Department of Pesticide Regulation
Environmental Monitoring Branch
1001 I Street, P.O. Box 4015
Sacramento, CA 95812-4015

Validating PREM performance for modeling outdoor uses of pyrethroids in residential areas of California

Yuzhou Luo, Robert Budd, Yina Xie, and Xuyang Zhang

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1 Introduction

Pyrethroid insecticides are highly toxic to aquatic organism and frequently detected in urban surface waters and sediments at levels that are deleterious to sensitive species (Budd et al., 2020; Ruby, 2013; Stehle et al., 2019; Sy et al., 2022). Over all detected pyrethroids, bifenthrin accounts for majority of detections and toxic response. Since 2012, a series of regulations have been adopted to reduce the applied mass of pyrethroids and associated runoff potentials from urban areas, including the surface water regulations by California Department of Pesticide Regulation (CDPR, 2012) and label changes by U.S. Environmental Protection Agency (USEPA, 2013). In addition to the regulations on pyrethroids, more restrictions are required for the use of bifenthrin according to the label amendment memorandum of agreement (MOA) (CDPR, 2011).

In 2020, USEPA issued the ecological risk mitigation proposal for 23 pyrethroids and pyrethrins chemicals (USEPA, 2020). The proposal refined and specified the requirements on the mitigation practices such as the dimension of spot treatment, applications before forecasted rainfall, and spray drift control. Compared to the previous regulations on urban outdoor uses, there were no significant changes especially on the restrictions intended to limit pyrethroid applications on impervious surfaces. In addition, the proposal is being incorporated into the new labels of pyrethroids products. Therefore, this study focuses on the "current" regulations which are supposed to be fully implemented in California field conditions and sufficiently represented by monitoring data, including the surface water regulation, 2013 label changes, and bifenthrin label amendment MOA.

In this study, the Pesticide Registration Evaluation Model (PREM) is configured to model the urban outdoor uses of pyrethroids in residential areas of California by following the mitigation practices required in current labels and regulations. The model predictions are compared with the measurements representing the "current conditions" of pyrethroids observed in California's urban waterways. The representative observations are derived as the upper percentiles of the measurements in water column and sediment from the urban monitoring network operated by CDPR's Surface Water Protection Program (SWPP). The modeling performance is evaluated based on a P/O ratio, where P is the model predictions reported as the estimated environmental concentration (EEC) and O is the representative concentration observed in monitoring data. As a

regulatory model, PREM is parameterized with conservative estimates of model input data for chemistry, pesticide applications, and environmental descriptions. Therefore, the model is expected to reasonably overestimate the observations, roughly defined as the P/O ratio between 1 to 10 (i.e., overestimation within an order of magnitude) (CDPR, 2017). The same criteria have been used in the previous studies for model validation for pyrethroids and other pesticides (Budd and Luo, 2016; CDPR, 2020; Luo, 2017a, b, c; Xie et al., 2018).

The objective of this study is to validate the modeling mechanisms and configurations incorporated in PREM for a reasonable representation of the use, fate, and transport of pyrethroids in the residential areas of California. The validated model with acceptable performance will be used to predict the relative changes of EEC before and after the implementation of proposed mitigation practices (i.e., mitigation effectiveness) to match the mitigation goal.

2 Modeling overview

2.1 Urban modeling approach in PREM

The PREM modeling on urban pesticide uses of pesticides is based on the California-specific modeling scenarios developed by SWMP (Luo, 2014a). An urban watershed of 10 ha is modeled with four types of surfaces: (1) pervious surfaces not subject to dry-weather runoff (including native vegetation and gardens with drip irrigation), (2) impervious surfaces not subject to dry-weather runoff (walls, roofs, roads), (3) pervious surfaces with dry-weather runoff (lawns), and (4) impervious surfaces with dry-weather runoff (paved areas adjacent to lawns such as sidewalk and part of driveway). Each type of surfaces is characterized according to the treated area fraction over the watershed. For example, broadcast applications to lawns are modeled on surface (3) with a treated area fraction of 12%, i.e., 12% of the 10-ha watershed will be treated and the treated area is modeled as surface (3).

Later, the consideration of hydrological connectivity was introduced (Luo, 2017d) for more realistic modeling on pesticide runoff from impervious areas. The updated model assumed that only the impervious surfaces in the front yard of a house could result in direct runoff into storm drains. Other impervious surfaces will drain through adjacent pervious surfaces. Therefore, the fifth type of surfaces for modeling is defined for pesticide applications to impervious surfaces that are not directly connected to the storm drains. For example, the applications on walls and walkways in the back yard are modeled by a treated area fraction on surface (5).

In summary, the PREM modeling for urban pesticide uses is based on a set of treated area fractions over the five types of surfaces according to the application methods required in the product labels. Common application methods and the corresponding treated are fractions have been predefined in PREM, including spot treatment or crack and crevice treatment, lawn treatment, perimeter treatment, and applications to general paved areas (Luo et al., 2019). For more complex application methods especially mitigation practices, PREM also allows user to manually adjust the treated area fractions according to the specific restrictions. In the previous modeling studies on fipronil (Budd and Luo, 2016; Budd et al., 2017) and bifenthrin (Luo, 2017b, c), for example, various application methods were evaluated by PREM for aquatic exposure assessments. The same approach is used in this study for mathematically representing

the mitigation practices for the urban outdoor uses of pyrethroids as required by the current labels and regulations.

2.2 Previous modeling efforts

The pyrethroid detections in the SWPP's urban monitoring network are grouped to represent the "historical" and "current" conditions of pyrethroid insecticides in the urban areas of California. The current condition represents the current pyrethroid application practices after the regulations intended to limit the applied mass and runoff potential of pyrethroids in urban areas, including the surface water regulations, label changes, and bifenthrin label amendment MOA. The historical condition reflects the historical pyrethroid application practices before the regulations.

The previous studies (Luo, 2017b, c) evaluated the PREM modeling capability to replicate the historical condition of pyrethroids (with bifenthrin as a test agent) derived from the monitoring data in 2012 and before. The historical application methods were modeled as perimeter treatments of 7 ft on horizontal surfaces and 3 ft on vertical surfaces (Jorgenson et al., 2013; USEPA, 2012). By comparing the model predictions and observation data, the resulting P/O ratio was 1.6, suggesting a conservative and reasonable estimation of the historical uses of bifenthrin in urban outdoor settings.

