**Estimating Bifenthrin Concentration in Urban Runoff Using PWC Model**

**Abstract**

The Sacramento-San Joaquin River Delta, which provides critical habitat for many fish and invertebrate species, is experiencing significant habitat loss due to increased pyrethroid use and its associated polluted urban storm runoff from upland urban areas such as the City Folsom and Roseville. The concentration of bifenthrin, one of the pyrethroids, was modeled for four storm-drain outlets from two main creeks throughout January 2009 to December 2014 and analyzed using the Pesticide in Water Calculator (PWC). For the study period, the total mass of bifenthrin applied in Sacramento and Placer County were 41364 and 8029kg respectively. From the mass applied, approximately 1.5% to 1.88% of bifenthrin was predicted to reach the urban creek in Roseville and Folsom through runoff and drift, with runoff accounting for more than 80% of the mass loss. Simulated daily bifenthrin concentrations were greatest in Alder Creek within the City of Folsom due to its high urban influence and associated application. The Alder Creek waters reached maximum concentrations of 73.2 ng/l bifenthrin. At the Pleasant Grove Creek in the City of Roseville, a maximum bifenthrin concentration of 44.8 ng/l was recorded for the sites. The Estimated Environmental Concentrations (EEC) results for 1-day (acute) and 4-day (chronic) averages indicated that bifenthrin would likely be responsible for paralysis or death to aquatic species (e.g. *H. azteca*) since its EECs are well 10 times more than the CALFED 2011 recommended values for risk assessment. Overall, the model demonstrated good performance in capturing the application patterns and concentration bifenthrin at the modeled sites. The well-calibrated model can appropriately be used for pyrethroid simulation and can efficiently support water resource management policies.

***Keywords****:* Pesticide in Water Calculator, Pyrethroid, Bifenthrin, Urban runoff, Estimated Environmental Concentration

# Introduction

Rivers and streams receiving urban runoff have been shown to be toxic to aquatic species (e.g. *H. azteca*) due to the increasing presence of pyrethroids (Budd et al., 2007; Weston and Lydy, 2010; Weston et al, 2014). Bifenthrin, a subset of the pyrethroids, is greatly toxic to aquatic species, with acute aquatic species mortality possible at even small concentrations of 1 ng/L (Weston et al., 2008; Weston et al., 2010), yet urban runoff regularly contains concentrations greater than 20 ng/L (Weston and Lydy, 2012). Generally, bifenthrin pesticides are widely used by professional pest control applicators for landscape application, or as perimeter treatments to keep pests out of structures in most urban environments. In urban environment, runoff often contains a considerable amount of bifenthrin after a storm event. The Sacramento-San Joaquin River Delta, one of the main water bodies in California, receives urban runoff after rainfall events. Studies have shown that the Sacramento–San Joaquin Delta is habitat for lots of aquatic species of concern, Delta Smelt, Threadfin Shad, San Francisco Longfin Smelt, and Striped Bass whose decline has been critical in recent times due to the presence of high bifenthrin concentration (Sommer and Mejia, 2013).

Werner et al. (2010) estimated that toxicity from bifenthrin can be as high as 117 ng/L, about 10 times the acute toxicity level for loss of motion to most aquatic Threatened and Endangered Species in the Sacramento-San Joaquin River Delta. To reduce pyrethroid contaminants to a safe level in the Delta, there is a need to monitor upstream urban rivers and creeks for the presence of these chemicals. However, current monitoring practices for pyrethroid detection are generally time consuming, expensive, and labor intensive (Amweg et al., 2005) resulting in a lack of adequate observed concentrations in water bodies for aquatic risk assessment (Luo et al., 2011). The use of exposure models becomes an effective mode of estimating pyrethroid concentration in water bodies. For environmental fate and transport modeling, water quality models are usually combined with field-scale models to provide the screening tool for pesticide-registration evaluation (Guo et al., 2004). Additionally, the data outputs from these models can be used to aid in the development of effective regulatory policies and mitigation strategies as in the development of Best Management Practices (BMPs) in reducing pesticide fluxes toward water bodies (Moore et al., 2002; Cho and Mostaghimi, 2009).

