Table 1.

Mass Balance of Neonicotinoids in Aqueous WWTP Process Flows. During the 5 day sampling period, the average concentrations (mean ± standard deviation) of imidacloprid, acetamiprid, and clothianidin detected in plant influent were 54.7 ± 9.3, 3.7 ± 0.8, and 149.7 ± 273.1 ng/L, respectively. These neonicotinoids entered the primary clarifier in which settling occurred, diverting 1% of the total volumetric flow away as sludge featuring a TSS content 17 times higher than that of the clarifier effluent. Resultant daily composite effluent samples of primary treatment contained similar levels to those found in raw sewage (influent) during the 5 day sampling period. Secondary treatment consisted of an activated sludge unit operation, a biological process aimed at breaking down organic compounds primarily by microbial degradation. Average concentrations of imidacloprid and clothianidin in secondary effluent were 48.6 ± 7.8 and 131.3 ± 170.8 ng/L, implying no discernible removal by processes including microbial degradation,

Table 1. Partitioning Properties, Method Detection Limits, and Detected Concentrations (mean ± SD) of Neonicotinoids in Wastewater Treatment and Wetland Streams

	partitioning properties		method detection limit (MDL)								detected concentration, ng/L						
			wastewater				biosolids				WWTP[a] process streams				wetland		
compound	log K_{OW}	log K_D	MDL, ng/L	LOQ, ng/L	absolute recovery, %	relative recovery, %	MDL, ng/g dw	LOQ, ng/g dw	absolute recovery, %	relative recovery, %	influent	primary effluent	secondary effluent	disinfection effluent	influent	effluent
imidacloprid	0.57	1.20	0.6	1.8	82 ± 20	116 ± 10	1.1	3.3	86 ± 12	111 ± 19	54.7 ± 9.3	58.4 ± 12.6[b]	48.6 ± 7.8	48.6 ± 8.4	48.2 ± 4.8	41.5 ± 11.5
clothianidin	0.91	1.20	0.9	2.7	90 ± 16	105 ± 10	1.4	4.2	95 ± 15	110 ± 8	149.7 ± 273.1[c]	163.8 ± 195.9[c]	131.3 ± 170.8[c]	116.7 ± 144.9[c]	124.8 ± 121.8	69.3 ± 53.9
Acetamiprid (A)	0.80	1.32	0.1	0.3	82 ± 3	95 ± 5	0.7	2.1	60 ± 3	97 ± 11	3.7 ± 0.8	3.4 ± 0.6	1.8 ± 0.4	1.7 ± 0.5	2.1 ± 0.5	2.0 ± 0.2
A-*N*-desmethyl	0.65	–	0.6	1.8	87 ± 9	N/A	1.9	5.7	88 ± 9	N/A	BDL	BDL	1.3 ± 0.3	1.3 ± 0.4	1.4 ± 0.3	1.6 ± 0.3
thiamethoxam	−0.13	0.37	0.3	0.9	99 ± 5	N/A	4.4	13.2	87 ± 12	N/A	BDL	BDL	BDL	BDL	BDL	BDL
thiadoprid	1.26	1.45	0.1	0.3	65 ± 4	N/A	1.6	4.8	69 ± 9	N/A	BDL	BDL	BDL	BDL	BDL	BDL
dinotefuran	−0.55	0.34	32.6	97.8	31 ± 3	N/A	86.5	259.5	34 ± 5	N/A	BDL	BDL	BDL	BDL	BDL	BDL

[a]WWTP, wastewater treatment plant. [b]Analyzed in triplicate. [c]80% detection frequency; N/A, not applicable (as isotope-labeled surrogate standard was not available); BDL, below detection limit; dw, dry weight; K_{OW}, *n*-octanol−water partition coefficient; K_D, sludge−water partition coefficient; LOQ, limit of quantification.

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hydrolysis, and oxidation in the aeration basin. Prior lab studies also had shown insignificant transformation of imidacloprid in both acidic and neutral water.[27] However, acetamiprid undergoes relatively fast dissipation in a neutral environment having an aqueous dissipation half-life of 4.7 days,[27] and corresponding results were observed during secondary treatment, with effluent concentration of acetamiprid (1.8 ± 0.4 ng/L) cut in half compared to influent, and the formation of acetamiprid-*N*-desmethyl being observed, thereby confirming transformation of acetamiprid in the aeration basin, presumably mediated in part by aerobic microorganisms. Secondary effluent showed average daily concentrations of acetamiprid-*N*-desmethyl of 1.3 ± 0.3 ng/L. Concentrations of acetamiprid-*N*-desmethyl in primary influent and primary effluent were below the detection limit (<0.5 ng/L). To meet microbial removal criteria, the wastewater facility examined herein uses chlorination at a chlorine dosage of 2.5 mg/L. Although chlorine has the potential to oxidize organic compounds, no change in concentrations of imidacloprid, acetamiprid, acetamiprid-*N*-desmethyl, and clothianidin were observed during this disinfection treatment process.