For the current application practices, the 2017 studies (Luo, 2017b, c) also modeled the mitigation effects of the label changes and regulations for urban outdoor uses of pyrethroids. At the time of the previous studies, however, the surface water monitoring data were not sufficient to validate the modeling results. Other modeling approaches for urban outdoor uses of pyrethroids under the current application practices were presented in the ecological risk assessments (ERAs) by USEPA and Pyrethroids Working Group (PWG) (Giddings et al., 2016; USEPA, 2016). Based on the reviews by SWPP (CDPR, 2017; Luo, 2017c), some of the modeling assumptions (e.g., only one application per year, underestimated area of treatment on impervious surfaces) may underpredict the concentrations of pyrethroids in the urban waterways of California.

2.3 Model configurations in this study

In this study, seven pyrethroids are selected for model simulations and validations in urban residential settings of California: bifenthrin (CHEM_CODE=2300), cyfluthrin (2223), cypermethrin (2171), deltamethrin (3010), esfenvalerate (2321), lambda-cyhalothrin (2297), and permethrin (2008). The selection of these chemicals is based on the considerations of the reported uses for structural pest control and landscape maintenance, the number of products registered for urban outdoor uses, and the availability of monitoring data in the SWPP's long-term monitoring sites. Isomers of the selected chemicals are also considered in the preparation of input data including product label review, physicochemical properties, Pesticide Use Reporting (PUR) data, and monitoring data. The same set of chemicals were modeled in the ERAs for urban outdoor uses of pyrethroids by USEPA and PWG (Giddings et al., 2016; USEPA, 2016). USEPA also modeled fenpropathrin, for which there is no active product registered in California for urban outdoor uses.

PREM is configured to predict the EECs of pyrethroids from their urban outdoor uses under the California residential settings. Model simulations are based on the residential settings for evaluating urban pesticide uses (Luo, 2014a). The PREM option for the adjustment on application extent is used for all pyrethroids modeling. With this option, it's assumed that 75.9% of households would use outdoor pest control products based on the survey results in California (Winchell, 2013). The mitigation practices required in the current regulations, especially those intended to limit the applications of pyrethroids on impervious surfaces, are mathematically represented in the modeling by adjusting the treated surface areas (Table 1).

Table 1. Application restrictions in the regulations and label changes for pyrethroids and their modeling representation in PREM

Surfaces	Application restrictions	Modeling representation in PREM
Impervious horizontal surfaces	"As a spot or crack and crevice treatment"	Modeled as spot or crack and crevice treatment over impervious horizontal surfaces.
Windows and doors	"(1) spot treatment, (2) crack and crevice treatment, or (3) pin stream treatment of one-inch wide or less"	Modeled as pin stream treatment of one-inch wide to garage doors. The same assumption was used in the ERAs for pyrethroids by USEPA (2016) to model applications around potential pest entry points.
Vertical structural surfaces	"Perimeter band treatment up to a maximum height of two feet above the grade level."	Modeled as two-foot perimeter treatment to walls.
(*Bifenthrin only*) Vertical non-porous surfaces	Prohibit applications to the "sections that abut driveways or sidewalks that's drain into streets."	Assume no applications to the walls and garage doors that that could results in runoff into storm drains.
Horizontal pervious surfaces	"Broadcast treatment but not within two feet from any horizontal impervious surface. Pin stream treatment of one-inch wide or less may be made within the two-foot area."	Assume no incidental applications to adjacent impervious surfaces during treatment to pervious surfaces (lawns, trees, and ornamentals).

Two separate modeling scenarios are developed for bifenthrin vs. other pyrethroids. The scenario for bifenthrin has been documented in the previous study for urban modeling of bifenthrin (Luo, 2017b). The difference between the two scenarios is that, in addition to the label changes and surface water regulations for all pyrethroids, bifenthrin is also regulated by the bifenthrin label MOA between CDPR and the bifenthrin manufacturers (CDPR, 2011). The surface water regulations allow pyrethroid applications to a garage door by spot, crack and crevice, or pin stream treatment, while the bifenthrin MOA prohibits bifenthrin applications to a garage door and other "sections that abut driveways or sidewalks that drain into streets". Therefore, bifenthrin is modeled with less treated area compared to other pyrethroids. The maximum treated area fractions, i.e., the treated area (on both horizontal and vertical surfaces) divided by the total watershed area, are 19.4% for bifenthrin and 21.0% for other pyrethroids. For comparison, the treated area fraction for the historical application methods of pyrethroids was 34.6%.

3 Input data for model simulation and validation

3.1 Representative observed concentrations for the current condition

SWPP has monitored pyrethroids in surface waters receiving urban runoff throughout California since 2009 (Budd et al., 2020; Ensminger et al., 2013). The surface water monitoring prioritization (SWMP) model (Luo and Deng, 2015) is used for a targeted design approach in the site selection by considering the reported pesticide uses in urban areas, physiochemical properties, aquatic life benchmarks, and watershed characteristics. The monitoring sites are located either at storm drain discharge points (site type as "storm drain") or within main stem receiving waters ("waterway"). This study uses the monitoring data in waterways for comparison with the PREM predictions (i.e., EECs in a template receiving water body). The same approach was used in the previous studies for exposure assessments and model validation (Budd et al., 2020; Luo, 2014a, 2017b).

This study is based on the monitoring data collected during 2009-2021. Measurements in the water column are reported as whole-water concentrations. For comparison with the modeling results of EECs predicted as aqueous concentrations (Young, 2019), the whole-water concentration is converted to freely dissolved concentration,

$$C_{dissolved} = \frac{C_{total}}{1 + (K_{OC} \times [POC]) + (K_{DOC} \times [DOC])}$$

where C_{total} (ng/L) is the reported whole-water concentration of a pyrethroid in the water sample, $C_{dissolved}$ (ng/L) is the converted freely dissolved concentration, K_{OC} (L/kg) is the organic carbon-water partition coefficient for the pyrethroid, K_{DOC} (L/kg) is the dissolved organic carbon-water partition coefficient (L/kg), and [POC] and [DOC] (kg/L) are the concentrations of particulate organic carbon and dissolved organic carbon in the water sample, respectively. [POC] is usually not reported in surface water monitoring, and could be estimated from the reported concentration of total organic carbon or [TOC] (kg/L) as [POC]=[TOC]-[DOC].

