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Methodology for Evaluating Pesticides for Surface Water Protection: Evaluation on Down-the-Drain Products

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1. Introduction

The transport of pesticides Down-the-Drain (DtD) is an important pathway that could ultimately lead into surface waters. Pesticide products such as spot-on, sprays, lotions, and shampoos for pets, treated textiles, indoor sprays, foggers, drain treatment products, and sewer root killers are applied in scenarios which could result in residual release of their active ingredients (AIs) into wastewater stream and ultimately discharges into surface waters (Moran and TenBrook, 2014, Shamim et al., 2014b, Sutton et al., 2018, Xie et al., 2021). The Surface Water Protection Program (SWPP) aims to provide consistent and transparent modeling approach to evaluating pesticide products submitted for registration with the California Department of Pesticide Regulation (CDPR) that have the potential to pose risks to aquatic organisms. As such, there is a need to expand capabilities to include a systematic modeling approach aiming to estimate the aquatic exposures and characterize the environmental risks for down-the-drain pesticides (Xie, 2018).

Presented is a DtD model which is designed to evaluate pesticide products for registeration with CDPR for select indoor uses that may result in pesticide transport to domestic wastewater treatment plants (WWTPs). Use patterns to be evaluated include pet products, impregnated materials, floor drain treatment, and indoor pest control (e.g., sprays and foggers). The model may also be applied to other products that are routed to SWPP for DtD concerns. As a screening-level tool, the model intends to predict the estimated environmental concentrations (EECs) that would result from all users in an idealized wastewater sewershed using the label-allowed maximum application rate and frequency. The model-estimated EECs will be compared to the lowest toxicity value of the active ingredient (AI) to generate a model-based recommendation for registration. This report documents the modeling methodology, data requirements, and model validation against past evaluations and monitoring data.

2. Modeling approach

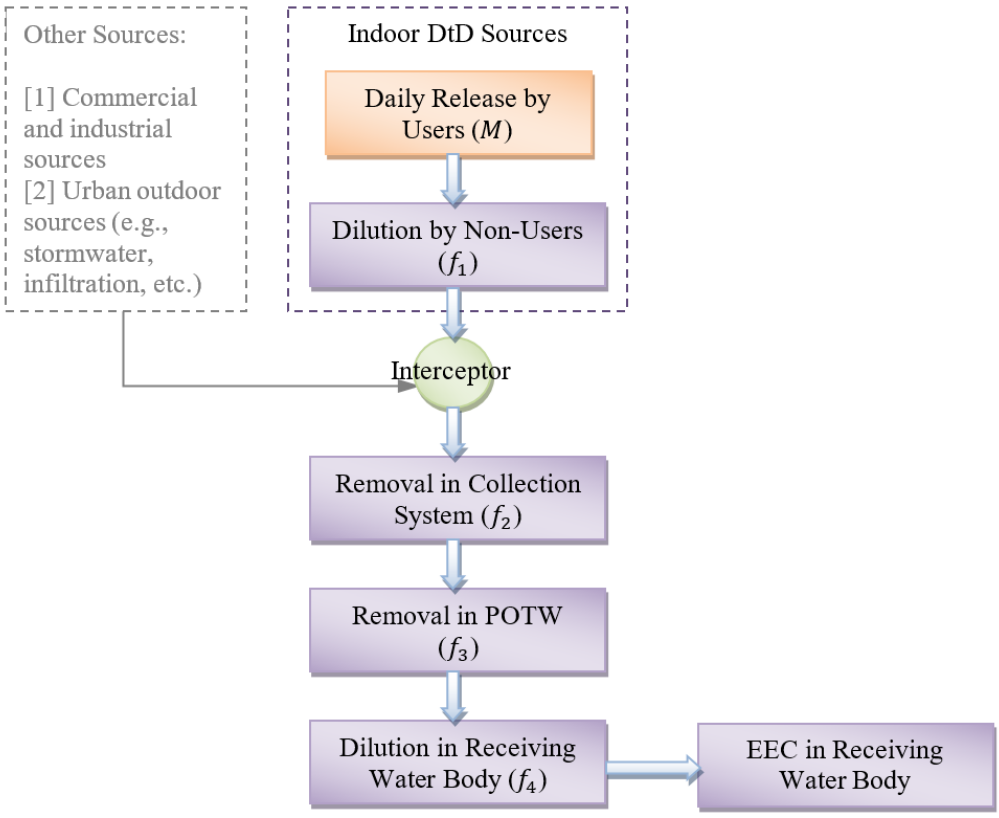
2.1 USEPA's exposure and fate assessment screening tool (E-FAST)

The DtD model presented is developed based on the US Environmental Protection Agency (USEPA) Exposure and Fate Assessment Screening Tool (E-FAST) Down-the-Drain module with additional modifications from SWPP. The E-FAST model is a screening-level consumer exposure model developed for assessing chemicals related to air, surface water, landfills, and consumer products in the U.S. EPA's Office of Pollution Prevention and Toxics (USEPA, 2007).

The DtD module of E-FAST is specifically designed to provide a conservative estimate of chemical residues in surface waters that may result from household uses of consumer products and the transport of chemicals into domestic wastewater (Shamim et al., 2014a, USEPA, 2016b). Conceptually, the model assumes that in a given year, the entire production volume of a chemical is parceled out on a daily basis to the entire U.S. population and converted to a mass release per capita, and subsequently, a daily per-capita release to a wastewater treatment facility. This mass is then diluted into the average daily volume of wastewater released per person to arrive at an estimated concentration of the chemical in wastewater prior to entering a treatment facility.

2.2 Model development

The SWPP DtD model is designed by following a similar conceptual model as E-FAST with a focus on utilizing registrant-submitted data and the product label to estimate the loading of AI to waste stream. Figure 1 demonstrates the conceptual model of DtD evaluation for pesticide registration evaluation in SWPP. The daily maximum pesticide loading from users (M) is estimated by using registrant-submitted data, application rate and frequency specified in product label, and other related data sources. The daily mass loading is then parceled out to the entire California population (i.e., converted to the per-capita daily loading) and diluted into the per-capita daily average volume of wastewater released in the State. There are four mechanisms considered in the model for pesticide removal and dilution from the DtD transport to entering surface waters. These are: (1) f_1 = dilution by wastewater discharge from non-users who have no pesticides released during the time-period of evaluation, (2) f_2 = removal in the collection system, (3) f_3 = removal during the wastewater treatment process, and (4) f_4 = dilution by other water sources in the receiving water body. Once the pesticide enters a receiving water body, the model simulates the fate of pesticide in environment and predicts the estimated environmental concentrations (EECs) in the water column and bed sediment.



Notes: Pesticide removal in collection system would occur anywhere in the system, but conceptually aggregated for demonstration purpose. Pesticide release from residential indoor uses is considered as a representative and conservative (in terms of concentration, not mass loading, of pesticides) source in estimating the POTW influent concentration. Other sources (shown in the box on the left, including commercial and industrial sources, and urban outdoor sources) are not explicitly included in the evaluation. Please see the model assumptions and considerations for more details.

Figure 1. Conceptual model of registration evaluation for DtD products.

To calculate the daily maximum whole-water (i.e., dissolved and particle-bound) concentration of AI in wastewater effluent, C_R (µg[AI] L^{-1}), the daily maximum DtD release rate of the pesticide from a person who is projected to use the product under review M (µg[AI] $person^{-1}$ day^{-1}) (Eq 1) must be calculated first. It is expressed as the product of three factors:

$$M = R_{max} \times Coef_{washoff} \times \frac{1}{Interval} \quad (1)$$

R_{max} (µg[AI] $person^{-1}$) is the maximum application rate of a treatment per user allowed by the product label. Note that application rate may not labeled on the per-capita basis. In this case, conversion is needed to obtain R_{max}, see section 3.2 for details.

$Coef_{washoff}$ (dimensionless) is the fraction of AI transported DtD in the washing or cleaning event, i.e., the wash-off coefficient.