Concentration (Table 1) data on neonicotinoids in aqueous process streams were used in conjunction with corresponding flow rate (Table S4) information to compute pesticide mass flow through the facility. On the basis of the daily average flow received by the treatment train, the total mass of analytes passing through the facility during the monitoring period was determined (Figure 1). Error values on the total mass are derived from maximum and minimum values of detected concentrations from two experimental replicates.

Mass in raw sewage of imidacloprid, acetamiprid, and clothianidin corresponded to 66.7 ± 3.0, 4.5 ± 0.4 g, and 183.0 ± 7.3 g/5 days, respectively. After primary treatment, the total mass leaving the primary clarifier in effluent was similar to those in influent (Figure 1), implying insignificant sorption of neonicotinoids onto sludge particulates, with the analytes persisting during primary treatment. The mass of imidacloprid and clothianidin leaving the secondary clarifier was 58.3 ± 6.3 and 159.6 ± 8.9 g/5 days, respectively. These data indicate persistence of both compounds during secondary treatment. The mass of acetamiprid leaving the secondary clarifier in the form of the parent compound was 2.1 ± 0.1 g/5 days, indicating a 53 ± 3% loss of acetamiprid in the aeration basin. The acetamiprid degradate, acetamiprid-*N*-desmethyl, accounted for 1.6 ± 0.2 g/5 days in effluent, which reduced the total mass removal estimate for acetamiprid and its major degradate to 18 ± 4%. Whereas relevant information on the toxicity of acetamiprid-*N*-desmethyl is unavailable, in theory this degradate could still impart toxicity to nontarget organisms via its cyano group, which is known to interact with the nAChR receptor of insects.[28,29] Similarly, a mass balance on chlorination treatment of imidacloprid, acetamiprid, acetamiprid-*N*-desmethyl, and clothianidin showed resistance of each of these compounds to oxidation under real-world conditions.

Paired *t*-tests were performed to compare the influent and effluent concentrations of the three analytes. The mean and standard deviation for imidacloprid for influent and effluent were 13.3 ± 2.4 and 11.7 ± 2.1, respectively. The mean daily influent and effluent mass loadings of imidacloprid detected over the sampling period were statistically indistinguishable (t = 1.88, p = 0.09, CI = 95%). The mean and standard deviation for acetamiprid for influent and effluent were 0.90 ± 0.21 and 0.73 ± 0.09, respectively. A mass balance over the WWTP showed total acetamiprid removal of 18 ± 4%

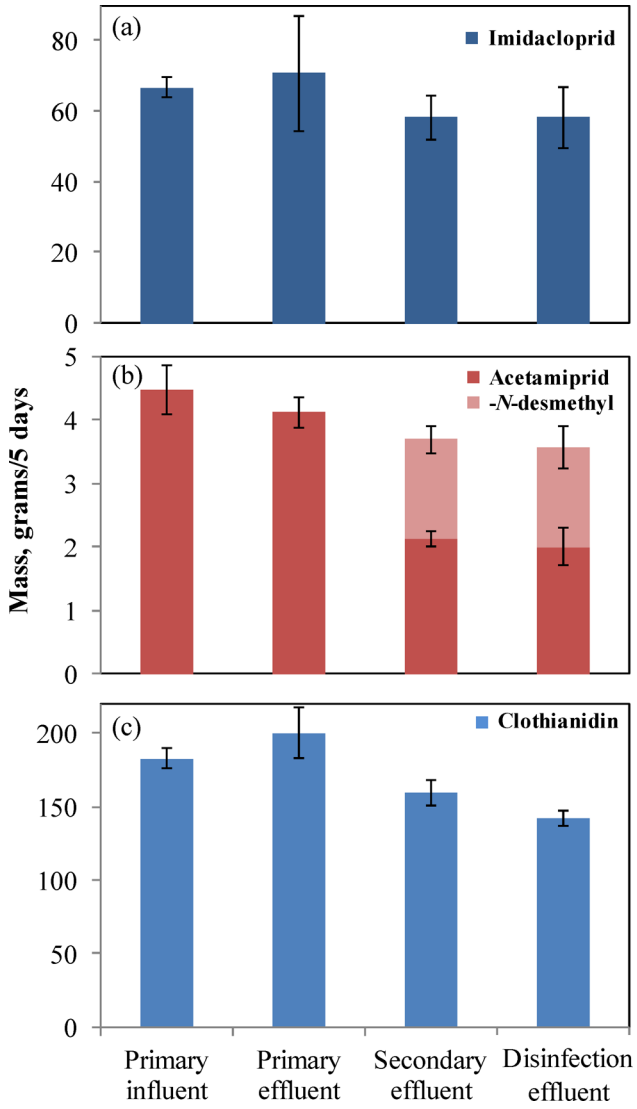

Figure 1. Total mass of imidacloprid (a), acetamiprid (b), and clothianidin (c) in wastewater unit operation flows over a 5 day period. Whiskers represent maximum and minimum values from two experimental replicates.