The same approach is used by the Central Valley Regional Water Quality Control Board (CVRWQCB, 2019) to convert the monitoring data for comparison with the water quality objectives. CVRWQCB suggested the use of K_{OC} and K_{DOC} values derived from solid-phase microextraction (SPME) (Table 2). Compared to the liquid-liquid extraction (LLE) method, the SPME technology is more suitable for hydrophobic chemicals like pyrethroids for the quantification of freely dissolved chemical concentrations (Chickering, 2014; Giddings et al., 2016).

Table 2. K_{OC} and K_{DOC} values (L/kg) derived from solid-phase microextraction (SPME) (Chickering, 2014; CVRWQCB, 2019)

Pyrethroid	K_{OC} (SPME)	K_{DOC} (SPME)
Bifenthrin	4,228,000	1,737,127
Cyfluthrin	3,870,000	2,432,071
Cypermethrin	3,105,000	762,765
Deltamethrin	4,350,000	1,002,076
Esfenvalerate	7,220,000	1,733,158
Lambda-cyhalothrin	2,056,000	952,809
Permethrin	6,075,000	957,703

The monitoring data in sediment are reported on a dry-weight (dw) basis (µg/kg[dw]), and converted in this study to organic carbon (OC)-normalized concentrations (µg/kg[OC]),

$$C(\mu g / kg[dw]) = \frac{C(\mu g / kg[OC])}{[TOC]}$$

Based on the converted monitoring data, the 90th and 95th percentiles are calculated for the samples collected in 2017 and after ("2017+"), and the results are considered as the representative observed concentrations for the current condition with the current labels and regulations. The approach for model validation with the upper percentiles of monitoring data has been widely used in the ecological risk assessments for pyrethroids by USEPA (2016), PWG (Giddings et al., 2015; Giddings et al., 2016), and CDPR (Luo, 2017a, b, c, 2019).

Table 3. Upper percentiles of monitoring data in 2017 and after for SWPP samples in urban waterways

	Freely dissolved concentration in water column (ng/L)		OC-normalized concentration in sediment (µg/kg[OC])	
	P90	P95	P90	P95
Bifenthrin	2.36	3.91	1650.4	1864.2
Cyfluthrin	0.64	1.21	217.6	304.1
Cypermethrin	0.42	1.67	54.1	92
Deltamethrin	1.06	3.25	832.1	905.4
Esfenvalerate	ND (P98=0.26)	ND (P99=0.38)	98.3	163.7
Lambda-cyhalothrin	0.27	0.61	119.9	195.3
Permethrin	1.47	3.69	326.5	568.2

Notes: P90 = the 90th percentile, and P95 = the 95th percentile. For esfenvalerate in the water column, both P90 and P95 are below the reporting limit (labelled as "ND"), so its 98th (P98) and 99th (P99) percentiles are used in the model validation.

In addition to model validation, the representative concentrations of the current condition would be also used to determine the relative reductions required to meet a given mitigation goal (usually provided as a set of toxicity thresholds or target concentrations). The required reductions are dependent on the selection of the toxicity value, which will be later determined in the

mitigation studies. The monitoring data in sediment and the conversion to OC-based concentrations are independent to the assumption and selection of partitioning coefficients (such as those in Table 2 for the water column), and thus would be more reliable in the determination of the required reductions.

The use of "2017+" to represent the current condition is justified by the following considerations. First, this is consistent with the previous model validation study for the uses of pyrethroids in agricultural areas of California (Luo, 2017a). A three-year transition period was assumed before the full implementation of label changes and required mitigation practices. For agricultural uses of pyrethroids, the label changes were required in 2008 (USEPA, 2008), so the monitoring data of 2012 and after were considered for the current conditions of pyrethroids in agricultural areas (Luo, 2017a). For urban uses, the latest regulation was proposed as label changes in 2013 (USEPA, 2013), so the monitoring data of 2017 and after are used to represent the current condition of pyrethroids in urban area.

Second, the data analysis results from the previous study (Budd et al., 2020) confirmed that no significant trends could be detected based on the monitoring data collected in the urban waterways of California during 2008 to early 2018. In this study, the proposed three-year transition period is further confirmed by the results of trend analysis on the monitoring data in sediment. Figure 1 showed the 90^{th} percentiles of bifenthrin over the periods after the regulations. Results for the 95^{th} percentiles and for other pyrethroids are provided in Appendix I. In each individual year, the monitoring data are not sufficient to derive reliable statistics. Therefore, the monitoring data over a period of consecutive years (such as 2015+ for the years of 2015 and after) are used to represent the overall conditions of pyrethroid concentrations in surface water for exposure assessments. In addition, the use of multi-year data would moderate the effects of hydro-climatologic dynamics over years on the pesticide runoff from the treated urban areas. A significant decrease of the resulting percentiles between two periods (such as 2015+ vs. 2016+ in Figure 1) indicates a high possibility that the high concentration measurements in the previous year were not observed in later years. It's worthy to note that the statistics for the recent years of 2018+ and 2019+ are associated with greater uncertainty due to the smaller sizes of available monitoring data, compared to other periods with more data.

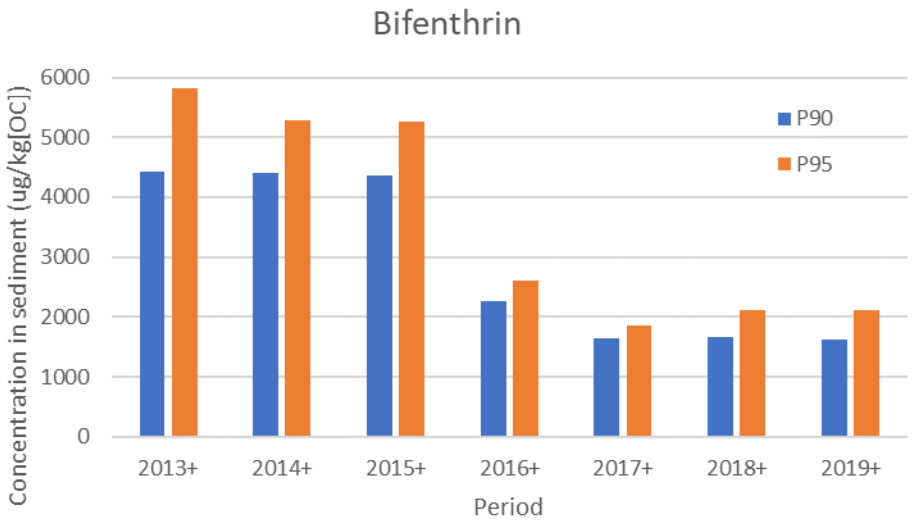

Figure 1. Sediment concentrations of bifenthrin (µg/kg[OC), reported as the 90th percentiles of monitoring data over various periods.