Interval (day) is the label allowed application interval. The reciprocal of *Interval* represents the chance that a user would wash or clean the treated subject in a day. Here we assume that there is one generic washing event between two applications and the chance for a user to apply the product in a day is evenly distributed across the label-allowed interval.

$$C_R = \frac{M}{W} \times f_1 \times f_2 \times f_3 \times f_4 \quad (2)$$

W (L person^{-1} day^{-1}) is the per-capita daily wastewater volume. Starting from September, 2014, the California State Water Resources Control Board (SWRCB) required detailed water use reporting from urban water suppliers in the state. Since the reports include both indoor and outdoor water used, the mid-winter use is a good representation of indoor water use. According to the reports from 2015 to 2020, January has the smallest average R-GPCD (residential gallon per capita day) within a year for California statewide (Appendix A). Therefore, the model uses the R-GPCD in January, i.e., 63.93 gallon capita^{-1} day^{-1} or 242 L capita^{-1} day^{-1} to represent the minimum volume of wastewater released in California. The value used in the model will evolve over time in accordance with the water use data.

f_1 (dimensionless) is the maximum fraction of population in California that is projected to use the product under review, indicating the dilution from non-users. The determination of values of f_1 is elaborated in Section 2.5.

f_2 (dimensionless) is the pesticide delivery coefficient in the wastewater collection system, which is calculated as one minus the removal rate. Pesticides could be removed in the collection system via aquatic degradation. However, this effect is fairly minor because the residence time of wastewater in the collection pipeline is typically hours (Goossens et al., 2016), which is much shorter than the aquatic degradation half-life (HL) for most pesticides. Therefore, a conservative assumption is made that pesticides are persistent in the wastewater collection system, i.e., f_2=1, unless additional studies for the product under review can provide evidence otherwise.

f_3 (dimensionless) is the pesticide delivery coefficient in the wastewater treatment facility, which is computed as one minus the removal rate. The removal rate can be determined based on registrant-submitted data or open literature values, for example, bench scale studies or plant scale monitoring data. If no such data is available, which is a common case for new AIs, the removal rate can be estimated from computational models. The Sewage Treatment Plant (STPWIN™) program of EPI Suite v.4.11 (USEPA, 2012a) is a modeling tool that is recommended by USEPA for estimating the wastewater removal efficiency for risk assessment of indoor pesticide uses (USEPA, 2016b). The STPWIN program has been widely used to predict the wastewater removal efficiency for pharmaceuticals and other organic pollutants with varying success (de García et al., 2013, Jones et al., 2002, Kim et al., 2009, Rojas et al., 2013, Seth et al., 2008); however, systematic validation has not been performed for pesticides. A theoretical review of the STPWIN model and a systematic evaluation on its performance in predicting removal efficiency for pesticides is presented in Appendix B. When using STPWIN in registration evaluation, reviewers should use the CDPR-approved values for model input. Detailed model inputs are discussed in Sections 3.1 and 3.5.

f_4 (dimensionless) is the dilution factor in the receiving water body to which the WWTP discharges, computed as the ratio of wastewater effluent to the sum of effluent volume and

stream flow. The USEPA E-FAST model recommended using a value of 4.1% for acute risk assessment and 0.7% for chronic risk assessment (USEPA, 2007). These values were derived from a national median factor of stream dilution at the 1Q10 condition (i.e., single day of lowest flow over a 10-year period) and the 7Q10 condition (i.e., 7 consecutive days of lowest flow over a 10-year period), respectively. The potential for dilution in California, however, has been shown to be much lower resulting in a greater value for the dilution factor. In a letter to USEPA, Tri-Tac (2007) asserted that there were water bodies in California that were predominately composed of wastewater effluent, especially during low flows. Rice and Westerhoff (2017) compared the WWTP design flow to the annual average streamflow of water bodies that receive wastewater effluent (retrieved from NHDPlus v.2 and USGS gauging stations) and reported that the median contribution from wastewater effluent to streamflow in California waterways was about 67.7%, and the 90th percentile was 97.1%, one of the highest numbers among the hydrologic regions in the nation. In small streams and creeks, the contribution percentage could be as large as 100% (i.e., zero stream dilution). Therefore, for the regulatory modeling, the USEPA (2016b) recommends using a stream dilution factor of 1 to represent the most conservative scenario, in which there was zero dilution effect in effluent dominated bodies of water or small receiving water bodies. Based on the evidence discussed above, a stream dilution factor of 1 is used in the SWPP DtD model.

Pesticides in wastewater effluent is discharged into a receiving water body. To describe the fate and transport of pesticide in receiving water body (e.g., partitioning, diffusion, degradation, photolysis, hydrolysis, etc.), the Variable Volume Water Model (VVWM), developed by USEPA (Young, 2016), is adopted into the DtD model. The USEPA standard pond scenario is used to represent the vulnerable receiving water body in California and estimate the EECs. Since it is assumed that there is no dilution in receiving water body, the initial concentration of pesticide in the water column of the standard pond is set to be the concentrations in effluent, i.e., C_R in Eq 1. With the VVWM simulations on the pesticide fate and transport processes, the daily average aqueous concentrations in the water column and benthic region are used for the risk characterization in the corresponding compartment of the receiving water body.

For the purpose of registration evaluation, the model-predicted EECs are compared to the lowest toxicity values in aqueous phase. For chemicals with K_{oc} greater than 1,000 L/kg[OC] the comparison is also made for the absorbed phase. When the resulting ratios (i.e., risk quotients) are greater than 0.5 the recommendation would be to deny registration.

2.3 Assumptions and considerations

The DtD model is developed based on the following assumptions and considerations.

First, the model only evaluates DtD transports from residential and selected commercial (e.g., floor drain in food/feed handling facility, animal kennels) applications.

Second, we assume that the concentration of DtD pesticide in sanitary wastewater (i.e., indoor) is higher than that in stormwater runoff (i.e., outdoor) for both dry and wet conditions. Specifically, the concentration of a pesticide in WWTP influent is mainly determined by the sanitary wastewater and will not be increased by the inclusion of stormwater runoff, by direct discharge in combined systems, or by infiltration in uncombined systems.

Third, DtD pesticides are evaluated during dry weather conditions, which minimize the total flow and maximize the concentration. Dry weather flow is estimated based on the statewide average per-capita daily water usage in Januaries, which is 242 L capita^{-1} day^{-1}, based on water usage data reported to the State Water Board. See Section 2.1 for details.

2.4 DtD scenarios to be evaluated by the model

Pesticides can be introduced to wastewater streams through multiple sources and pathways (Moran and TenBrook, 2014, Sutton et al., 2018, Xie et al., 2021). Considering data availability and registration evaluation patterns, SWPP's DtD model includes evaluation for selected use patterns, as follows:

(a) Pet products (e.g., spot-on, spray, and shampoos).

(b) Impregnated materials (e.g., impregnated fabrics and fibers, and pesticide preserved garments, gears and apparels).

(c) Floor drain products.

(d) General indoor pest control products (e.g., foggers, and indoor sprays to pet and human beddings, floors, carpets, rugs, and upholsteries).

Additional products may be routed to SWPP on a case-by-case basis for special DtD use patterns, depending on request from outside stakeholder or at the discretion of registration branch. Examples include spray for animal kennels, secondary treatment of portable water, etc. The model may be able to assess additional scenarios where there is sufficient data.

3. Data requirements

3.1 Overview of model inputs

Input data required by the DtD model are illustrated in Table 1. The model is composed of three components, including the DtD loading model, the USEPA EPI Suite STPWIN program used to estimate the f_3 factor, and the VVWM model used to estimate EECs and make final recommendation.

Table 1. Input data requirement and data sources for DtD model.

Parameter	Definition	Unit	Value
DtD Loading			
R_{max}	Daily maximum per user release rate	μg[ai] person^{-1}	See Section 3.2
$Coef_{washoff}$	Maximum fraction of AI washed off in a single washing event	-	See Section 3.3
Interval	Time interval between two applications/wash events	day	Product label
W	Per-capita daily wastewater volume	L person^{-1} day^{-1}	242 (See Section 2.2)

f_1	Dilution factor from non-users	-	See Section 3.4
f_2	Removal coefficient in wastewater collection system	-	1 OR Registrant-submitted data
f_3	Removal coefficient in wastewater treatment	-	EPI Suite STPWIN OR Bench scale/monitoring study
f_4	Stream dilution factor	-	1
EPI Suite STPWIN			
VP	Vapor pressure	torr	Registrant-submitted data approved by CDPR
SOL	Water solubility	mg L^{-1}	Same as above
LogKow	Octanol/water partition coefficient	-	Same as above
Henry	Henry's law constant	atm-m^3 mol^{-1}	Same as above
Bio_HL	Biodegradation HL	hours	10,000
SMILES	Simplified molecular-input line-entry system	-	EPI Suite database
Receiving Waterbody Model			
SOL	Water solubility	mg L^{-1}	Registrant-submitted data approved by CDPR
KOC	Organic carbon-normalized soil adsorption coefficient	L kg[OC] $^{-1}$	Same as above
HYDRO	Hydrolysis half-life	day	Same as above
AERO_W	Aerobic aquatic metabolism half-life	day	Same as above
ANAER_W	Anaerobic aquatic metabolism half-life	day	Same as above
MWT	Molecular weight	g mole $^{-1}$	Same as above
VP	Vapor pressure	torr	Same as above
AQPHOT	Aqueous photolysis half-life	day	Same as above
TOX	Lowest toxicity value for water toxicity (acute)	µg L^{-1}	Same as above
TOXSED	Lowest toxicity value for sediment toxicity	µg kg[dry sediment] $^{-1}$	Same as above

3.2 Daily maximum per user release rate (R_{max})

Typically, the daily maximum per-capita loading to wastewater (R_{max}) is not readily available in registrant-submitted data. Conversion is needed to translate information specified in the label to the desired model input. Table 2 shows the conversion from label-allowed application rate to R_{max} (µg[ai] $person^{-1}$) as follows.

$$R_{max} = Label\ Rate\ (in\ units\ in\ Table\ 2) \times Subject\ per\ Capita\ Conversion\ Factor \quad (3)$$

Table 2. Conversion from label-allowed application rate to R_{max} assumptions and references follow in the body of the report.

Subject Treated	Unit of Label Rate	No. of Subjects	Subject per Capita Conversion Factor
Dogs	µg[ai]/dog	8,885,121	0.22
Cats	µg[ai]/cat	9,706,690	0.25
Floor drains	µg[ai]/drain	7,620,100	0.19
Impregnated materials	µg[ai]/subject	NA	1 [a]
Indoor sprays	µg[ai]/house	NA	0.25

[a] The default value is 1 for subjects such as apparels. It could be changed to a user-specified value in other cases.