(t = 3.31, p = 0.01, CI = 95%), with 45 ± 4% of the initial mass being discharged as acetamiprid and 37 ± 4% as its degradate, acetamiprid-*N*-desmethyl. Strong variations in the loading of clothianidin during the sampling period stood in the way of conducting a firm mass balance; nevertheless, notable persistence (>70%) of the compound during treatment was firmly established.

Neonicotinoids in Sludges and Biosolids. As primary sludge and waste activated sludge represented 2% of the total facility flow, the mass of neonicotinoids accumulated in sludge was assessed as part of the mass balance analysis. Partitioning of neonicotinoids to wastewater solids was not a major factor for their fate during treatment, however. Levels of imidacloprid, acetamiprid, acetamiprid-*N*-desmethyl, and clothianidin were all below their respective MDLs of 1.1, 0.7, 1.9, and 1.4 μg/kg dry weight sludge. Despite these nondetect values, refined concentration estimates were obtained by analyzing the decanted liquid of sludges and using the established partition coefficients (Table 1) to calculate the approximate neonicotinoid concentrations on dry weight solids. As shown in Table S6, the

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resultant concentrations were low and inconsequential for the mass balance analysis (<1% of total mass).

Fate of Neonicotinoids in a Constructed Wetland. Availability of sunlight, an average water depth of only about 1.5 m, low TSS concentrations (10−15 mg/L), and a HRT of about 4.7 days made the constructed wetland a location of potential photolysis of neonicotinoids. Imidacloprid concentrations entering and leaving the engineered wetland after 5 days were 54.4 ± 3.4 and 49.9 ± 14.6 ng/L, respectively, with corresponding mass loading and discharge of 15.1 ± 0.9 and 11.4 ± 3.3 g/day. Though lab studies have shown that the photolysis half-life of imidacloprid in water is less than 1 day,[30] no significant removal of imidacloprid was observed. During the sampling period (5 days), average concentrations of imidacloprid entering and leaving the engineered wetland were 48.2 ± 4.8 and 41.5 ± 11.5 ng/L, respectively; the corresponding average daily mass loading and output values were 13.6 ± 1.1 and 10.2 ± 2.7 g/day. Thus, no significant removal of imidacloprid was observed in the wetland regardless of whether average concentrations or daily concentrations off set by the HRT were compared. Similar results were found for acetamiprid and acetamiprid-*N*-desmethyl (Figure S3). Notable changes in loading of clothianidin made it impossible to draw any firm conclusions about potential losses in the wetland (Table S3).

Environmental Emissions and Potential Impacts of Discharged Neonicotinoids. Considering the high toxicity of neonicotinoids to aquatic communities at low concentrations, it is necessary to consider WWTP effluent as a source of pesticides to the environment. Therefore, to better define the discharge of neonicotinoids into United States surface waters nationwide and to confirm that the observed behavior is not plant specific, composite wastewater samples were collected from 12 United States WWTPs between January and December 2015 and analyzed. The WWTPs analyzed were located in the western (n = 4), southern (n = 6), and midwestern (n = 2) regions of the United States, featuring diverse microbial communities, suspended solids, sludge age, and hydraulic retention time. Influent and effluent concentrations (Figure 2a) of neonicotinoids coincided with the conducted mass balance. Facilities 2, 5, and 12 performed tertiary treatment by filtration, and facilities 2, 6, and 12 performed UV disinfection instead of chlorination. All other facilities performed conventional treatment, i.e., secondary treatment followed by chlorine disinfection. Regardless of treatment strategy investigated, neonicotinoids persisted in each case without notable differences. The average concentrations discharged (including information on minimum, maximum, and median values in ng/L as well as detection frequency) were 62.6 ng/L (18.5, 146.4, 52.7, 100%) for imidacloprid, 1.9 ng/L (0.6, 5.7, 1.3, 67%) for acetamiprid, and 12.1 ng/L (9.9, 13.4, 12.5, 33%) for clothianidin. Thiamethoxam, thiacloprid, and dinotefuran were not detected in any of the samples examined, with MDLs of 0.3, 0.1, and 32.6 ng/L, respectively. On the basis of the detected concentration of neonicotinoids in influent and the population served by the studied treatment facilities, the total neonicotinoid annual loading in sewage is estimated to range from 3.1 to 10.7 mg/person/y, a value reflecting both known domestic and unknown agricultural insecticide uses in the respective sewersheds. Accordingly, the mass of neonicotinoids discharged into United States surface waters nationwide is estimated to be on the order of approximately 1.0−3.4 t of imidacloprid [United States population is considered 318.9 million (2014) (Source: United States Census Bureau)]. No estimates are provided for acetamiprid and clothianidin here because of low concentrations (<10 ng/L) and relatively low detection frequencies. The nationwide estimate provided here could be improved upon by future studies featuring a larger number of seasonal samples taken at a greater number of plants.