For most of the pyrethroids, a decreasing trend of sediment concentrations was not observed in 2013-2015 immediately after the regulations. However, significant reductions of sediment concentrations have been observed since 2016 and 2017 compared to the previous years (Figure 1). Since there are no additional regulations on urban uses of pyrethroids after 2013, the observed concentration reductions are attributed to the implementation of current regulations. Therefore, the data of 2017+ better represent the conditions with the currently required mitigation practices, and thus are more appropriate for comparison with simulation results under the modeling scenarios developed for the current regulations.

Concentrations of pyrethroids in the water column may have a quicker response to the mitigation practices compared to those measured in sediment. For example, the 90th percentile of freely dissolved concentration of bifenthrin was 2.54 ppt for the year 2012 and prior ("2012-"), compared to 1.77 ppt for 2013+ or 1.74 ppt for 2014+. However, this trend is not able to be confirmed for other pyrethroids due to the significant changes of the reporting limits (RLs). For example, the RL for cyfluthrin was 15 ppt in 2010, which was changed to 5 ppt in 2011 and then 2 ppt after 2013. So, the monitoring data in the water column cannot be simply compared before and after the regulations. With relatively higher RLs before 2012, the 90th percentile of concentrations in the water column for 2012- were below RLs for most of the pyrethroids, including cypermethrin, deltamethrin, esfenvalerate, lambda-cyhalothrin, and permethrin.

For the period 2013-2021 with lower RLs, there is no general trend detected for concentrations in the water column for the selected pyrethroids. To be consistent with the data analysis on sediment concentrations, therefore, monitoring data for the same period of 2017+ are used to generate representative concentrations in the water column (Table 3).

3.2 Physicochemical properties and environmental fate data

Listed in Table 4 are the physicochemical properties and environmental fate data of the pyrethroids modeled in this study. KOC (SPME) values are taken from a PWG study (Chickering, 2014). The same values have been used by the CVRWQCB (2017) and in this study (Table 2) to convert whole-water concentrations to freely dissolved concentrations. Other properties and half-lives for pyrethroids are taken from the ERA for pyrethroids (USEPA, 2016) as complied in the previous study (Luo, 2017a). The 2017 study was developed for agricultural uses of pyrethroids, so did not use soil photolysis half-lives (SPHOT). In this study, SPHOT values are extracted from the USEPA 2016 ERA, Attachment III "Environmental fate assessments": bifenthrin (page 562, as the average of 147 and 98.5 days), cyfluthrin (p. 652), cypermethrin (p608), deltamethrin (p573), esfenvalerate (p626), lambda-cyhalothrin (p637), and permethrin (p586).

Table 4. PREM input parameters for physicochemical properties of the selected pyrethroids

Pyrethroid	SOL	K_{OC}	HYDRO	AERO	AERO_W
Bifenthrin	1.40E-05	4,228,000	Stable	169.2	466.2
Cyfluthrin	2.32E-03	3,870,000	Stable	72.68	44.58
Cypermethrin	9.00E-03	3,105,000	210	219	23.5
Deltamethrin	2.00E-04	4,350,000	Stable	50.5	86.1
Esfenvalerate	6.00E-03	7,220,000	Stable	225	80.4
Lambda-cyhalothrin	5.00E-03	2,056,000	Stable	52	47.87
Permethrin	5.50E-03	6,075,000	Stable	211	56.7

Pyrethroid	ANAER_W	MWT	VP	AQPHOT	SPHOT
Bifenthrin	650.2	422.9	1.80E-07	49	123
Cyfluthrin	25.59	434.29	1.80E-08	0.7	5.6
Cypermethrin	53.1	416.3	1.70E-09	36.2	55
Deltamethrin	138.6	505.2	9.32E-11	86	Stable
Esfenvalerate	138.3	419.9	4.70E-07	9	30
Lambda-cyhalothrin	426	449.86	1.56E-09	13	Stable
Permethrin	193	391.3	1.48E-08	94	106

Notes: SOL (ppm) = water solubility, KOC (L/kg[OC]) = organic carbon (OC) normalized soil adsorption coefficient and SPME = solid-phase microextraction, HYDRO (day) = hydrolysis half-life (HL), AERO (day) = aerobic soil metabolism HL, AERO_W = aerobic aquatic metabolism HL, ANAER_W (day) = anaerobic aquatic metabolism HL, MWT (g/mol) = molecular weight, VP (torr) = vapor pressure, AQPHOT (day) = aqueous photolysis HL, and SPHOT (day) = soil photolysis HL.

3.3 Agronomic inputs

3.3.1 Maximum label rates

SWPP reviewed the pyrethroid products registered in California for urban outdoor uses. The maximum label rates for pest control on outside surfaces and around buildings are used in the

modeling (Table 5). Also provided in the table are the label rates used for the modeling studies in the ERAs by USEPA (2016) and PWG (Giddings et al., 2016). The application rates modeled in this study are generally consistent with those by USEPA and/or PWG, except for cypermethrin with a higher rate from the review by SWPP. In the cypermethrin product labels, there is no sufficient information for "outdoor surfaces and around buildings". So, the rate of cypermethrin (3.814 kg/ha) was determined based on the use directions for "barrier treatment", i.e., up to 5 oz product per 1000 ft^2.

Table 5. The maximum label rates (kg/ha) of pyrethroids for pest control on outside surfaces and around buildings

	Label review by SWPP (used in this study)	Label review by USEPA [1]	Label review by PWG [2]
Bifenthrin	0.254	0.247	0.224
Cyfluthrin	0.206	0.215	0.430
Cypermethrin	3.814	1.01	2.018
Deltamethrin	0.240	0.235	0.235
Esfenvalerate	0.206	0.206	0.213
Lambda-cyhalothrin	0.336	0.269	0.336
Permethrin	19.53	19.3	1.950

Data sources: [1] Section 5.4 in Part II of the ERA report (USEPA, 2016), application rates modeled for urban residential uses of California. [2] Table 90 in the ERA report (Giddings et al., 2016), rates on foundation perimeter, driveway, and patio/walkway.