Note that the label-allowed application rate may not necessarily follow the units listed in Table 2. Specifics about determining application rate appropriate for model input are shown below.

(a) For dog/cat products, if the label contains multiple application rates for small, medium, large, or extra-large pets; the medium application rate is used for model input. This is consistent with the model design where the f_1 factor was determined based on pesticide sales data for medium-sized dogs/cats. Otherwise, the rate specified in the label is used.

(b) For floor drain products, the per-floor-drain application rate is usually not explicitly specified in the product label. As a part of indoor structural pest control, the rate on floor drains follows the indoor application rate. Here, we assume that the surface area of a drain is about 1 ft^2, the mass applied per drain can be calculated as the mass applied per ft^2.

(c) For indoor spray products, the label rate is typically in the unit of µg[ai]/ft^2. The per house application rate = label rate * indoor treatable area per house. The indoor treatable area is assumed to be 1500ft^2 * 2.5% = 37.5ft^2, where 1500ft^2 is the reported square footage for "inhabitable" areas of a house unit according to the American Housing Survey (AHS) standards, and the 2.5% is the model-assumed impervious (i.e., treatable) percentage of indoor square footage, derived from Luo (2014). It is also assumed that there are four persons in a household (Luo, 2014), and the daily maximum pesticide load is adjusted by dividing four accordingly.

Except for impregnated materials, the subject per capita conversion factor is determined as the number of subjects divided by CA population, where CA population = 39,557,045 as of July 1, 2018, according to the US Census Bureau. The number of subjects is determined as follows.

(a) The number of dogs or cats in California were derived from the national pet ownership survey conducted by the American Veterinary Medical Association (AVMA) in 2018 (AVMA, 2018), which is 8,885,121 dogs and 9,706,690 cats.

(b) The number of floor drains was estimated by using the best available data, as follows. The floor drain products are typically applied in food/feed handling establishments. According to the 2016 California Plumbing Code (CPC) Section 418.3, floor drains shall be installed in toilet rooms and commercial kitchens of food/feed handling facilities. There is no data on the number of floor drains in California; however, the National Restaurant Association reports number of restaurants in California, which is 76,201 according to the 2019 survey (NRA, 2019). This number could be used to estimate the

number of floor drains. According to CPC and plumbing practices, we assumed that there were ten floor drains in a restaurant. The number of floor drains in restaurants is 76,201*10 = 762,010. This number was multiplied by ten to include all food/feed handling establishments, which yields the number of floor drains in California = 762,010*10 = 7,620,100.

For indoor spray, we assumed that there are four persons per household, therefore the subject per capita conversion factor is ¼ or 0.25.

Note that since the population, number of pets, and number of restaurants in California would be updated over time, the subject per capita conversion factor will evolve in accordance with the data.

3.3 The wash-off coefficient ($Coef_{washoff}$)

The wash-off coefficient ($Coef_{washoff}$) of the product under review is typically available from registrant-submitted data, especially for impregnated materials. In the case when no data is available, the maximum value reported in existing studies for products with similar use patterns was recommended for model input (Table 3). Note that the default values would be updated regularly as new information becomes available. For pet treatment products, the default value of the wash-off coefficient is suggested to be 0.21. Teerlink et al. (2017) reported that an average 21±22% of the mass of fipronil applied to dogs via spot-on products could be washed off in 2 days after application. The percentage decreased to 16±13 and 4±5% if dogs were washed 7 and 28 days after application, respectively. Since fipronil is a highly soluble chemical (solubility = 1.9 ppm, K_{oc} = 668.75), the wash-off coefficient is considered to be a conservative representative of other pet product AIs. The high-end value (0.21) is recommended for model use for pet products except that the wash-off coefficient for pet shampoos is one. For floor drain products, the wash-off coefficient is assumed to be 1 unless a specific value is available from the registrant-submitted data. For indoor pest control products, a conservative assumption of 100% mass being washable (i.e., wash-off coefficient = 1) is used when no wash-off data is available. Note that a 100% wash-off for indoor pest control products is an extremely conservative assumption.

Table 3. Values of wash-off coefficient recommended when no data is available.

Use Pattern	**Wash-off Coefficient ($Coef_{washoff}$)**
Pet Products (except shampoos)	0.21 OR request for wash-off study
Pet Shampoos	1
Impregnated materials	Request for wash-off study
Floor Drains	1
Household Indoor Pest Control	1 OR request for wash-off study

3.4 Determination of the f_1 factor

The f_1 factor determines the dilution effect from non-users to pesticide loading. In some cases, the value is available from registrant-submitted data or open literature. For pet products in particular, since no readily data is available, f_1 was derived from the sales data of similar

products, see Appendix C for details. Table 4 provides a suggested value for f_1 in each DtD category.

Table 4. Model suggested value of f_1 factor for each DtD use pattern.

DtD Use Pattern	Suggested Value for f_1 Factor
Dog Treatment	0.07 [a]
Cat Treatment	0.05 [a]
Impregnated materials	Case-specific
Floor Drains	0.76 [b]
General Indoor Pest Control	0.76 [b]

[a] See Appendix C.

[b] The value 0.76 was derived from survey data for outdoor pest control Luo (2014), and adopted here for indoor uses.

3.5 Determination of the f_3 factor

For some existing AIs, the value of f_3 factor may be available in plant-scale or bench-scale studies. In the case of no data available, or for new AIs, the f_3 factor can be determined by using the STPWIN™ program of EPI Suite v.4.11. See Section 2.3 and Appendix B for a full description of the program. The model requires an input of several chemical properties of the AI, including logKow, solubility, vapor pressure, and Henry's law constant. Reviewers should use CDPR-approved values for model input.

4. Model validation

4.1 Model validation against past evaluation

In this section, we demonstrate the registration evaluation for several products by using the DtD model depicted in this report and show an evaluation of how well the new model matches the decision made by professional judgement for past evaluations. Table 5 elaborates the model input and results for six products designated for various DtD use patterns, including impregnated fabrics/fibers, floor drain treatment, indoor spray, drinking water treatment, and spray for animal kennels. These products were evaluated in the past by SWPP staff based on the drafted version of the DtD model and professional judgement. By re-evaluating them with the finalized model, a same modeling result and recommendation were achieved, indicating that the finalized model presented in this report is consistent with the previous methodology.

Table 5. Comparison of registration recommendation between the DtD model and past evaluations.

Parameter	Unit	Product 1	Product 2	Product 3	Product 4	Product 5	Product 6
Use pattern		Impregnated socks	Floor drain	Floor drain	Indoor spray	Drinking water treatment	Animal housing treatment
Product AI		Copper	Fipronil	Deltamethrin	Deltamethrin	Copper	Indoxacarb
R_{max_label}	µg[AI] subject^{-1} day^{-1}	1.16E+06	2.80E+04	2.55E+05	1.88E+04	NA	3.13E+06
Subj/Capita	Dimensionless	1	0.02	0.02	0.25	NA	9.38E-06
$R_{max} = R_{max\_label}$ * *Subj/Capita*	µg[AI] person^{-1} day^{-1}	1.16E+06	5.39E+02	4.91E+03	4.7E+03	NA	2.94E+01
$Coef_{washoff}$	Dimensionless	0.0013	1	1	1	NA	1
Interval	day	7	30	180	180	1	1
M	µg[AI] person^{-1} day^{-1}	2.15E+02	1.8 E+01	2.73 E+01	2.61 E+01	1.94E+05	2.94 E+01
W	L person^{-1} day^{-1}	242	242	242	242	242	242
f_1	Dimensionless	0.01 [a]	0.76 [a]	0.022 [a]	0.022 [a]	0.338 [a]	1 [a]
f_2	Dimensionless	1	1	1	1	1	1
f_3	Dimensionless	0.18	0.8697	0.1238	0.1238	0.18	0.3638
f_4	Dimensionless	1	1	1	1	1	1
C_R	µg[AI] L^{-1}	1.60E-03	0.05	3.08E-04	2.94E-04	48.67	4.41E-02
TOX	µg[AI] L^{-1}	0.48	0.14	0.0037	0.0037	0.48	54.2
RQ (Dissolved)	Dimensionless	5.24E-05	0.34	8.01E-03	7.65E-03	1.59	7.56E-04
TOXSED	µg[AI]/kg[dry weight]	151000	NA	3.8	3.8	151000	720
RQ (Adsorbed)	Dimensionless	8.50E-06	NA	3.17E-03	3.03E-03	0.26	1.29E-03
Recommendation		Support	Support (Watch list)	Support	Support	Denial	Support
Consistent with Previous Decision?		Yes	Yes	Yes	Yes	Yes	Yes

References: product 1 (Xie and Deng, 2014), product 2 (Xie and Singhasemanon, 2016), products 3 and 4 (Xie, 2020), product 5 (Evaluation decision pending), and product 6 (Budd, 2019).