The Pesticide in Water Calculator (PWC), an environmental fate and transport model developed by the United States Environmental Protection Agency (USEPA) -Office of Pesticide Program (OPP) as a regulatory tool for risk assessment, was used in this study. The model simulates pesticides concentration in surface water for aquatic exposure assessments (USEPA, 2016b) and contains two main simulation engines: The Pesticide Root Zone Model (PRZM version 5.02), and the Variable Volume Water Model (VVWM version 1.02) (PWC Manual, 2015). The model accommodates specific characteristics of the modeled chemical and includes more site-specific information regarding the application method and impact of local daily weather on the treated site for long-term simulations (typically 30 years or more).

The PRZM5 (Young and Fry, 2016) included in PWC is an update of PRZM3 (Suraez, 2005) and has many advantages over PRZM3, including bug fixes, an improved volatilization routine and a more modern input interface (Young and Fry, 2016). PRZM5 is a continuous simulation model, which uses multiple years of rainfall data to cover year-to-year variability in runoff; secondly, PRZM5 predicts daily edge-of-field loadings of pesticides in both dissolved (in runoff water) and adsorbed forms (sorbed to sediment) (USEPA, 2016b).

The VVWM is an updated model of the EXposure Analysis Modeling System (EXAMS). Unlike the EXposure Analysis Modeling System (EXAMS) simulation engine (Burns, 2000), which assumes constant water volume and does not allow the water bodies within the watershed to vary in response to precipitation, runoff, evaporation, and overflow (USEPA, 2016b), VVWM simulates the USEPA standard water bodies and allows for variations in water body volume on a daily basis due to runoff, precipitation, overflow, and evaporation (USEPA, 2016b).

Although PWC has many advantages compared to previous models such as FIRST (FQPA Index Reservoir Screening Tool) and GENEEC (GENeric Estimated Environmental Concentration) (Parker et al. 1995, USEPA, 2016b), the PWC model has not been thoroughly evaluated, and there are no journal publications regarding the use of the model in simulating pesticide concentration in surface water for risk assessment. In this study, the PWC was used to simulate the acute and chronic bifenthrin EECs in storm drain outfalls on the Pleasant Grove Creek and Alder Creek within Placer and Sacramento Counties, respectively. Storm drain outfalls are the main source of pyrethroid wash-off to the urban creeks which eventually ends up in large rivers and streams. The specific objectives of this study are: (1) to evaluate how accurately the PWC model predicts daily and longer term EEC of bifenthrin in urban runoff at the sampling outlets; and (2) to compare the model-derived acute and chronic EECs at the urban sites to the reported 2011 CALFED aquatic Threatened and Endangered Species values, which provide useful information for exposure-related decision making and management.

We decided to look at bifenthrin because it is among the highest-use pyrethroids in the region (CDPR Database, 2014) and also most often contribute to the increased toxicity in the study area urban creeks (TDC, 2010; Amweg et al., 2005), which eventually end up in the Sacramento-San Joaquin River and Delta. Finally, monitored bifenthrin concentration is available for the model evaluation.

# Materials and Methods

## PWC Model and Aquatic Exposure Risk Assessment

Since PRZM5 and VVWM are the two main engines of the PWC, a brief introduction of PRZM5 and VVWM is provided below. In the PWC model, PRZM5 is dynamically (file transfer-) linked to the VVWM for the estimation of pesticide concentrations in surface waters for aquatic ecosystem exposure assessments. PRZM5 is a one-dimensional hydrology, heat and solute transport model, developed for pesticide simulations in unsaturated soil systems within and underneath the root zone of plants (Young and Fry, 2016). PRZM5 model simulates descending movement of water by a tipping bucket concept, where water is always moving downward. It is designed to evaluate the influence of climate, soil properties, and management practices on pesticide transport and transformation processes (e.g., surface runoff, leaching, erosion, and volatilization). The model has the capacity to simulate up to three chemicals as separate chemicals or as a parent and daughter mixes and allows the simulation to be conducted using multiple years of rainfall data to cover year-to-year climate variability. This added feature gives the user the alternative to observe the impacts of various chemicals without making extra runs, or the capacity to enter a mass change component from a parent chemical to daughter chemicals.