3.3.2 Application frequency

For *bifenthrin*, the application frequency for modeling has been determined as "four applications on a monthly interval" in the previous study (Luo, 2017b). Multiple applications are allowed for bifenthrin products, but the application interval and the maximum number of applications are not well defined in the labels. To estimate the application frequency, the following two assumptions are considered based on the results of use/usage surveys (PWG, 2010; Winchell, 2013):

1) Monthly applications of outdoor pest control products (with all insecticides including bifenthrin); and
2) About 30% of the applications are associated with the use of bifenthrin.

Note that the probability of 30%, called an "adoption rate" or "%AI", is not specific to bifenthrin, but determined from the survey results for the most popular insecticides used in California: 26.3% for fipronil and 27.1% for bifenthrin (Winchell, 2013). Although the numerical numbers (e.g., 26.3%, 27.1%, etc.) from surveys are associated with great uncertainty, it's a reasonable and conservative assumption to set 30% as the upper bound of the probability for products containing a certain pesticide used for outdoor pest control (Luo, 2014b). The implied assumption is that the adoption rate for bifenthrin has not been significantly changed during the last decade. There were no new survey studies to update this value. The available data such the PUR data, pesticide sales data, and survey results in retail stores are not sufficient to estimate the adoption rates. Therefore, the assumption of 30% is used in the modeling for the

current application practices of bifenthrin after the label changes and regulations, and will be verified during model validation.

With the assumptions of monthly applications and adoption rate of 30% for bifenthrin, the total number of applications per year is estimated as 12×30%=3.6 (where 12 months/year is the potential number of monthly applications of any insecticide for outdoor pest control per year). Finally, the maximum number of bifenthrin applications per year is conservatively set as "four" for modeling. For comparison, USEPA modeled only one to six applications per year (USEPA, 2012, 2016), and PWG modeled eight applications on a six-week interval or four applications on a 12-weekly interval (Giddings et al., 2016).

For *other pyrethroids*, the same application frequency (four applications on a monthly interval) is modeled, and the modeling results are adjusted by the corresponding adoption rate of a pyrethroid normalized by that of bifenthrin (i.e., "relative adoption rate"). The relative adoption rate is 100% for bifenthrin, and less than 100% for other pyrethroids. For example, if a pyrethroid has a relative adoption rate of 50%, its modeling results based on four monthly applications will be multiplied by 0.5 before being used in model validation. The relative adoption rates for the modeled pyrethroids are estimated in the next section.

3.3.3 Adoption rates relative to bifenthrin

The adoption rates for some pyrethroids were first estimated from surveys conducted in 2009 (PWG, 2010). For example, deltamethrin was estimated with an adoption rate of 14.5%, so its relative adoption rate is 54% (=14.5% normalized by the adoption rate of 27.1% for bifenthrin estimated in the same study). In order to better represent the current conditions with mitigation practices required in label changes and regulation, the adoption rates for pyrethroids relative to bifenthrin are updated in this study with PUR data in and after 2017.

PUR data of 2017-2020 are queried for SITE_CODE=10 (structural pest control), and summarized as annual average uses. The time period is consistent with that used for monitoring data analysis (Section 3.1). The Surface Water Monitoring Prioritization (SWMP) model (Luo et al., 2013) was used to facilitate the data query and reporting. Note that some of the monitoring data used in this study were sampled in 2021, but the PUR data for year 2021 is not officially released by CDPR at the time of this study.

Table 6. Annual average uses reported in PUR data of 2017-2020 for structural pest control (SITE_CODE=10) and estimated relative adoption rates (post-2017).

	Max label rate (kg/ha)	Uses (pounds/year)	Relative adoption rate
Bifenthrin	0.254	58357	100%
Cyfluthrin	0.206	18383.4	38.84%
Cypermethrin	3.814	22096	2.52%
Deltamethrin	0.240	13175.6	23.89%
Esfenvalerate	0.206	3631.9	7.53%
Lambda-cyhalothrin	0.336	11368.9	14.55%
Permethrin	19.53	32313.8	0.72%

The relative adoption rate of a pyrethroid (p) is calculated as,

$$\text{Relative }\%\text{AI(p)} = \frac{\text{USE(p)/RATE(p)}}{\text{USE(bifenthrin)/RATE(bifenthrin)}}$$

where USE is the annual average use amount (Table 6) and RATE is the maximum label rate (copied from Table 5). By definition, the relative adoption rate for bifenthrin is 100%, and the rates for other pyrethroids ranges from 0.72% (permethrin) to 38.84% (cyfluthrin). The ratio USE/RATE, with a unit of a hectare, is the estimated total treated areas covered by the corresponding chemical. Therefore, the relative adoption rate from the above equation conceptually represents the probability for a pyrethroid, relative to bifenthrin, to be used in outdoor pest control.

The relative adoption rates in this study (Table 6) and those from the PWG survey in 2009 are derived based on different approaches, spatial scales, and time periods. However, they are generally consistent with each other by considering the changes of the reported use data between the corresponding time periods (2017-2020 in this study and the years before the current labels and regulations for the PWG survey). For example, the annual average uses of deltamethrin and esfenvalerate are increased, so are their relative adoption rates compared to those from the 2009 survey. The relative adoption rate for permethrin in this study is significantly lower than that from the survey in 2009. This could be related to the decreased use of permethrin in urban areas of California. Comparing the PUR data during 2017-2020 (Table 6) vs. 2009, annual average use of permethrin for structural pest control has decreased by about 80%.

PUR data for both structural pest control (SITE_CODE=10) and landscape maintenance (30) are also tested for the calculation of the relative adoption rate. The reported uses for structural pest control were significantly higher than those for landscape maintenance. Therefore, the relative adoption rates derived from both sites are very similar to those from structural pest control only. See Appendix II for more details.

4 Model results and performance

PREM reports the EECs of pyrethroids as 1-in-10-year daily average aqueous concentrations (ng/L) in the water column and pore water (Table 7). The EECs in pore water are converted to the equilibrium concentrations in sediment. For bifenthrin as an example, the OC-based EEC in sediment is calculated as: EEC (pore-water) × K_{OC} = 0.822 ng/L × 4,228,000 L/kg[OC]= 3475.4 µg/kg[OC], where the K_{OC} value is taken from Table 2.