[a] Sources: product 1 = registrant-submitted data; product 2 = Table 4; products 3-4 = 0.76 * 28.9% = 0.022, where 28.9% is the adjustment factor for deltamethrin-containing consumer products based on the survey conducted by the Pyrethroid Working Group (Winchell, 2013); product 5 = California Water Use Report by the State Water Board; and product 6 = conservative assumption made by the reviewer.

4.2 Model validation against monitoring data

For the receiving water body component, the model uses VVWM to estimate EECs in the USEPA farm pond. While VVWM with the farm pond scenario has been proved to be an appropriate tool to model the most conservative exposure in California's urban and agricultural waterways for outdoor runoff modeling (Luo, 2014, Xie et al., 2018, Xie et al., 2019), whether or not it is suitable for wastewater modeling has not been validated. To evaluate the performance of the model, the model-estimated EECs were compared to the corresponding monitoring data and a reasonable overestimation indicated a good model fit for a conservative modeling at the screening level. Twelve pesticides that have effluent monitoring data reported in California (Markle et al., 2014, Parry et al., 2015, Sadaria et al., 2016, Sadaria et al., 2017, Weston and Lydy, 2010, Weston et al., 2013) were selected for the analysis. The collection of pesticides represents a wide range of physiochemical properties and environmental fate. The 99th percentile of concentration in effluent was taken to represent the worst-case discharge from WWTPs to receiving water body, and used as model input, i.e., C_R in equation (1). Ideally, the model-estimated EECs should be compared to the observed concentrations downstream of the effluent; however, there is a lack of data to perform this analysis. Therefore, we used a proximate method, which compared the model output to monitoring data collected from California's waterways. In this analysis, monitoring data recorded in CDPR's Surface Water Monitoring Database as of April, 2020 (CDPR, 2020) was used. To be consistent with the model input, the 99th percentile of monitoring data was derived to represent the worst-case exposure in the real world.

Figure 2 shows the comparison of the model-estimated aqueous EEC resulted from the 99th percentile of concentration reported in California's wastewater effluent to the 99th percentile of observed concentrations in California's surface waters. The model generally overestimates the concentration in receiving water body for most of the selected pesticides (i.e., red points are below the 1:1 blue line) except acetamiprid. In the case of acetamiprid, the model-estimated EEC was 2.12 µg/L versus the 3.09 µg/L value that was observed. The model slightly underestimates the concentration. This result may be due to the relatively small sample size (i.e., five samples), which might lead to an increased uncertainty in the observed effluent concentration for model input and the value used for model input might not capture the worst-case concentration in effluent. In general, the VVWM with farm pond scenario is a suitable tool to estimate EECs for registration evaluation of DtD pesticides.

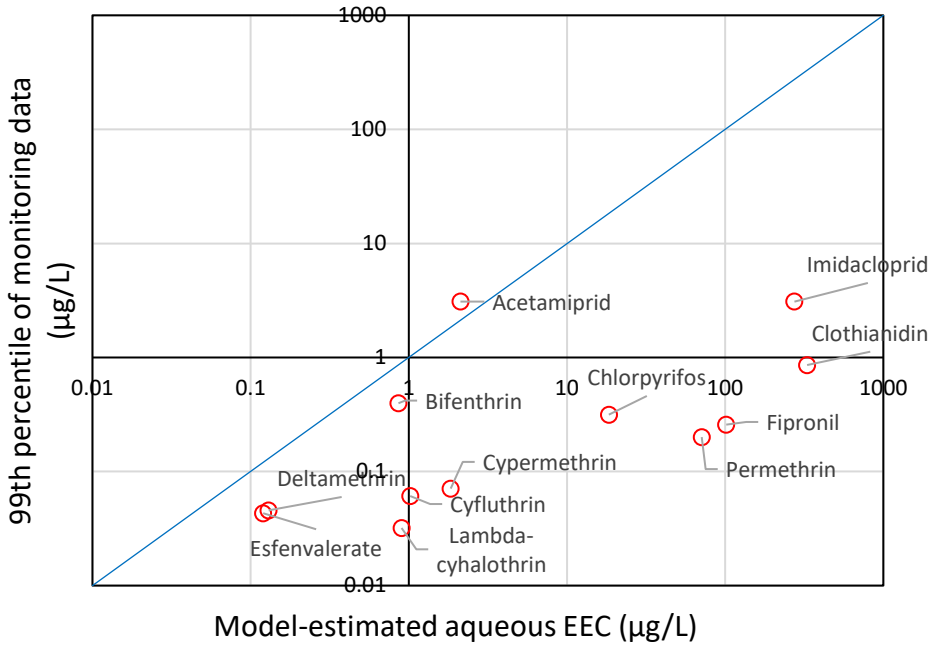


Figure 2. Comparison of the model-estimated aqueous EEC resulted from the 99th percentile of concentration in wastewater effluent to the 99th percentile of monitoring concentration in California's waterways. Data and references are presented in Appendix D.

5. Summary

This study report presents a working version of the DtD model that is developed to evaluate the aquatic risk of pesticide products submitted for registration with CDPR for uses with potentials of down-the-drain transport. This model is parameterized as a screening-level tool and intends to generate a conservative estimate of EECs for the proposed uses and provide a registration recommendation for the product under review. Use patterns to be evaluated include pet products, impregnated materials, floor drain treatments, indoor pest control, and any other products routed to SWPP with DtD concerns. Additionally, this model simulates processes such as pesticide loading to wastewater, dilution in the sewershed, removal in collection system and during wastewater treatment process, dilution in stream, and the fate in receiving water body. This report documents the modeling methodology, data requirements, and model validation for SWPP's DtD model.

Acknowledgements

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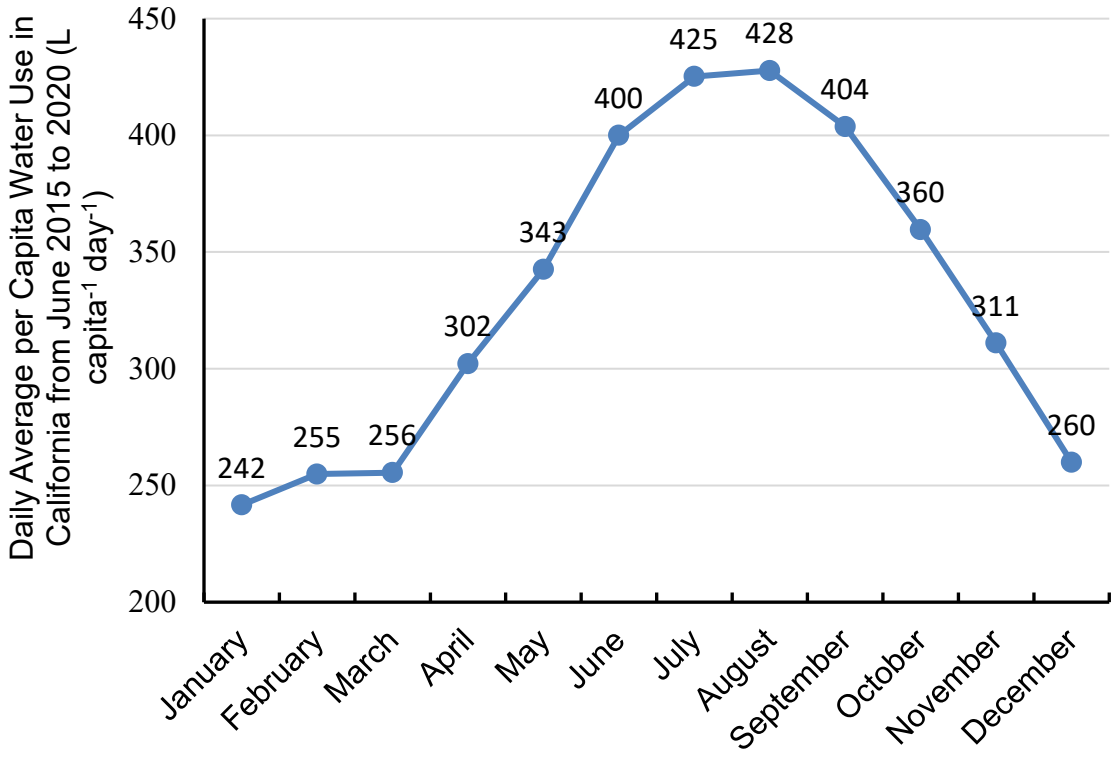
Appendix A: Daily average per-capita water use in California by month during 2015-2020



Source: California State Water Resources Control Board (http://www.waterboards.ca.gov/water_issues/programs/conservation_portal/conservation_reporting.shtml#monthly_archive).

Appendix B: Theoretical review and validation of the Sewage Treatment Plant (STPWIN™) program of EPI Suite v.4.11

The Estimation Program Interface (EPI) Suite is a Windows-based suite of physical/chemical property, aquatic toxicity, and environmental fate estimation program jointly developed by the USEPA's Office of Pollution Prevention and Toxics and the Syracuse Research Corporation (SRC) (USEPA, 2012a). The Sewage Treatment Plant (STPWIN^{TM}) program is one of the modules from EPI Suite (Card et al., 2017). The STPWIN is a version of the of the Sewage Treatment Plant (STP) model originally developed by Mackay and coworkers at the University of Toronto (Clark et al., 1995). The STPWIN model is formulated based on the fugacity approach (Clark et al., 1995), and predicts the fate of organic chemicals in the conventional WWTP with activated sludge. The model is based on a standard system design and set of default operating conditions. It assumes thermodynamic equilibrium between water and suspended solids in three treatment compartments – primary clarifier, aeration vessel, and settling tank. An estimate of total removal is given by accounting for three removal processes – biodegradation, sorption to sludge, and air stripping. A schematic diagram of the model is described in Figure B1. Note that pesticides can also be removed through abiotic degradations such as photolysis and hydrolysis (Margot et al., 2015); these processes however are not explicitly considered in the model.