The PRZM5 model calculates runoff based on the Natural Resources Conservation Services (NRCS) Curve Number (CN) method (NRCS, 2003). In using the CN method, irrigation water, and snowmelt is treated as having the same effect as precipitation (rain). Hence, precipitation in the above equations is the sum of rain, snowmelt, and irrigation. The CN used to compute daily runoff is adjusted on a daily basis according to the soil moisture (Young and Fry, 2016). PRZM5 has two options for erosion calculation (Young and Fry, 2016); the Modified Universal Soil Loss Equation (MUSLE) (Williams, 1975) and the Small watershed version of MUSLE (MUSS) (Kinnell, 2004).

In PRZM5, chemicals are simulated through the vertical movement of water in the soil compartment (Young and Fry, 2016). The soil water content in the water column, at any point of the simulation, is first calculated from the amount of infiltrating water from the layer above. At any point, if the soil water content exceeds the field capacity, the excess water is used as flow into the next compartment for the chemical simulation that compartment. This process continues throughout the soil column chemical simulation with the aid of precipitation, irrigation and snowmelt infiltration.

The VVWM simulation engine of the PWC model, the successor of the EXAMS model (Burns, 2000), is an important water quality model used to assess the fate, transport, exposure, and persistence of pesticides in aquatic systems (Xie, 2014). In the VVWM model, the receiving water body is divided into two parts – the littoral zone and the benthic zone, which are coupled by completely mixing with dispersive and advective transports and first-order mass transfer process (Burns, 2000; Young, 2014). Classic processes, such as pesticide adsorption and desorption, photolysis, hydrolysis and redox, biolysis, and volatilization are involved in the VVWM model. The model allows users to define custom water bodies within their study area. The main difference between the VVWM model and the EXAMS model is based on the assumption of the volume of the receiving water body in the region of study. That is, the EXAMS model assumes constant water volume whereas the VVWM model allows the water volume to vary in response to precipitation, runoff, evaporation, and overflow.

The advantages of the VVWM coupled with the ability of PRZM5 to simulate relevant processes of pesticide transport, and its use by regulatory agencies in their pesticide exposure assessments (USEPA, 2010) aided in the selection of the PWC for this study. In addition, California has also developed urban scenarios to aid in the application of the PWC model in aquatic risks assessment (CALFED Report, 2011). These scenarios specify the urban land application site percentages (pervious and impervious) for structural, landscape maintenance, and other urban land uses, and soil properties.

To assess the risks to aquatic species, the PWC model in this study estimated acute and chronic EEC of bifenthrin in the surface runoff. These EECs were obtained from the PWC model as 1 and 4-day average concentration in the 1-in 10 -year return simulation period. The model’s estimated acute and chronic concentrations were compared to the 2011 CALFED report established benchmark for bifenthrin. The 2011 CALFED report benchmark was obtained as 1/10th of the USEPA benchmark for aquatic species (CALFED, 2011). This comparison was in-line with the proposed toxicology threshold established in the 2011 CALFED Report for Threatened and Endangered Species.

## Study Area

Sacramento and Placer Counties, California have experienced increased population growth, and within the past few years, thousands of homes have been built on land that was initially grassland (Weston et al., 2012). The City of Roseville and Folsom are two of many such urban communities. These communities are made up of numerous single-family homes, most of which are less than 20 years old. Roseville and Folsom were selected because they are active sampling sites of CDPR and have observed bifenthrin concentration for model evaluation. In addition, the sites are urban areas with no agricultural land use. They are also upstream of the Sacramento–San Joaquin Delta and a contributor to water quality in the Delta.

This study area contains four storm drains which receives runoff from the Roseville and Folsom sites (Fig. 1). In the city of Folsom, one storm drain is located near open space at Brock Circle (CDPR-FOL002) with a drainage area of 0.26 km2 . The other storm drain is located near Outfall at Marsh Hawk Drive between Donnelly Circle Widgeon Court (CDPR-FOL003) with a drainage area of 0.11 km2. ,The storm drains serve approximately 295 and 91 single-family homes, respectively. Discharge water from both storm drains lead into Alder Creek. The area is mostly characterized by a dry season from May through October with an average annual high temperature of 23.8 oC and low temperature of 9.9 oC. Precipitation mostly occurs from November through April resulting in an annual average of 625 mm.