Table 7. Modeling results of EECs in the water column and pore water, and converted EECs in sediment

	EEC (ng/L) in the water column	EEC (ng/L) in pore water	Converted EEC (µg/kg[OC]) in sediment
Bifenthrin	6.51	0.82	3475.4
Cyfluthrin	12.65	0.28	1095.2
Cypermethrin	314.80	9.49	29466.6
Deltamethrin	16.60	0.71	3084.2
Esfenvalerate	7.20	0.34	2483.7
Lambda-cyhalothrin	51.28	4.14	8522.1
Permethrin	906.00	49.40	300105.0

The model predictions are adjusted by the relative adoption rate for each pyrethroid (Table 8).

Table 8. Adjusted EECs in the water column and pore water

	Relative adoption rate (from Table 6)	Adjusted EEC (ng/L) in the water column	Adjusted EEC (µg/kg[OC]) in sediment
Bifenthrin	100%	6.51	3475.4
Cyfluthrin	38.84%	4.91	425.4
Cypermethrin	2.52%	7.94	743.1
Deltamethrin	23.89%	3.97	736.9
Esfenvalerate	7.67%	0.55	190.6
Lambda-cyhalothrin	14.73%	7.55	1255.1
Permethrin	0.72%	6.52	2161.2

For model validation, the adjusted EECs are compared to the representative concentrations of monitoring data in Table 3. A set of four P/O ratios are generated for each pyrethroid. Taking bifenthrin as an example, the calculations are demonstrated below:

1) P/O (bifenthrin, water column, P90) = 6.51/2.36 = 2.8
2) P/O (bifenthrin, water column, P95) = 6.51/3.91 = 1.7
3) P/O (bifenthrin, sediment, P90) = 3475.4/1650.4 = 2.1
4) P/O (bifenthrin, sediment, P95) = 3475.4/1864.2 = 1.9

where 6.51 ng/L and 3475.4 µg/kg[OC] are adjusted EECs, respectively, in the water column and sediment from Table 8, and the denominators are the representative concentrations at the 90th and 95th percentiles of monitoring data in the water column (2.36 and 3.91 ng/L) and sediment (1650.4 and 1864.2 µg/kg[OC]) (Table 3).

The above procedures are repeated for each of the pyrethroids, resulting in 28 P/O ratio values for model validation (Table 9), where 28=7 pyrethroids × 2 environmental compartments (water and sediment) × 2 percentiles (the 90th and 95th).

Table 9. P/O ratios for model validation

	P/O (water, P90)	P/O (water, P95)	P/O (sediment, P90)	P/O (sediment, P95)
Bifenthrin	2.8	1.7	2.1	1.9
Cyfluthrin	7.7	4.1	2.0	1.4
Cypermethrin	18.9	4.8	13.7	8.1
Deltamethrin	3.7	1.2	0.9	0.8
Esfenvalerate	2.1	1.5	1.9	1.2
Lambda-cyhalothrin	28.0	12.4	10.5	6.4
Permethrin	4.4	1.8	6.6	3.8

Notes: P90 = the 90^{th} percentile, and P95 = the 95^{th} percentile.

Most of the P/O ratios are within or close to the range of 1 to 10. For model validation, there is no preference for the use of the 90^{th} or 95^{th} percentiles in the calculation of P/O ratios. Therefore, the two resulting ratios, based on the 90^{th} and 95^{th} percentiles, define the range of model performance for comparison with the expected range of 1 to 10. For cypermethrin as an example, the range of the predicted P/O rates is from 4.8 to 18.9 (Table 9), which overlaps with the expected range of 1 to 10, and thus considered as satisfactory model simulations. The prediction of lambda-cyhalothrin in the water column is the only case where the model significantly overestimates the observations at both percentiles (P/O ratios = 28.0 and 12.4).

Modeling results for bifenthrin are also used to verify the assumption in the model configurations on the reference adoption rate for bifenthrin (Section 3.3.3) which was derived from the 2009 survey results. The model well predicts the monitoring data of bifenthrin in the water column and sediment with the R/O ratios ranging from 1.7 to 2.8. The results support the use of the previously determined adoption rate for modeling the current application practices of bifenthrin.

Compared to the modeling results in the ERAs by USEPA (2016) and PWG (Giddings et al., 2016), the modeling approach and configurations implemented with PREM show better performance in predicting urban outdoor uses of pyrethroids. The previous ERAs underestimated the concentrations of pyrethroids especially in sediment. The median P/O ratio in sediment was about 0.3 in the previous ERAs, compared to 2.1 in this study. See Appendix III for more details.

By considering the overall performance, in conclusion, PREM provides satisfactory model simulations on outdoor uses of pyrethroids in the urban residential settings of California. The model and its urban configurations can be used in scenario analysis for evaluating the effectiveness of mitigation measures. Note that the overestimation in model predictions does not affect the scenario analysis for mitigation modeling. The goal of mitigation, presented as the required concentration reduction, is determined from the monitoring data and regulatory target concentrations, which are independent to modeling.