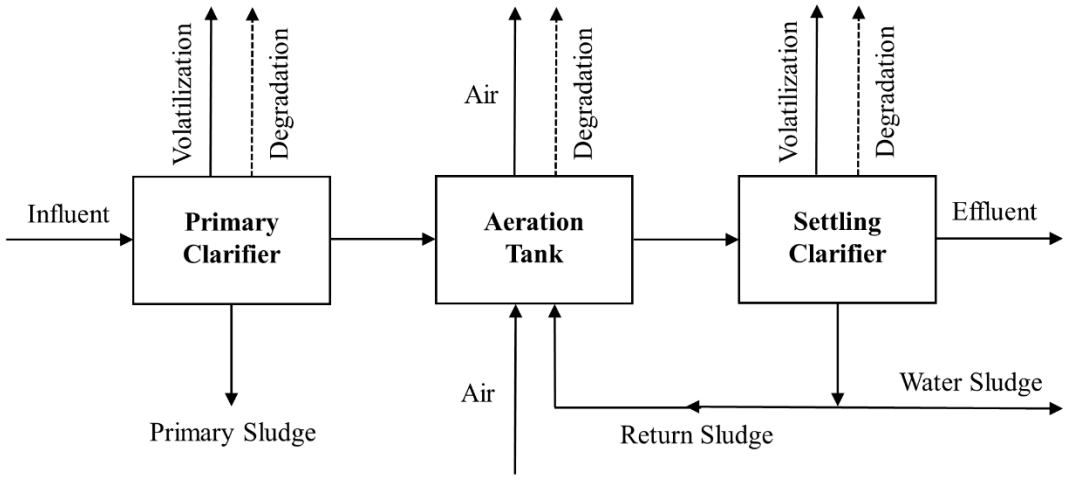


Figure B1. Schematic diagram of STPWIN program. Adapted from Fig. 1 in Clark et al. (1995).

The most critical variables in STPWIN model are the biomass-water partition coefficient (K_{BW}) and the pseudo-first order biodegradation rate. The K_{BW} describes pesticide partitioning to biomass and estimates the removal through sorption to sludge. The model predicts K_{BW} using the octanol-water partition coefficient (Kow) by the following equation:

$K_{BW} = 0.2Kow + 0.8$

The value of Kow can be determined from the chemical structure of the pesticide by using the chemical computational approach built in EPI Suite, or from user-specified value. Biodegradation is another removal mechanism. The biodegradation rate, or the HLs, is the most uncertain variable. The model Help Manual recommended setting the biodegradation HLs to be

10,000 hours, which leads to a small biodegradation rate and a conservative estimate of the removal. Given the uncertainty in the biodegradation rate, the recommended assumption is appropriate for the screening-level risk assessment. However, users can enter customized HLs if available to refine the estimate. Besides, the biodegradation HLs can also be determined based on the estimated biodegradability from the BIOWIN program of EPI Suite and the USEPA default classification of HLs (Meylan and Howard, 1995). This method intends to provide a more realistic setup of the HLs, compared to the conservative assumption. Other key model inputs include the solubility, Henry's law constant, and vapor pressure of the chemical. These input values can either be estimated from EPI Suite or be determined with customized data. For registration evaluation, reviewers should use CDPR-approved values for model inputs wherever possible. In the case of no data available, users can enter the Simplified Molecular Input Line System (SMILES) into EPI Suite and the model will estimate the required values. A complimentary database that contains 112,000 entry records of the CAS number, chemical name, and the corresponding SMILES notation of a compound is available with EPI Suite. If the SMILES notation of the AI under review is not included in the database, use public libraries (e.g., https://pubchem.ncbi.nlm.nih.gov/) or software to retrieve the information

The STPWIN program has been widely used to predict the wastewater removal efficiency for pharmaceuticals and other organic pollutants with varying success (de García et al., 2013, Jones et al., 2002, Kim et al., 2009, Rojas et al., 2013, Seth et al., 2008); however, no systematic validation has been done for pesticides. Although the USEPA has adopted the model to evaluate the aquatic risk of pyrethroid indoor products with DtD concerns, it remains unclear that how well the model results are sufficiently conservative for the screening level assessment. In order to evaluate the model performance, the model estimated removal rates were compared to the measured rates collected from the existing literature (Fig. B2). Studies that reported plant-scale removal efficiencies for pesticides were examined (Table B2) and the range of the reported values is presented in Fig. B2. These included removal efficiencies for eight pesticides observed in WWTPs in the US and another 32 pesticides around the world (may include US). The plants sampled were mainly secondary treatment plants with some tertiary plants. The model estimated removal rates were obtained by using two different biodegradation HLs – the USEPA recommended values (i.e., HLs = 10,000h, red circle in Fig. B2) and the BIOWIN estimates (blue cross in Fig. B2). Detailed model inputs were demonstrated in Table B1. Since the USEPA recommended HLs were usually much longer than the BIOWIN estimates, the estimated removal rates were typically smaller and more conservative. The estimated removal and measured removal were the comparable for some pesticides, including bifenthrin, fipronil, lambda-cyhalothrin, and propanil, indicating a low biodegradability for these chemicals. The removal rates estimated from the USEPA method were typically on the lower end of or below the range of the observed values, meaning that the model results were conservative. There were a few exceptions. In the USA WWTPs samples, the model predicted removal rates for bifenthrin and lambda-cyhalothrin were about 0.67% and 3.69% greater than the observed maximum values, respectively. The model slightly overestimated the removal rate for the two chemicals, but the difference between the estimated and observed values was not significant. In the worldwide samples, the model overestimated the removal rate for three out of the 32 pesticides. These included buprofezin, dichlorfenthion, and penconazole, and the model estimates were about 1.3, 0.67, and 0.32 times more than the maximum observed rate, respectively. The difference was slightly significant, but considered acceptable given the high variation in removal efficiency for the reported plants (Campo et al., 2013, Stamatis et al., 2010). In general, the STPWIN program

under the USEPA recommended setup was able to provide a worst-case estimate of wastewater removal efficiencies for pesticides. It was a viable tool to be used by SWPP for the screening-level aquatic risk assessment for products with DtD concerns.