The international regulatory framework for neonicotinoids is still immature. In the United States, there currently are no binding regulations in place for neonicotinoid residues in treated wastewater. The Dutch government has established maximum permissible risk threshold levels for ecosystems ranging from 8 to 13 ng/L,[7] and other published ecological reference values[7,11,31−34] for aquatic invertebrates are about 30−40 ng/L. The imidacloprid concentrations in discharged treated wastewater established in this study (18.5−146.4 ng/L) exceed the above-mentioned thresholds (Figure 2b). Risk posed by wastewater-borne neonicotinoids will be most pervasive in situations where the discharge receiving stream is effluent-dominated, as is the case in the southern locations examined here. Fate of discharged neonicotinoids will be influenced by vegetation downstream, water depth, and pH, among other factors.[35] In this study, the fate of the discharged neonicotinoids was traced with a comprehensive sampling campaign at one WWTP only, and significant persistence was observed. Whether WWTP effluent-borne neonicotinoids pose related threats to

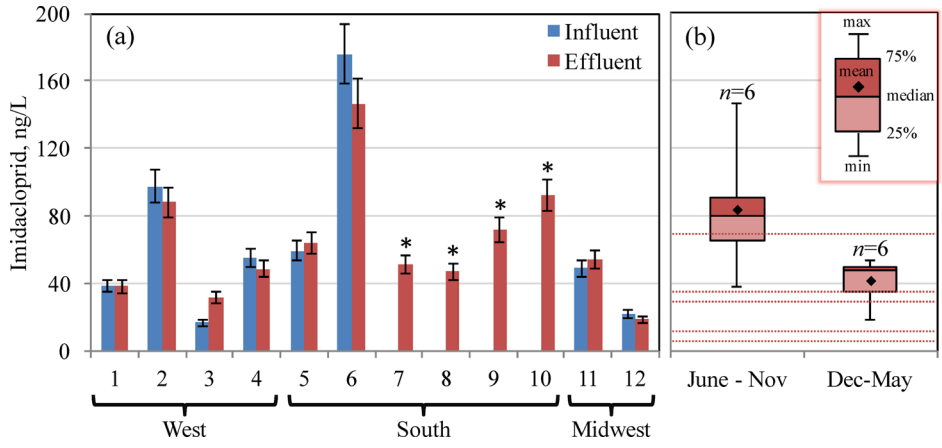

Figure 2. Imidacloprid concentrations detected in 12 United States wastewater treatment plants (a); for WWTPs 7−10 (∗), only effluent was analyzed. Also shown is a comparison of published ecological toxicity benchmark values for chronic and acute exposure (red dotted lines) with discharged effluent concentration of imidacloprid at different times of year (b). Appropriate in-stream dilution factors for receiving surface water bodies need to be considered for risk assessment and may be as small as unity in effluent-dominated streams.

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plants and wildlife in wetlands and aquatic ecosystems downstream of WWTP discharge locations is currently unknown and deserves further study. Aside from posing direct toxicity to aquatic species, these systemic pesticides also can be taken up by plants and circulated throughout the plant tissues;[5] this represents a potential pathway for exposure of pollinator species and other susceptible, nontarget organisms upon accumulation of insecticide mass in pollen and nectar.[36] During this one time sampling event at each facility, it was observed that relatively higher concentrations were discharged in the period of June to November when compared to the December to May time frame; however, regional time series analysis is required to confirm and elucidate this phenomenon.

Consistent loading of imidacloprid (influent concentration of 54.7 ± 9.3 ng/L) during sampling for 5 consecutive days (not coinciding with seasonal pesticide applications in the region) and 100% detection frequency at various locations throughout the year suggest that nonagricultural neonicotinoid uses also should be considered as contributors. Neonicotinoids have been detected in urine samples of Japanese adults and children without occupational spraying histories, suggesting exposure from daily lives and consumables.[37−39] In recent years, nonagricultural applications of neonicotinoids have expanded. Some of the best selling canine and feline flea control products in United States contain around 10% imidacloprid as an active ingredient. Termicide products often contain up to 25% acetamiprid. Neonicotinoids also are being used in household sectors as fly bait, roach bait, and ant bait, and to eradicate bed bugs. These uses could potentially contribute to the loadings in sewage observed here. However, lack of inventory and application rate for such nonagricultural usage of these active ingredients is a major knowledge gap to study their contribution, transport, and impact on nontarget organisms.[40]

In summary, the present work adds much needed data to the occurrences and fates of neonicotinoid pesticides in the built water environment. Imidacloprid, thiamethoxam, clothianidin, and acetamiprid are frequently detected neonicotinoids in global surface waters.[7,17−21,41−43] According to a recent study, 74% of global surface waters exhibited concentrations of individual neonicotinoids exceeding 35 ng/L (n = 17).[7] Yet, the role of real-world, conventional pollution control infrastructure in attenuating sewage-borne neonicotinoids was until now ill defined.