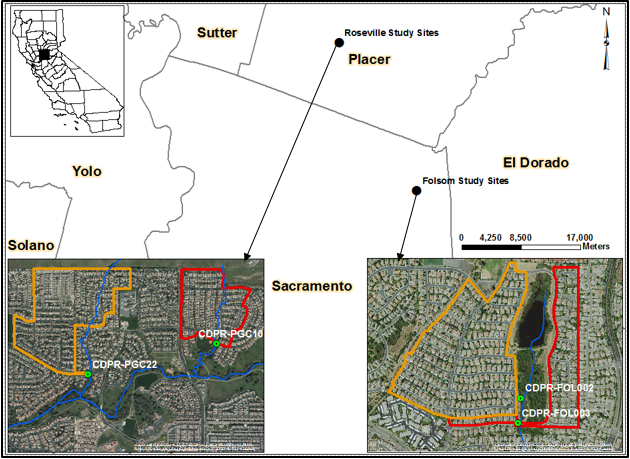


Fig. 1. Location of The Pleasant Grove Creek Study Area in Placer County and The Alder Creek Study Area in Sacramento County Upstream of the Sacramento-San Joaquin Delta.

In the city of Roseville, there is one storm drain in Dugan Park on Diamond Woods Circle (CDPR-PGC010) with a drainage area of 0.23 km2 . The second storm in Roseville is located at Opal and Parkside Way (CDPR-PGC022) with a drainage area of 0.45 km2. CDPR-PGC010 and CDPR-PGC022 serve about 250 and 375 single-family homes, respectively. These two sites drain to the Pleasant Grove Creek, the main watercourse within this area, with Kaseberg Creek as one of its main tributaries to Sacramento–San Joaquin. Precipitation usually occurs between November and March with an annual value of about 711 mm. With almost similar climatic conditions, the primary source of water to the drains is runoff from residences during storm events and over irrigation of landscapes and lawns during the summer. Numerous storm drains from the urban residential discharge to Alder Creek and Pleasant Grove Creek, and tributaries, along much of their lengths.

These four sites, all of which have relatively small drainage areas and predominantly urban land use, are active sites established by the California Department of Pesticide Regulation for monitoring bifenthrin concentration from urban water bodies due to high urban pesticide usage. Monitoring of bifenthrin in the study area was mostly done after storm events, limiting the amount of monitored data available. However, there was no associated runoff monitoring for the study periods. Between 2009 and 2014, the total number of monitored bifenthrin data is about 57 samples for the four sites. That is, 21 for (CDPR-FOL002), 11 for (CDPR-FOL003), 19 for (CDPR-PGC010), and 16 for (CDPR-PGC022). Since runoff was not monitored at the study sites, observed runoff from the nearest USGS station number 11447360 at Arcade C NR Del Paso was modeled and compared to the PWC simulated runoff in terms of trend and magnitude (<https://waterdata.usgs.gov/nwis/uv?site_no=11447360>). This USGS site has a large drainage area of about 81 km2 compared to the study sites and is made up of about 90% urban and 10% agricultural land use (Vecchia et al., 2008).

Though the study was focused on the urban sites sampling outlets within the City of Roseville and the City of Folsom in Placer and Sacramento County respectively, there are many similar sites as these. In this regard, PWC model could be an important tool for simulating bifenthrin concentrations in similar sites.

The study area dimensions were digitized based on a predefined study area by Ensminger, (2014). The water body dimensions in PWC are “User Defined.” Dimensions were derived from GIS analysis (ArcGIS 10.4) of the study site with water body physical parameters based on USEPA OPP default values (Table 2).