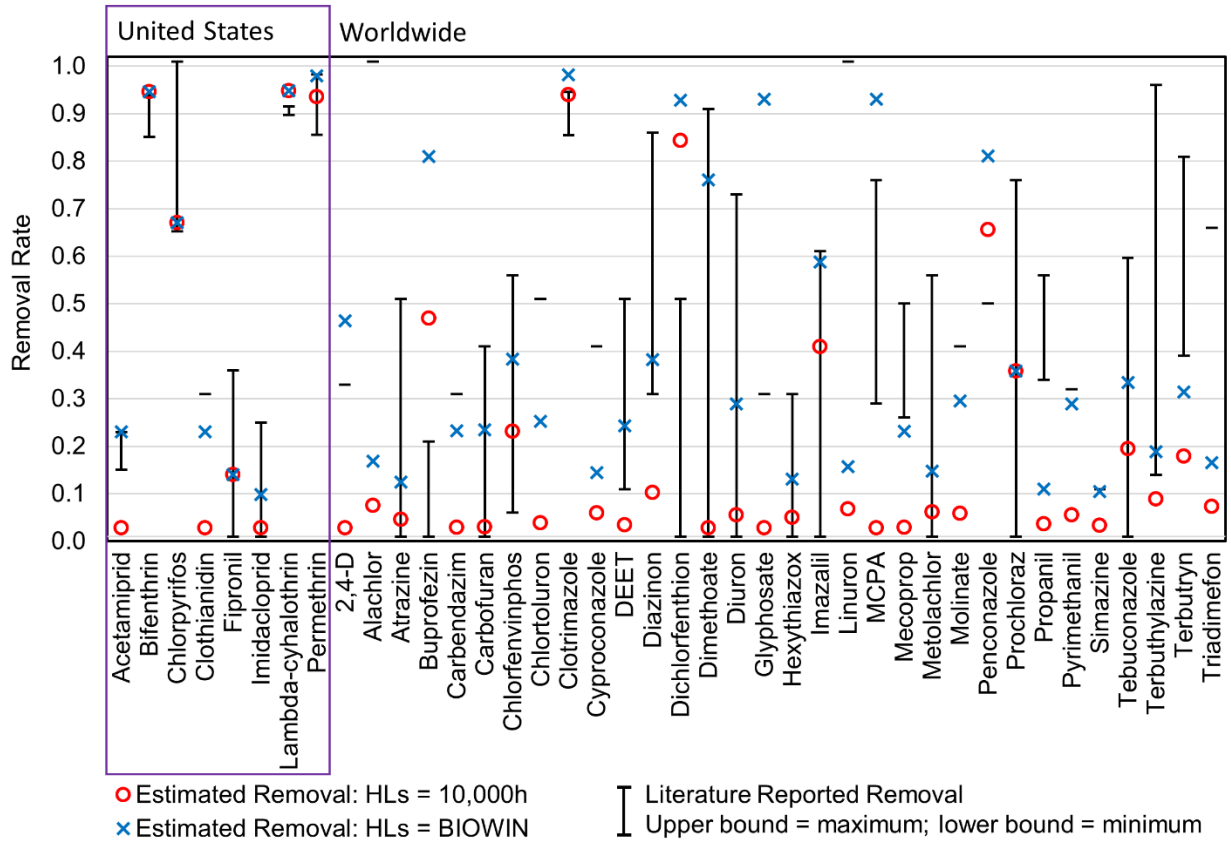


Figure B2. Comparison of pesticide removal rate between STPWIN estimates and literature reported values. References to reported removal: (Campo et al., 2013, Heidler and Halden, 2009, Köck-Schulmeyer et al., 2013, Luft et al., 2013, Luo et al., 2014, Margot et al., 2015, Rodriguez-Mozaz et al., 2015, Sadaria et al., 2016, Sadaria et al., 2017, Stamatis et al., 2010, Supowit et al., 2016, Weston et al., 2013). Detail information on model input (i.e., SMILES notation, logKow, solubility, vapor pressure, and Henry's Law constant) and reported removal efficiencies is presented in Tables C1-2.

Table B1. SMILES notation and physiochemical properties of the pesticides.

Chemical Name	Type	SMILES	Log Kow	Vapor Pressure	Solubility	Henry's Law Constant
Unit	-	-	-	mm Hg	mg/L	atm-m3/mol
Acetamiprid	Neonicotinoid	c1cc(Cl)ncc1CN(C)C(C)=NC#N	0.80	1.30E-09	3720	5.30E-13
Bifenthrin	Pyrethroid	c1ccccc1c2c(C)c(COC(=O)C3C(C)(C)C3C=C(Cl)C(F)(F)F)ccc2	6.40	1.63E-07	0.000014	7.20E-03
Chlorpyrifos	Organophosphate	CCOP(=S)(OCC)Oc1nc(Cl)c(Cl)cc1Cl	4.70	2.44E-05	1.39	6.60E-06
Clothianidin	Neonicotinoid	CN=C(NCC1=CN=C(S1)Cl)N[N+](=O)[O-]	0.70	1.00E-07	259	0.00E+00
Fipronil	Insecticide	Clc1cc(C(F)(F)F)cc(Cl)c1N2C(N)=C(S(=O)C(F)(F)F)C(C#N)=N2	3.50	2.80E-09	1.9	8.47E-11
Imidacloprid	Neonicotinoid	c1nc(Cl)ccc1CN2C(=NN(=O)=O)NCC2	0.57	1.00E-07	514	6.50E-11
Lambda-cyhalothrin	Pyrethroid	FC(F)(F)C(Cl)=CC1C(C)(C)C1C(=O)OC(C#N)c2cc(Oc3ccccc3)ccc2	7.00	3.78E-06	0.005	1.82E-07
Permethrin	Pyrethroid	CC1(C)C(C=C(Cl)Cl)C1C(=O)OCc3cccc(Oc2ccccc2)c3	6.10	1.42E-08	0.07	7.55E-08
2,4-D	Herbicide	O=C(O)COc(c(cc(c1)Cl)Cl)c1	-0.19	1.40E-07	29900	1.76E-12
Alachlor	Herbicide	CCc1cccc(CC)c1N(COC)C(=O)CCl	3.09	1.40E-05	200	2.48E-08
Atrazine	Herbicide	n(c(nc(n1)NC(C)C)NCC)c1Cl	2.65	2.34E-07	32.5	1.97E-09
Buprofezin	Insecticide	c1ccccc1N2CSC(=NC(C)(C)C)N(C(C)C)C2(=O)	4.31	6.65E-06	0.46	5.85E-06
Carbendazim	Fungicide	c1ccc2nc(NC(=O)OC)nc2c1	1.49	5.44E-09 *	2589 *	1.49E-12 *
Carbofuran	Insecticide	O=C(Oc(c(OC(C1)©C)c1cc2)c2)NC	1.66	2.00E-05	351	1.10E-06
Chlorfenvinphos	Organophosphate	CCOP(=O)(OCC)OC(=CCl)c1ccc(Cl)cc1Cl	4.15 *	9.41E-06 *	3.022 *	5.17E-08 *
Chlortoluron	Herbicide	CN©C(=O)Nc1ccc©c(Cl)c1	2.58 *	8.84E-06 *	329.1 *	7.94E-10 *
Clotrimazole	Fungicide	Clc1ccccc1C(c2ccccc2)(c3ccccc3)n4ccnc4	6.26 *	2.13E-09 *	0.02984 *	3.12E-08 *
Cyproconazole	Fungicide	c1cc(Cl)ccc1C(O)(C©C2CC2)Cn3ncnc3	3.25 *	5.71E-08 *	148 *	1.72E-10 *
DEET	Insect Repellent	O=C(N(CC)CC)c(cccc1C)c1	2.26 *	3.31E-03 *	666 *	2.08E-08 *
Diazinon	Organophosphate	O(P(OCC)(Oc(nc(nc1C)C(C)C)c1)=S)CC	3.30	2.40E-04	6	8.70E-07
Dichlorfenthion	Phosphorothioate	CCOP(=S)(OCC)Oc1ccc(Cl)cc1Cl	5.20 *	9.37E-05 *	0.408 *	4.12E-05 *
Dimethoate	Organophosphate	O=C(NC)CSP(OC)(OC)=S	0.70	1.85E-06	39800	1.40E-11
Diuron	Herbicide	O=C(N(C)C)Nc(ccc(c1Cl)Cl)c1	2.84	6.90E-08	36.4	5.10E-10
Glyphosate	Herbicide	OC(=O)CNCP(O)(O)=O	-4.77 *	7.50E-08	1160	1.44E-12
Hexythiazox	Ovacide	c1cc(Cl)ccc1C2SC(=O)N(C(=O)NC3CCCCC3)C2C	2.75	1.00E-08	0.12	2.29E-09 *
Imazalil	Fungicide	c1cc(Cl)cc(Cl)c1C(OCC=C)Cn2cncc2	4.20	2.69E-02	0.02	7.25E-08 *

Linuron	Herbicide	O=C(N(OC)C)Nc(ccc(c1Cl)Cl)c1	3.01	1.40E-06	77.2	5.80E-09
MCPA	Herbicide	O=C(O)COc(c(cc(c1)Cl)C)c1	0.02	3.00E-06	160100	5.50E-10
Mecoprop	Herbicide	O=C(O)C(Oc(c(cc(c1)Cl)C)c1)C	1.18	8.98E-04	734	3.46E-07
Metolachlor	Herbicide	CCc1cccc(C)c1N(C(C)COC)C(=O)CCl	2.93	3.14E-05	492.5	2.40E-08
Molinate	Herbicide	CCSC(=O)N1CCCCCC1	2.88	5.00E-03	970	1.30E-06
Penconazole	Fungicide	n1cncn1CC(c2c(Cl)cc(Cl)cc2)CCC	4.67 *	3.60E-05 *	1.547 *	4.49E-06 *
Prochloraz	Fungicide	Clc1cc(Cl)cc(Cl)c1OCCN(CCC)C(=O)n2cncc2	4.13 *	1.60E-08 *	1.344 *	7.58E-12 *
Propanil	Herbicide	CCC(=O)Nc1ccc(Cl)c(Cl)c1	2.29	7.78E-07	152	1.47E-09
Pyrimethanil	Fungicide	c1ccccc1Nc2nc(C)cc(C)n2	3.19 *	1.03E-04 *	165.8 *	2.46E-06 *
Simazine	Herbicide	n(c(nc(n1)NCC)NCC)c1Cl	2.09	2.21E-08	6.15	5.40E-10
Tebuconazole	Fungicide	c1cc(Cl)ccc1CCC(O)(C(C)(C)C)Cn2ncnc2	3.70	1.64E-08	32	1.24E-10
Terbuthylazine	Herbicide	n(c(nc(n1)NC(C)(C)C)NCC)c1Cl	3.27 *	1.61E-05 *	55.4 *	5.94E-09 *
Terbutryn	Herbicide	CCNc1nc(NC(C)(C)C)nc(SC)n1	3.65	1.68E-06	22	1.47E-08
Triadimefon	Fungicide	CC(C)(C)C(=O)C(Oc1ccc(Cl)cc1)n2cncn2	3.07	3.01E-07	64	9.00E-10

* Values were not available in CDPR's internal chemistry database and estimated by using EPI Suite based on SMILES.

Table B2. Plant-scaled removal efficiencies collected from literatures.