This study adds to the present state of knowledge by furnishing the first mass balance for three neonicotinoids—namely, imidacloprid, acetamiprid and clothianidin—in a full-scale, conventional wastewater treatment plant and constructed wetland in the United States, using previously established methods to obtain reliable data.[44,45] Adding to prior fate studies including a recent nationwide assessment of neonicotinoids in United States streams,[46,17] we here provide the first nationwide reconnaissance on the occurrence and fate of neonicotinoid insecticides during wastewater treatment. Acetamiprid-*N*-desmethyl was identified as a major degradate formed during activated sludge treatment. The present work establishes the presence of neonicotinoids in urban sewersheds, demonstrates significant recalcitrance of these compounds during conventional and advanced wastewater treatment, and indicates risk to the effluent-dominated ecosystems. An order-of-magnitude estimate of the discharge load to surface waters in the United States indicates that successful management of risks posed by neonicotinoid compounds will have to take sewage sources into consideration, even for urban, nonagricultural geographical settings.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b01032.

Information as mentioned in the text. (PDF)

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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

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

Introduction

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

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

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

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

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

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

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

Regulatory Framework Relevant to Urban and Consumer Pesticide Applications

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

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

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

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

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

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

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

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

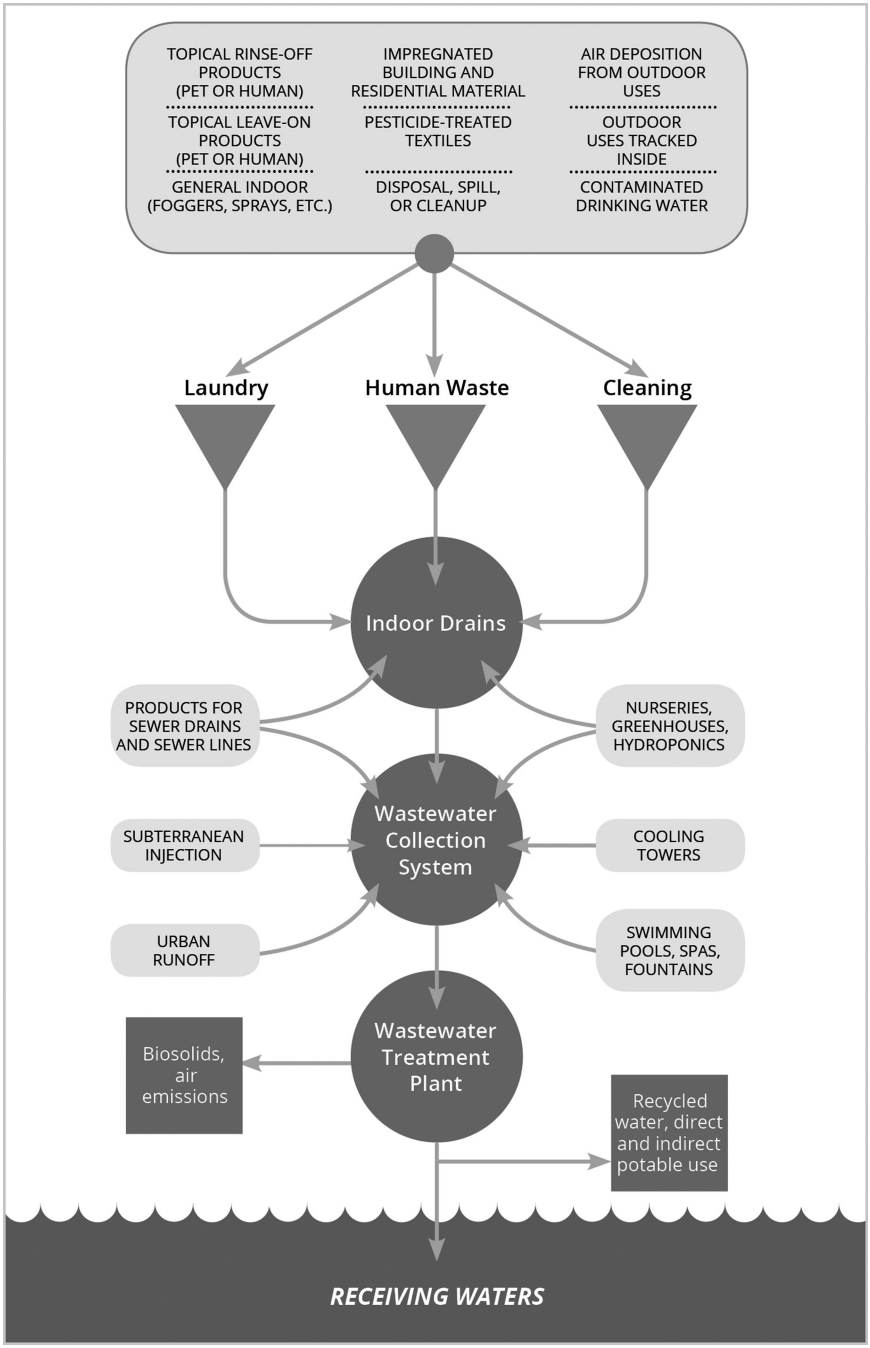

Figure 1. Conceptual model of sources of current-use pesticides to municipal wastewater. Black text is used to describe sources.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Relative Ecotoxicity of Pesticides in Effluent

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

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

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

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

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

Case Studies Illustrating Use of WWTP Monitoring Data and Conceptual Models

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

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

Case Study: Diazinon and Chlorpyrifos

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Priority Data Gaps

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

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

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

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

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

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

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

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

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

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

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

Conclusion

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

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

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Disclaimer

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

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Will Pesticides Prevent Publicly-Owned Wastewater Treatment Plant Effluent from Becoming a Much-Needed Drinking Water Supply?