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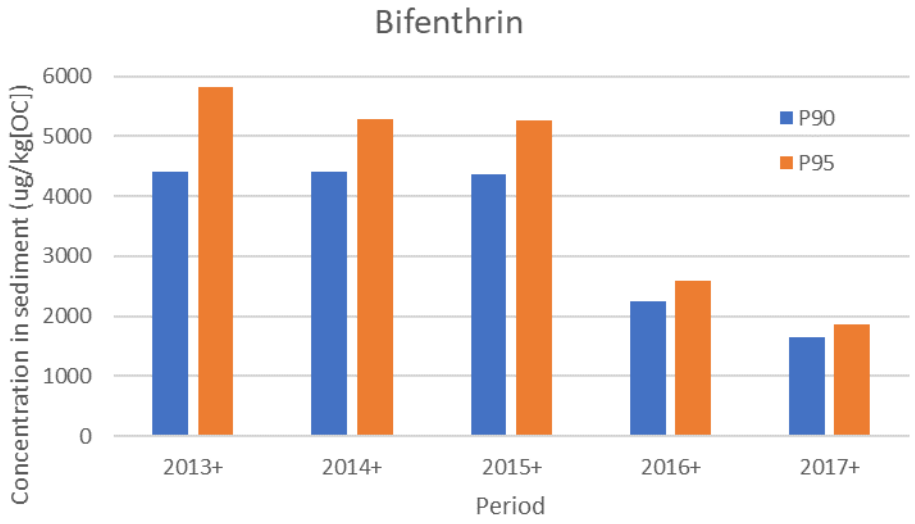
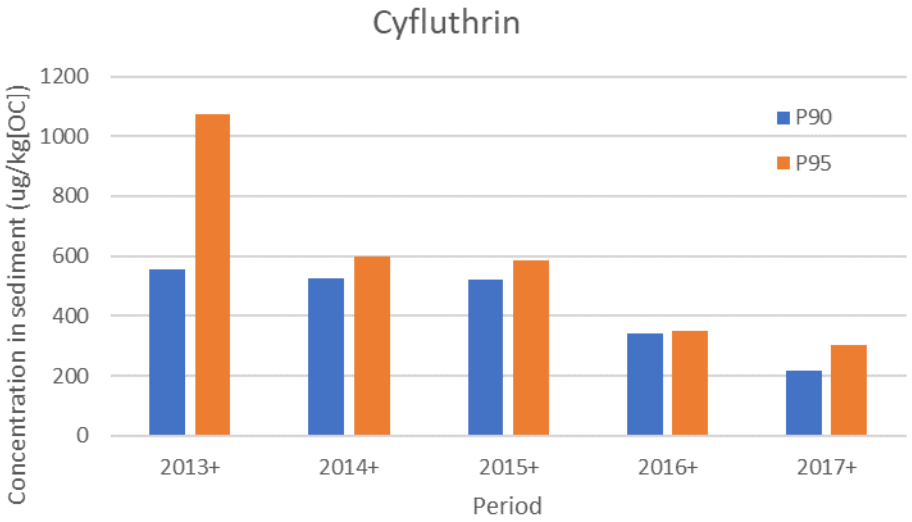
Appendix I. The 90th and 95th percentiles of the concentrations of pyrethroids in sediment