Chemical Name	Removal Efficiency (%)		Treatment Type	No. of Facility	Location	Sample Year	References
	Min	Max					
Acetamiprid	14	22	Secondary + optional tertiary	1	US	2014	(Sadaria et al., 2016)
Bifenthrin	84.2	93	Secondary	1	US	2010-2012	(Weston et al., 2013)
Chlorpyrifos	64.29	100	Secondary	1	US	2010-2012	(Weston et al., 2013)
Clothianidin	30	30	Secondary + optional tertiary	1	US	2014	(Sadaria et al., 2016)
Fipronil	0	35	Secondary	34	US	2005-2015	(Heidler and Halden, 2009, Sadaria et al., 2017, Supowit et al., 2016)
Imidacloprid	0	24	Secondary + optional tertiary	9	US	2014-2015	(Sadaria et al., 2016, Sadaria et al., 2017)
Lambda-cyhalothrin	88.8	90.5	Secondary	1	US	2010-2012	(Weston et al., 2013)
Permethrin	84.6	97.2	Secondary	1	US	2010-2012	(Weston et al., 2013)

2,4-D	32	32	Secondary + optional tertiary	3	Spain	2007-2009	(Köck-Schulmeyer et al., 2013)
Alachlor	100	100	Secondary + optional tertiary	3	Spain	2007-2009	(Köck-Schulmeyer et al., 2013)
Atrazine	0	50	Secondary + optional tertiary	Multiple	EU & WW	2008-2013	(Campo et al., 2013, Luo et al., 2014, Margot et al., 2015)
Buprofezin	0	20	Secondary + optional tertiary	4	Spain	2010	(Campo et al., 2013)
Carbendazim	30	30	Secondary	Multiple	WW	2008-2013	(Margot et al., 2015)
Carbofuran	0	40	Secondary + optional tertiary	4	Spain	2010	(Campo et al., 2013)
Chlorfenvinphos	5	55	Secondary + optional tertiary	4	Spain	2010	(Campo et al., 2013)
Chlortoluron	50	50	Secondary + optional tertiary	3	Spain	2007-2009	(Köck-Schulmeyer et al., 2013)
Clotrimazole	84.5	93.6	Secondary + optional tertiary	Multiple	EU	2008-2013	(Luo et al., 2014)
Cyproconazole	40	40	Secondary	1	Greece	2007-2008	(Stamatis et al., 2010)
DEET	10	50	Secondary	Multiple	WW	2006-2015	(Merel and Snyder, 2016)
Diazinon	30	85	Secondary + optional tertiary	Multiple	EU & WW	2007-2013	(Campo et al., 2013, Köck-Schulmeyer et al., 2013, Luo et al., 2014, Margot et al., 2015, Rodriguez-Mozaz et al., 2015)
Dichlorfenthion	0	50	Secondary + optional tertiary	4	Spain	2010	(Campo et al., 2013)
Dimethoate	0	90	Secondary + optional tertiary	7	Spain	2007-2010	(Campo et al., 2013, Köck-Schulmeyer et al., 2013)
Diuron	0	72	Secondary + optional tertiary	Multiple	EU & WW	2007-2013	(Campo et al., 2013, Köck-Schulmeyer et al., 2013, Luo et al., 2014, Margot et al., 2015)
Glyphosate	30	30	Secondary	Multiple	WW	2008-2013	(Margot et al., 2015)
Hexythiazox	0	30	Secondary + optional tertiary	4	Spain	2010	(Campo et al., 2013)
Imazalil	0	60	Secondary + optional tertiary	4	Spain	2010	(Campo et al., 2013)
Linuron	100	100	Secondary	1	Spain	2009	(Rodriguez-Mozaz et al., 2015)
MCPA	28	75	Secondary + optional tertiary	Multiple	EU & WW	2007-2014	(Köck-Schulmeyer et al., 2013, Margot et al., 2015, Rodriguez-Mozaz et al., 2015)
Mecoprop	25	49	Secondary + optional tertiary	Multiple	EU & WW	2007-2014	(Köck-Schulmeyer et al., 2013, Margot et al., 2015, Rodriguez-Mozaz et al., 2015)

Metolachlor	0	55	Secondary + optional tertiary	4	Spain	2010	(Campo et al., 2013)
Molinate	40	40	Secondary + optional tertiary	4	Spain	2010	(Campo et al., 2013)
Penconazole	49	49	Secondary	1	Greece	2007-2008	(Stamatis et al., 2010)
Prochloraz	0	75	Secondary + optional tertiary	4	Spain	2010	(Campo et al., 2013)
Propanil	33	55	Secondary + optional tertiary	7	Spain	2007-2010	(Campo et al., 2013, Köck-Schulmeyer et al., 2013)
Pyrimethanil	31	31	Secondary	1	Greece	2007-2008	(Stamatis et al., 2010)
Simazine	10	10	Secondary + optional tertiary	3	Spain	2007-2009	(Köck-Schulmeyer et al., 2013)
Tebuconazole	0	58.7	Secondary + optional tertiary	Multiple	EU	2007-2013	(Luo et al., 2014, Stamatis et al., 2010)
Terbuthylazine	13	95	Secondary + optional tertiary	Multiple	EU	2007-2014	(Köck-Schulmeyer et al., 2013, Margot et al., 2015, Rodriguez-Mozaz et al., 2015)
Terbutryn	38	80	Secondary + optional tertiary	Multiple	EU	2010-2014	(Campo et al., 2013, Luft et al., 2013, Margot et al., 2015)
Triadimefon	65	65	Secondary	1	Greece	2007-2008	(Stamatis et al., 2010)

Appendix C: Methodology for estimating f_1 for pet products

Here we show the methodology for estimating f_1 for pet products based on the statewide sales data reported to CDPR. The method is based on the assumption that the number of users projected to use the new AI would not exceed the maximum number of users who are currently using an existing AI registered for a similar use pattern. The use of existing AIs for the similar use pattern could be estimated from CDPR's statewide product sales data. Note that the sales data is not externally available. The f_1 factor for pet products is determined as a function of the number of pets treated with the existing most popular AI and the number of treated pets that would be washed during an application interval. The calculation is shown as follows.

First, products registered for treatments on dog/cat were identified from CDPR's Product/Label database. The criteria used for product identification is demonstrated in Table C1 and C2. Note that products with combined use on pet and livestock (and their premises) were not included. Pet products were further divided into cat products and dog products by using criteria demonstrated in Table C1.

Table C1. Criteria used to identify dog/cat treatment products from CDPR's Product/Label database.

Use Pattern	Criteria
Pet Treatment	1. Site Code = PET (Table A-2) ONLY 2. If Site Code = PET + Other Sites, then Product Name contains [DOG(S), CAT(S), PUPPIES, KITTENS, PET(S)] AND not contain [HORSE(S), GARDEN, YARD, REPELLENT, FARM, POULTRY, GOAT, BARN, CATTLE, LIVESTOCK, MASTER LABEL]
Cat product	Site code = CAT (Table A-2: Cat = X) ONLY
Dog product	Difference between pet products and cat products

Table C2. Site codes associated with dog/cat products.

Site Code	Description	Dog	Cat
54000	PETS (ALL OR UNSPEC)	X	X
54001	CATS (KITTENS) (PET)		X
54002	CATS (ALL OR UNSPEC) (PET)		X
54003	DOGS (ALL OR UNSPEC) (PET)	X	
54004	DOGS (PUPPIES) (PET)	X	
54005	CANINES (PET)	X	
54007	DOGS (ADULT) (PET)	X	
54008	CATS (ADULT) (PET)		X
56002	DOGS (SPECIAL – E.G. MILITARY, SHOW)	X	
56011	DOGS (LAB)	X	
56028	CATS (LAB)		X

Second, the statewide sales data in 2014-2016 was retrieved for the identified pet products and the annual average mass of AIs sold for pet products was calculated by using the product sales data and the AI percentage of the product. Table C3 shows the top-3 sales AIs found in California for dog and cat products, respectively. To determine the number of pets treated by

each of the AIs, the most popular product corresponding to the AI was identified from the sales data and the label-allowed maximum application rate and frequency were retrieved from the product label. The number of dogs or cats treated by an AI was calculated as the annual average mass of the AI sold divided by the product of the maximum application rate and the frequency of the top-sales product corresponding to the AI. Here we used the most popular product to represent the general application rate and frequency of other dog or cat products that contain the same AI. The number of dogs or cats that are treated with the top-3 sales AIs is demonstrated in Table C3. The maximum number (highlighted in gray) was considered to be the best available estimate of the maximum number of pets that would be treated by a new AI with similar use patterns.

Table C3. Number of cats and dogs treated by the top-3 sales AIs.

Pet	AI	Avg. Mass Sold (kg[AI]/yr) *	Median Appl. Rate (kg[AI]/trt) **	Appl. Freq. (trt/yr)	No. of Pets Treated
Cat	Etofenprox	7844	6.21E-04	12	1,052,966
	Fipronil	1143	5.02E-05	12	**1,896,600**
	S-Methoprene	897	6.05E-05	12	1,235,926
Dog	Permethrin	31287	1.10E-03	12	2,370,066
	Etofenprox	12855	1.32E-03	12	811,298
	Fipronil	6000	2.01E-04	12	**2,488,673**

* Note that for wet-formulation products, the mass sold is reported in the unit of gallon. Conversion to the unit of kg was conducted by using the equation: $Q_{lbs} = Q_{gallon} \times 8.33 \times SpecGravity$, where Q_{lbs} and Q_{gallon} are the mass of product sold in the unit of pounds and gallon, respectively. *SpecGravity* is the specific gravity of a product. The same conversion was also applied to application rate which is measured in the unit of US fluid ounces or ml.
** The label-allowed maximum application rate varies as a pet's age and weight. The median application rate is used here to represent the average use.