Table 2. Parameters Required for Defining the Receiving Water Body.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Parameter | DPR-FOL002 | DPR-FOL003 | DPR-PGCO10 | DPR-PGC022 |
| Watershed and Water Body Dimensions | **User Defined** | **User Defined** | **User Defined** | **User Defined** |
| Field Area (m2) | 263046 | 109265 | 226624 | 453248 |
| Water Body Area (m2) | 35000 | 35000 | 32000 | 30000 |
| Initial Depth (m) | 2 | 2 | 2 | 2 |
| Maximum Depth (m) | 2 | 2 | 2 | 2 |
| Hydraulic Length (m) | 2400 | 2400 | 2000 | 2000 |
| Water Body Physical Parameters – Water Column | **USEPA Pond** | **USEPA Pond** | **USEPA**  **Pond** | **USEPA Pond** |
| DFACa | 1.19 | 1.19 | 1.19 | 1.19 |
| Water Column SSb (mg/L) | 30 | 30 | 30 | 30 |
| Chlorophyll (mg/L) | 0.005 | 0.005 | 0.005 | 0.005 |
| Water Column FOCc | 0.04 | 0.04 | 0.04 | 0.04 |
| Water Column DOCd (mg/L) | 5 | 5 | 5 | 5 |
| Water Column Biomass (mg/L) | 0.4 | 0.4 | 0.4 | 0.4 |

*Table edited from Young, 2014.*

*aDFAC = VVMM-defined distribution factor associated with photolysis*

*bWater Column SS = Concentration of suspended sediment in water column*

*cWater Column FOC = Fraction of organic carbon in water column*

*dWater Column DOC = Concentration of dissolved organic carbon in water column*

## Site Specific Input Parameters

Daily weather data required by PRZM5 are rainfall, temperature, wind speed, and solar radiation. The daily weather data for both deterministic and probabilistic simulations was retrieved from the Camino weather station operated by the California Irrigation Management Information System (CDWR, 2016). This station is the nearest weather station to the study area. The CN required for runoff calculation, soil physical properties, USLE required parameters such as USLE cover factor (USLE\_C), USLE practice factor (USLE\_P), USLE soil erodibility factor (USLE\_K), and the topographic length-slope factor were obtained from the CALFED Report (2011). The soil properties data were based on Soil Survey Geographic (SSURGO) database (USDA-NRCS, 2009). Soil property input values used for deterministic simulations are shown in Table 1. These values were used because they are recommended values in the CALFED 2011 report. The CALFED 2011 report is based on the “Spatial and Temporal Quantification of Pesticide Loadings to the Sacramento River, San Joaquin River, and Bay-Delta and serves as a Guide to Risk Assessment for Sensitive Aquatic Species.”

Table 1. Environmental Properties Used in The PRZM 5 Deterministic Simulation.



|  |  |  |  |
| --- | --- | --- | --- |
| **Parameter** | **Description** | **Input Value** | **Range** |
| **USLE\_C** | **USLE cover factor** |  | 0.123 – 0.396 |
| **USLE\_K** | **USLE soil erodibility factor** |  | 0.02 – 0.55 |
| **USLE\_LS** | **USLE topographic factor** |  | 0.0 - 22.12 |
| **USLE\_P** | **USLE practice factor** |  | **0.0 – 1.0** |
| **CN2** | **SCS runoff curve number** |  | 0.58 - 100 |
| **PFAC** | **Pan factor** |  | 0.7 - 0.77 |
| **ED** | **Evaporation depth** |  | 10.0 - 17.5 |



Table 3. Surface Media Fraction.

|  |  |  |  |
| --- | --- | --- | --- |
| **Modeled Surface Media** | | | **SMF** |
| **Landscape** | Grass | Pervious | 0.866 |
| **Landscape** | Concrete | Impervious | 0.114 |
| **Structural** | Grass | Pervious | 0.5 |
| **Structural** | Concrete | Impervious | 0.35 |
| **Structural** | Building | Impervious | 0.15 |
| **Other** | Grass | Pervious | 1 |

*Source: Modified from CALFED Report, 2011*

2.3.1 Bifenthrin Input Parameters

The physicochemical properties of bifenthrin, sorption constant (Kd), aerobic soil metabolism half-life, and solubility (SOL) in Table 4 are the governing factors for pesticides runoff potential in both dissolved and absorbed for phases (Goss, 1992; Luo and Zhang, 2010). Degradation of pesticides in soil involves processes such as hydrolysis, photolysis, and microbial decay, simulated by PRZM5, is based on a combined single decay rate and assumes first-order kinetics (Luo and Zhang, 2009).