Kelly Moran, Ph.D., TDC Environmental, LLC
Melody LaBella, P.E., Central Contra Costa Sanitary District

- The byproduct of potable reuse treatment – reverse osmosis concentrate – could contain pesticides at concentrations that will prevent its discharge to surface water. This increases cost, potentially preventing potable reuse implementation.
- Monitoring data are urgently needed to inform management measures.
- Both RO concentrate treatment and modifying uses of persistent mobile pesticides may be necessary.

Informed pesticide product design, regulation and mitigation measures may be needed to allow society to obtain the full benefits of its soon-to-be necessary new urban water supplies.

Presenters

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TDC Environmental, LLC

Melody LaBella, P.E.
Central Contra Costa Sanitary District

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Drinking water supplies are under stress

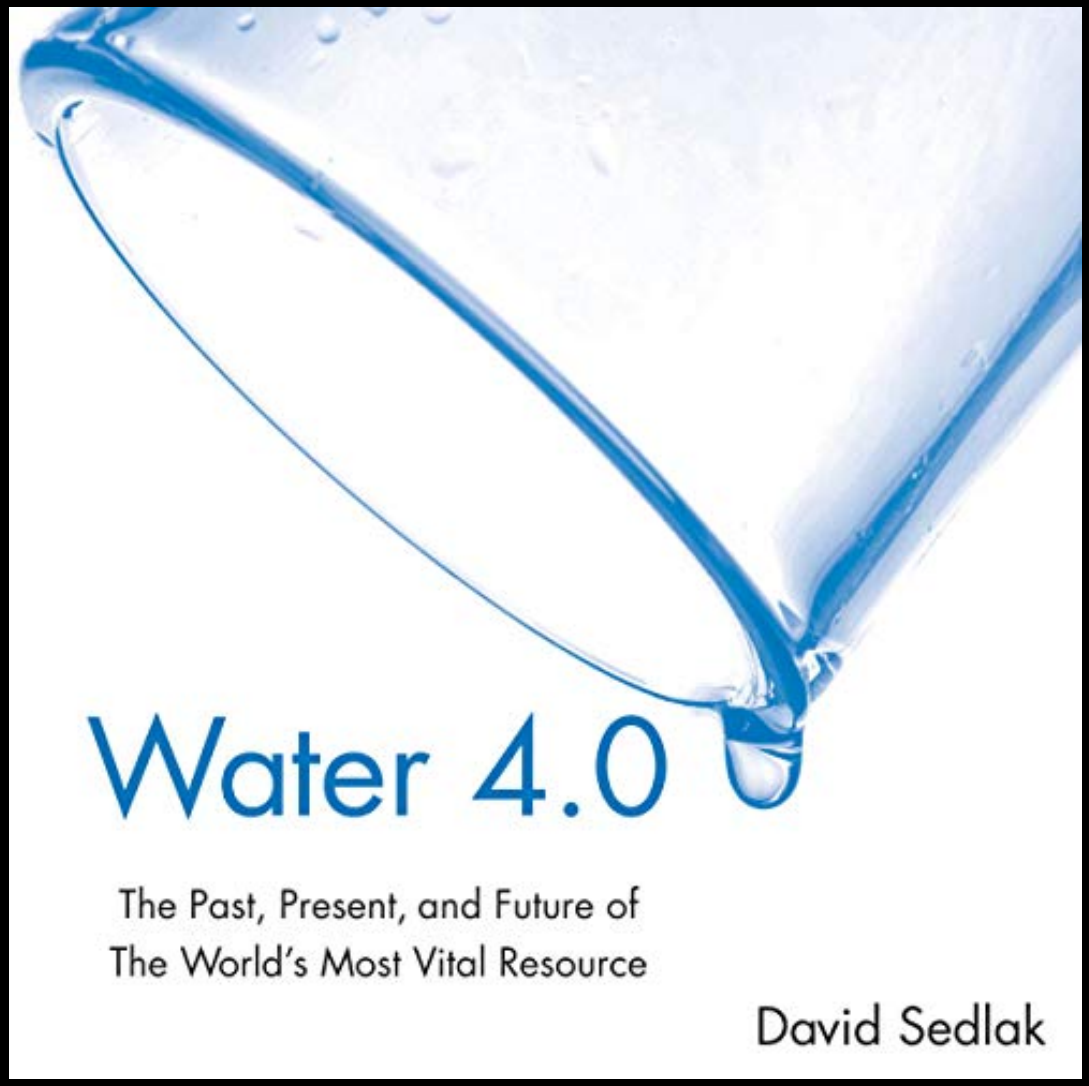
- Climate change = Weather extremes = Drought
- Increasing urbanization of the world's population