At last, the value of f_1 for pet products was computed as the maximum number of dogs or cats treated by the most popular existing AI divided by the total number of dogs or cats in California. The numbers of pets in California were derived from the national pet ownership survey conducted by the American Veterinary Medical Association (AVMA) in 2018 (AVMA, 2018). Table C4 shows the number of pet-owning households and pets in California. The numbers were derived from the AVMA national pet ownership statistics based on California population. With the number of pets treated with the most popular existing AI (Table C3), we obtained the fraction of pets treated with the most popular existing AI, which is a proxy to the fraction of pets that is projected be treated with the AI under review. The pets need to be washed in order for the pesticides to be transported DtD. According to Teerlink et al. (2017), it is reasonable to assume that up to 25% of the treated pets would be washed during an application interval, which is about one month for pet products. As such, the factor f_1 can be computed as the product of the fraction of pets treated with the most popular existing AI (0.2 and 0.28 for cat and dog products, respectively) and the fraction of treated pets that would be washed during an application interval (0.25), which yielding $f_1 = 0.05$ and 0.07 for cat and dog products, respectively.

Table C4. Pet ownership in California and the estimation of f_1 for pet products.

Statistics	Cats	Dogs
Number of pet-owning households *	4,625,131	5,553,201
Number of pets *	9,706,690	8,885,121
Number of pets treated with the most popular existing AI	1,896,600	2,488,673

Fraction of pets treated with the most popular existing AI	0.2	0.28
Fraction of treated pets that would be washed during an application interval	0.25	0.25
Factor f_1	**0.05**	**0.07**

* The numbers were derived from the national pet ownership statistics obtained by the AVMA 2018 survey and converted to the California-based data based on population in California. The estimate population in CA as of July 1, 2018 is 39,557,045, according to the US Census Bureau.

Appendix D: Data and references used for model validation.

Table D1. Values of model input variables used for model validation against CDPR's previous registration evaluation.

(a) Physiochemical properties, e-fate variables, and ecotoxicity

Pesticide	SOL	KOC	HYDRO	AERO	ANAER	FD	AERO_W	ANAER_W	MWT	VP	AQPHOT	SPHOT	TOX	TOXSED
Unit	mg/L	L/kg[OC]	day	day	day	day	day	day	g/mole	torr	day	day	µg/L	µg/L
Deltamethrin	0.0002	533750	0	23.55	33.9	54.5	86.1	139	505.2	9.30E-11	74.85	9.745	0.0037	3.8 [a]
Fipronil	1.9	668.75	28	379	123	131	16.42	160	437.14	2.80E-09	0.33	34	0.14	NA
Indoxacarb	0.2	4928.571	38	25.225	190	20.1	37.05	211.75	527.8	1.00E-07	1	139	54.2	720 [a]

Metal	SOL	Land-phase Kd	Water-phase Kd	TOX	TOXSED
Unit	mg/L	L/kg[particle]	L/kg[particle]	µg/L	µg/kg[dry weight]
Copper	1	501	15849	0.48	151000

[a] TOXSED is available in unit µg/kg[dry weight].

References for physiochemical properties and e-fate variables: CDPR's internal Pesticide Chemistry Database (Bergin, 2010). If multiple values were reported, the median was used for model input. For parameters that were not readily available in the database, including KOC, AERO_W, ANAER_W, and MWT, values were retrieved from the USEPA ERA reports – deltamethrin and permethrin (USEPA, 2016b), fipronil (USEPA, 2011a), imidacloprid (USEPA, 2016a), and indoxacarb (USEPA, 2017b). For etofenprox, all values were from USEPA (2008). References for ecotoxicity: fipronil (CDPR, 1998), permethrin (USEPA, 2016b), etofenprox (USEPA, 2008), imidacloprid (USEPA, 2016a), indoxacarb (USEPA, 2017b).

(b) EPI Suite STPWIN input variables and model results

Chemical	log Kow	Vapor Pressure	Solubility	Henry	SMILES	Waste water Removal			
Unit	-	mm Hg	mg/L	atm-m3/mol	-	Total	biodegradation	Sludge adsorption	Air
Deltamethrin	5.43	1.00E-07	0.0002	3.30E-04	CC1(C)C(C=C(Br)Br)C1C(=O)OC(C#N)c3cccc(Oc2ccccc2)c3	0.8762	0.0073	0.8584	0.0105

Fipronil	3.50	2.80E-09	1.9	8.47E-11	Clc1cc(C(F)(F)F)cc(Cl)c1N2C(N)=C(S(=O)C(F)(F)F)C(C#N)=N2	0.1303	0.0018	0.1285	0
Indoxacarb	4.65	1.00E-07	0.2	6.00E-10	COC(=O)C12CC3=C(C1=NN(CO2)C(=O)N(C4=CC=C(C=C4)OC(F)(F)F)C(=O)OC)C=CC(=C3)Cl	0.6362	0.0058	0.6305	0

Table D2. Values of physiochemical properties and e-fate variables of selected pesticides inputted to the DtD model for validation against monitoring data.

Pesticide	SOL	KOC	HYDRO	AERO	ANAER	FD	AERO_W	ANAER_W	MWT	VP	AQPHOT	SPHOT
Unit	mg/L	L/kg[OC]	day	day	day	day	day	day	g/mole	torr	day	day
Acetamiprid	3720	244.8929	52.9	28.7	330	13.55	1974	4116	222.68	1.31E-09	34	17
Bifenthrin	1.40E-05	371000	0	191	179.5	109.5	466.2	650.2	422.9	1.63E-07	11.1	104
Chlorpyrifos	1.39	6040	72.1	86.2	135.5	46	91.2	202.7	350.57	2.44E-05	52.65	10
Clothianidin	259	123.3333	0	830	26.7	561.5	180.05	27	249.7	1E-07	0.138	8.21
Cyfluthrin	0.0023	124000	193	59.5	33.6	13.5	44.6	25.6	434.29	1.5E-08	8.36	4.35
Cypermethrin	0.004	310000	555	23	76.65	27	25.5	53.1	416.3	1.30E-09	272	29.55
Deltamethrin	0.0002	533750	0	23.55	33.9	54.5	86.1	139	505.2	9.30E-11	74.85	9.745
Esfenvalerate	0.00131	436515.8	0	105	142.5	31.05	80.4	138	419.9	1.50E-09	9	1391
Fipronil	1.9	668.75	28	379	123	131	16.42	160	437.14	2.80E-09	0.33	34
Imidacloprid	514	266	0	997	27.1	64.8	159	33	255.7	1.00E-07	0.04	38.9
Lambda-cyhalothrin	0.005	297500	480	61	128	23.35	47.9	6080	449.86	1.56E-09	13	274
Permethrin	0.07	76800	0	211	50.05	38.35	56.7	193	391.3	1.42E-08	106.55	289

Value of parameters were retrieved from CDPR's internal Pesticide Chemistry Database (Bergin, 2010). If multiple values were reported, the median was used for model input. For parameters that were not readily available in the database, including KOC, AERO_W, ANAER_W, and MWT, values were retrieved from the USEPA ERA reports – acetamiprid (USEPA, 2012b), bifenthrin, cyfluthrin, cypermethrin, deltamethrin, esfenvalerate, lambda-cyhalothrin, and permethrin (USEPA, 2016b), chlorpyrifos (USEPA, 2017a), clothianidin (USEPA, 2011b), fipronil (USEPA, 2011a), and imidacloprid (USEPA, 2016a).

Table D3: Model inputs and outputs, and comparison to monitoring data

Pesticide	99th percentile of concentrations in effluent	Effluent sample size	Aqueous EEC	99th percentile of monitoring concentrations
Unit	µg/L	#	µg/L	µg/L
Acetamiprid	2.096	5	2.12	3.09
Bifenthrin	7.184	92	0.86	0.40
Chlorpyrifos	19.68	27	18.39	0.32
Clothianidin	338.948	5	329.6	0.86
Cyfluthrin	3.288	90	1.02	0.06
Cypermethrin	13.44	90	1.84	0.07
Deltamethrin	1.58	81	0.13	0.05
Esfenvalerate	1.22	81	0.12	0.04
Fipronil	105.65	16	101.56	0.26
Imidacloprid	300.364	13	274.11	3.09
Lambda-cyhalothrin	5.1	81	0.9	0.03
Permethrin	161.1	90	71.09	0.20

Sources of concentrations in effluent: acetamiprid (Sadaria et al., 2016), bifenthrin (Markle et al., 2014, Parry et al., 2015, Weston and Lydy, 2010, Weston et al., 2013), chlorpyrifos (Weston and Lydy, 2010, Weston et al., 2013), clothianidin (Sadaria et al., 2016), cyfluthrin, cypermethrin, permethrin (Markle et al., 2014, Weston and Lydy, 2010, Weston et al., 2013), deltamethrin, esfenvalerate, lambda-cyhalothrin (Markle et al., 2014, Weston and Lydy, 2010), fipronil (Sadaria et al., 2017), imidacloprid (Sadaria et al., 2016, Sadaria et al., 2017).