Professional bifenthrin application data for Sacramento and Placer County for 2009 to 2014 were downloaded from the PUR database maintained by CDPR (CDPR, 2016) and quantified. The PUR database reports all daily agricultural uses of registered pesticides by active ingredient and non-agricultural uses at the county level. For this study, structural - impervious (concrete) and pervious (grass), landscape maintenance - impervious (concrete) and pervious (grass); and other - pervious (grass) of non-agricultural use category in PUR were selected for the study area

The bifenthrin application apportionment was based on assumed impervious and pervious application surfaces percentages from research conducted by CDPR, Pyrethroid Working Group (PWG) and TDC regarding licensed applicators usage of the chemicals. For structural applications, it was assumed that 50% of bifenthrin was applied to impervious (35% of concrete and 15% of buildings) and 50% to pervious surfaces. For landscape treatments, based on an assumption of 3-ft overspray onto sidewalks, roads, and driveways, 11.4% of bifenthrin was applied to impervious and 86.6% to pervious (TDC, 2010). For other surfaces besides landscape and structural, bifenthrin application was assumed to be 100% for pervious surfaces. In this work, these values will be termed Surface Media Fractions (SMFs) as shown in Table 3. Application timing and days of application were based on monthly pesticide volume in the PUR and randomly assigned dates respectively. For this study, bifenthrin were assumed to be entirely outdoor use and above ground application.

Homeowner use of bifenthrin is not reported in the PUR database; however, an approximate amount of use can be inferred from sales data. Approximately 80% of bifenthrin use in the study area is estimated to be applied by professional applicators (TDC, 2010). Therefore, homeowner use of bifenthrin was assumed to be 25% of professional use (20/80=0.25) of bifenthrin. Homeowner use was assumed to follow professional use patterns with respect to allocation to structural versus landscape maintenance, distribution to pervious and pervious surfaces, and therefore separate model simulations were not required for homeowner applications.

The PUR database provides urban pesticide use data at the county-level. In other to effectively simulate bifenthrin concentration in the urban environment, there is no need to redistribute bifenthrin over all known urban areas in the county, but only those urban areas that fall within the study area. To determine the fraction of urban land within the study area, a GIS overlay analysis was performed. This was done using the 2011 United States Geological Survey National Land Cover Dataset (USGS NLCD, 2011) to represent urban areas within study area. Determining the urban area was performed in two phases. First, the study area was overlaid on the NLCD data and then extracted. Last, the total urban area within the extracted portion was calculated.

The bifenthrin application rate (kg/ha) was calculated based on the size of the extracted urban study area. Application efficiency and drift were set to 99% and 1% (CALFED Report, 2011) for aboveground application method. In PUR database, reported entries for structural pest control and landscape maintenance uses are usually dated as the first day of the month regardless of the actual application dates. The application was made to occur for every year from the first year to the last year of precipitation data.

Table 4. Physicochemical Property for only Bifenthrin (CALFED Report, 2011)

|  |  |  |
| --- | --- | --- |
| \*Physicochemical Properties | Bifenthrin | Sources |
| Pervious Kd (mL/g) | 48 | J |
| Impervious Kd (mL/g) | 48 | J |
| Water Column Metabolism Half-life (day) | 323.6 | C |
| Water Reference Temperature (oC) | 20 | - |
| Benthic Metabolism Half-life (day) | 647.2 | C |
| Benthic Reference Temperature (oC) | 20 | - |
| Aqueous Photolysis half-life (day) | stable | E |
| Photolysis Reference Latitude(o) | 40 | - |
| Hydrolysis Half-life (day) | stable |  |
| Soil half-life (day) | 161.8 | E |
| Soil Reference (oC) | 20 | - |
| MWT (g/mol) | 422.9 | E |
| Vapor Pressure (torr) | 1.80E-03 | E |
| Solubility (mg/L) | 0.000014 | E |
| Henry's Constant (m3/mol) | 7.20E-03 | E |

***SOURCES:*** *J = Jorgenson and Young, 2010, E = EPA RED/IRED, C = CALCULATED*

## Deterministic Simulation Design

A deterministic simulation was performed to provide a single concentration estimate for each sampling site over the studied time period. Deterministic simulations do not incorporate a random component because a single set of input values are used to model the output rather than considering a range of possible values for each input parameter.