Photo: Pouya Dianat/The Atlanta Journal-Constitution

Photo: Silicon Valley Advanced Water Purification Center

Prettyboy Reservoir During 2002 Drought (LJWorld)

New water supply – potable use of municipal wastewater effluent



Resilient, continuous supply of partially-treated water

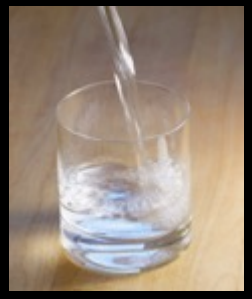
Municipal wastewater is an upcoming water supply

Sewer

Municipal wastewater treatment plant

Effluent

Continuous discharges



Planned & constructed potable use of wastewater treatment plant effluent (2017)

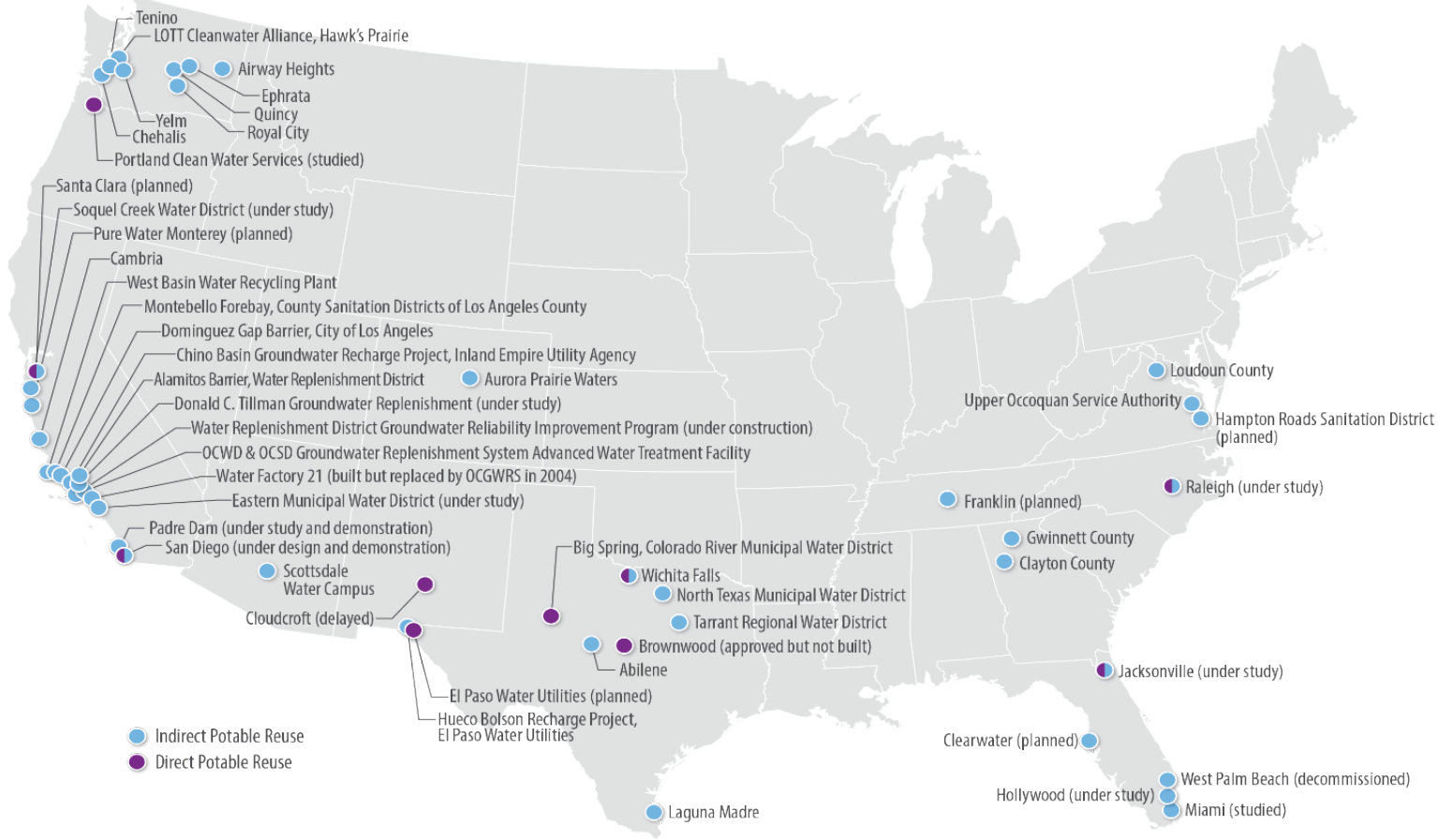


Figure 2-1. Planned and constructed IPR and DPR projects in the United States as of 2017