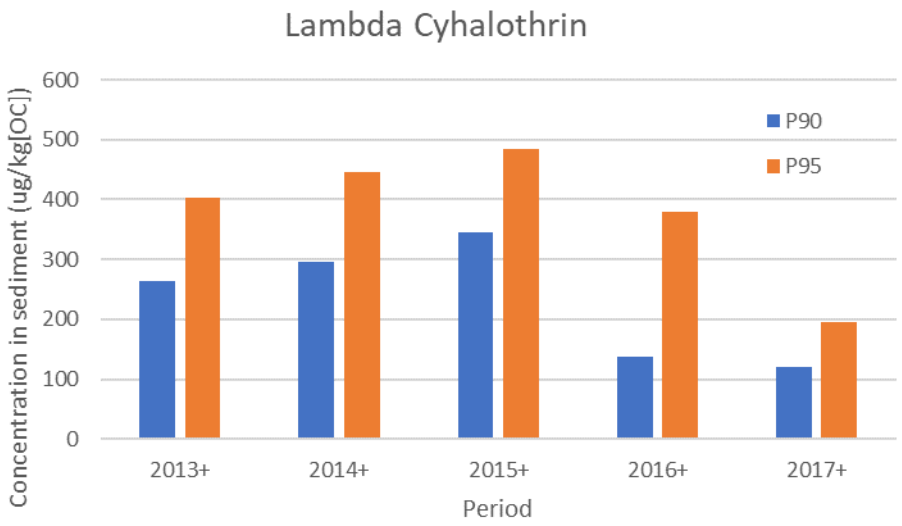
(a) Bifenthrin



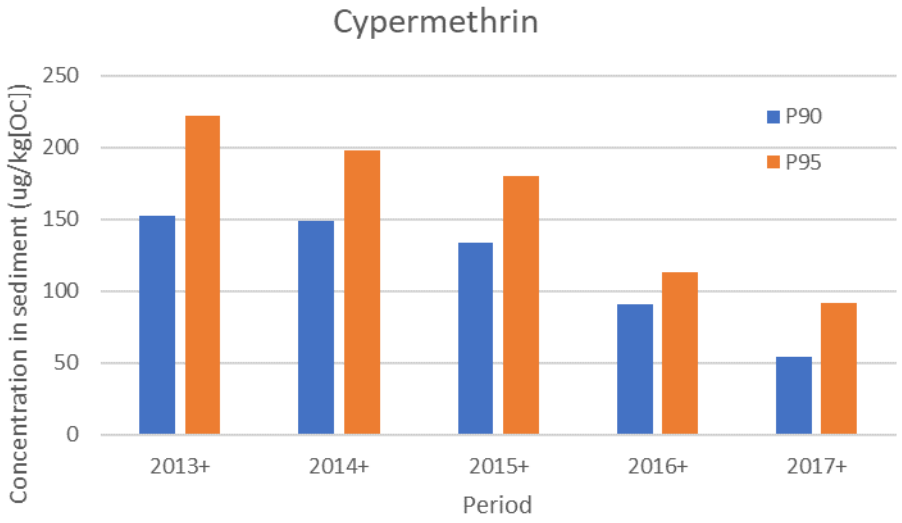
(b) Cyfluthrin



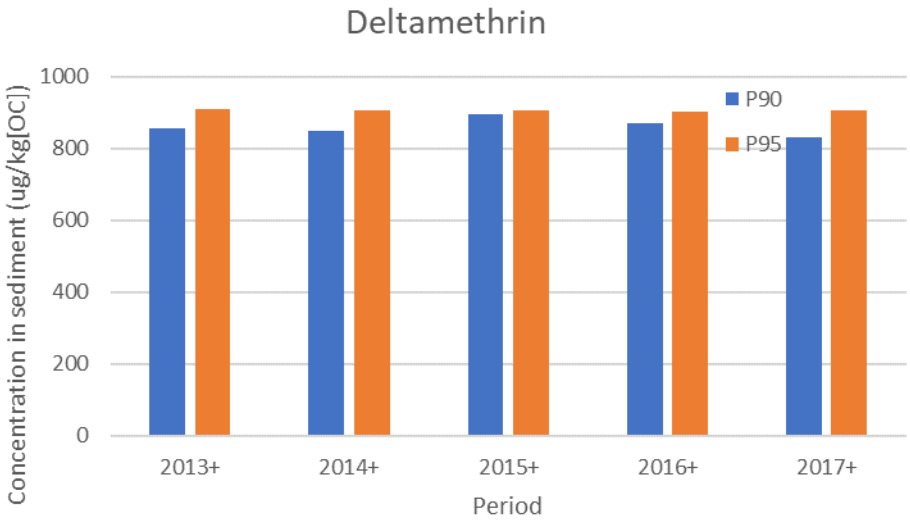
(c) Lambda-cyhalothrin



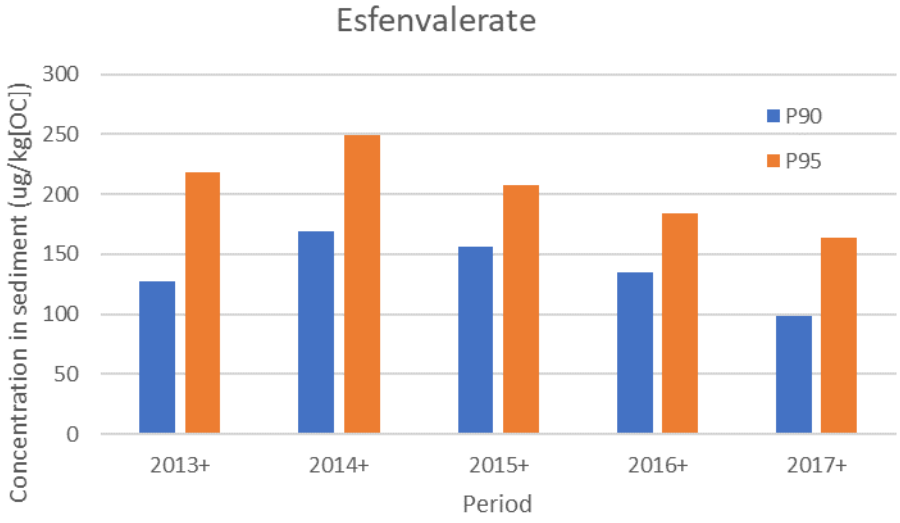
(d) Cypermethrin



(e) Deltamethrin



(f) Esfenvalerate



(g) Permethrin

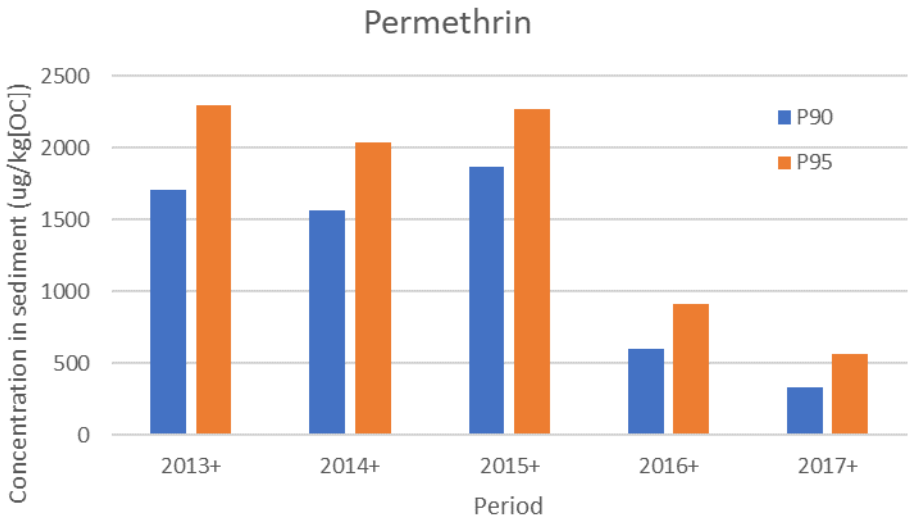


Figure 2. Sediment concentrations of pyrethroids (µg/kg[OC), reported as the 90th (P90) and 95th (P95) percentiles of monitoring data over various periods.

Appendix II. Additional data analysis for relative adoption rates

Table 10. Annual average uses (pounds) reported in PUR data of 2017-2020 for structural pest control (SITE_CODE=10) and landscape maintenance (30) and calculations for the relative adoption rates

	Max label rate (kg/ha)	Annual average uses	Relative adoption rate
Bifenthrin	0.254	61888.9	100%
Cyfluthrin	0.206	19546.1	38.94%
Cypermethrin	3.814	22665.4	2.44%
Deltamethrin	0.24	13207.7	22.59%
Esfenvalerate	0.21	3643.3	7.12%
Lambda-cyhalothrin	0.34	11511.7	13.90%
Permethrin	19.53	37832.1	0.80%

Appendix III. Modeling results from the ERAs by USEPA and PWG

Table 11. Model predictions from the previous ERAs for urban outdoor uses of pyrethroids in California residential settings

	EECs from USEPA [1]		EECs from PWG [2]	
	Water column (ng/L)	Sediment (µg/kg[OC])	Water (ng/L)	Sediment (µg/kg[OC])
Bifenthrin	4.04	25.25	0.95	220
Cyfluthrin	1.07	3.01	1.89	39
Cypermethrin	52.8	217	10.6	250
Deltamethrin	1.19	5.34	0.96	55
Esfenvalerate	6.61	48.3	0.56	42
Lambda-cyhalothrin	1.18	52.25	2.45	88
Permethrin	745	5275	5.97	670

Data sources: [1] Tables 37-43 in Part II of the ERA report (USEPA, 2016), modeling results for California residential lots. [2] Tables 53 and 54 in the ERA report (Giddings et al., 2016), modeling results for California current residential scenarios.

Table 12. P/O ratios based on the model predictions in the previous ERAs (Table 11) and the representative concentrations in California urban waterways (Table 3)

	P/O based on the EECs from USEPA				P/O based on the EECs from PWG			
	Water P90	Water P95	Sediment P90	Sediment P95	Water P90	Water P95	Sediment P90	Sediment P95
Bifenthrin	0.4	0.2	0.1	0.1	1.7	1.0	0.02	0.01
Cyfluthrin	3.0	1.6	0.2	0.1	1.7	0.9	0.01	0.01
Cypermethrin	25.2	6.3	4.6	2.7	125.7	31.6	4.0	2.4
Deltamethrin	0.9	0.3	0.1	0.1	1.1	0.4	0.01	0.01
Esfenvalerate	2.2	1.5	0.4	0.3	25.4	17.4	0.5	0.3
Lambda-cyhalothrin	9.1	4.0	0.7	0.5	4.4	1.9	0.4	0.3
Permethrin	4.1	1.6	2.1	1.2	506.8	201.9	16.2	9.3