US EPA Office of Water (2017). Potable Reuse Compendium

Municipal wastewater contains pesticides

Sewer

- *Conventional wastewater treatment technologies are generally ineffective at removing pesticides from wastewater*
- *Aquatic life reference values can be exceeded in undiluted effluents*
- *Limited monitoring data available*
- *Municipal wastewater treatment plants cannot regulate pesticides*

Sutton et al. (2019). “Occurrence and Sources of Pesticides to Urban Wastewater and the Environment “ in Goh et al.; Pesticides in Surface Water: Monitoring, Modeling, Risk Assessment, and Management ACS Symposium Series; American Chemical Society: Washington, DC, 2019.

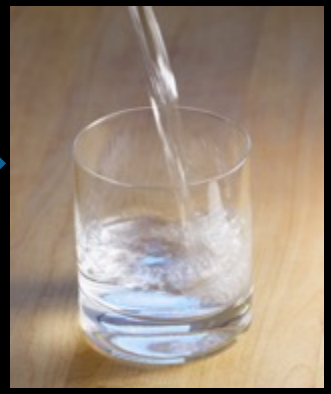
Pesticides and advanced treatment of municipal wastewater for potable use

Treated Wastewater (contains trace chemicals)

Reverse Osmosis (RO) Treatment

~80% of Flow

UV Disinfection & Advanced Oxidation



Smaller persistent mobile chemicals (e.g., 1,4-Dioxane, PFAS)

"RO Concentrate" ("RO reject")
Concentrates pollutants ~5 times

Larger persistent, mobile chemicals (e.g., imidacloprid, fiproles)

~20% of Flow

Challenges of RO Concentrate

- *Large volume (millions of gallons per day) requiring disposal*
- *Limited disposal options*
  - Typically discharged to the ocean (if nearby) or inland surface waters
  - Little or no dilution of discharged water in regions most in need of this new water supply
  - Discharges must comply with Clean Water Act
- *Treatment challenging, costly, and unlikely to sufficiently remove every one of the pesticides present*

Photo: David Sedlak

Pesticides in RO concentrate likely to exceed toxicity thresholds

Pesticide	RO Concentrate (ng/L)	Toxicity Threshold (ng/L)	Reduction Needed
Imidacloprid	53 – 1080	10	81.1 – 99%
Fipronil	12 – 280	7.5	37.5 – 97.3%
Fipronil Sulfone	15 – 49	2.6	82.7 – 94.7%
Fipronil Sulfide	<1 – 13.2	4.6	0 – 65%
Bifenthrin	*5 – 50 (est.)*	0.05	*99 – 99.9% (est.)*
Permethrin	*5 – 100 (est.)*	2.4	*52 – 97.6% (est.)*
Cypermethrin	<1 – 85 (est.)	0.05	75 – 99.7%

RO concentrate values from King et al 2020 Water Res. 176: 115744; UC Berkeley, Stanford, & San Francisco Estuary Institute (2020). *Reverse Osmosis Concentrate Treatment Research Results and Context for San Francisco Bay*. Italicized values are estimates (effluent concentration x 5) based on data in Sutton et al 2019. Toxicity threshold from US EPA Office of Pesticide Programs (invertebrate Aquatic Life Benchmark or most sensitive invertebrate aquatic toxicity endpoint used in most recent risk assessment)

Other pesticides that may exceed toxicity thresholds in RO concentrate

Based on municipal wastewater effluent monitoring data

- Carbaryl
- Chlorpyrifos
- Clothianidin
- Cyfluthrin
- Cypermethrin
- Deltamethrin
- Diazinon
- Diuron
- Esfenvalerate
- Imazapyr
- Lambda-cyhalothrin
- Propiconazole

Most pesticides have not been monitored. Antimicrobials are the biggest data gap.

Source: Effluent concentrations reported in Sutton et al 2019 x 5 compared to toxicity threshold from US EPA Office of Pesticide Programs (invertebrate Aquatic Life Benchmark or most sensitive invertebrate aquatic toxicity endpoint used in most recent risk assessment).

Conclusions

1. RO concentrate could contain pesticides at concentrations that will prevent its discharge to surface water.
2. Pesticides in RO concentrate may increase cost or – in the most difficult cases – entirely prevent potable reuse of wastewater effluent.
3. Modifying uses of persistent mobile pesticides in ways that avoid sewer discharges may be the best (and perhaps only) means to allow society to access this future water supply.

Recommendations

1. Conduct pesticides monitoring of municipal wastewater effluent and RO concentrate
2. Pesticides registration should address risks and costs associated with potable reuse of municipal wastewater effluent
3. Examine if cost-effective treatment alternatives exist for RO concentrate
4. Modify uses of persistent mobile pesticides in ways that avoid sewer discharges

Informed pesticide product design, regulation and mitigation measures may be needed to allow society to obtain the full benefits of its soon-to-be necessary new urban water supplies.