The deterministic simulation was performed for bifenthrin in the urbanized residential monitoring sites from 2009 to 2014. “Nonstandard” scenarios developed for California in 2007 for non-agricultural uses, based on the Tier-II modeling scenarios by USEPA designed for registration evaluation and risk assessment of pesticides (USEPA, 2013b) were used. The main PWC model components are the land phase, simulated by PRZM5 and water phase, simulated by VVWM. For PRZM5, the “nonstandard” scenarios are based on non-agricultural uses (pervious and impervious urban residential land-uses) in California taking into account studies for California Red-legged frog (USEPA, 2013a). For VVWM, three modeling scenarios are available: the USEPA standard farm pond for aquatic ecosystem risk assessment, the USEPA standard index reservoir for drinking water exposure assessment, and a “User Defined” scenario (PWC Manual, 2015). The “User Defined” water body (Table 2) was used for simulation in this study. In the scenarios modeling, parameters were formatted for the PWC for urban pesticides simulation.

The model set-up for bifenthrin was carried out to calibrate the model for use in simulating bifenthrin at the other sites of concern (DPR-PGC010, DPR-PGC022and DPR-FOL003). The SMF information for impervious and pervious surfaces for bifenthrin was used to conduct a baseline simulation to estimate a reasonable and conservative concentration of bifenthrin relative to the proportion of the amount of monthly bifenthrin active ingredient (A.I.) used and sites of application (landscape maintenance, structural pest control, and others). Monthly applications were used to incorporate the effects of climatic and hydrologic variations on bifenthrin movement.

Modeling results from the PWC are reported as time series concentrations at a daily scale, 1-day and 4-day average EEC of bifenthrin in the urban waters, which was simulated as a custom (User Defined) water body (Table 2). In order to evaluate the performance of the PWC model, the same day predicted bifenthrin concentrations were compared to the reported CDPR-SURF observed concentrations at the four urban storm drain outlets using the coefficient of determination, means, and graph to determine the agreements between the observed and simulated output. T Test of equality of means was also performed to determine if there is a difference between the observed and simulated bifenthrin mean. The approach used in modeling bifenthrin in this study is in line with USEPA standards for exposure and risk assessment.

## Probabilistic Simulation Design

The probabilistic simulation uses the deterministic simulation’s set of input parameters and assumptions. However, the probabilistic simulation utilizes pre-determined distributions for each input parameter to allow for variability across the simulations. This approach randomly draws input variables from their respective distribution during each simulation to yield x model outputs (where x is the number of probabilistic simulations). A probabilistic sensitivity analysis (SA) then searches the entire parameter space to identify critical parameters on the model output. The SA can also aid in reducing overall model variation and uncertainty by focusing efforts on the critical input parameters.

The probabilistic SA included 5000 simulations and \_\_\_ input parameters. Input parameters were sampled using the Latin Hypercube technique with the “lhs” R package (Carnell, 2016). The Latin Hypercube technique samples parameters evenly across their distribution range. Table \_\_\_ displays the sampled PWC input parameters, their descriptions, their distribution ranges, and the sources used to determine these ranges. The partial correlation coefficient (PCC) statistic was computed with the “sensitivity” R package to quantify the parameters’ impact on the model output, therefore serving as the primary sensitivity analysis metric (Pujol et al., 2017). The PCC statistic measures the strength of the linear relationship between the model output and each input parameter while accounting for changes in all other input parameters. It ranges from -1 to +1 with the sign denoting a negative or positive relationship, respectively, between the model output and input parameter. A Monte Carlo shell wrapper was developed using R version 3.6.1 to execute PRZM and VVWM (PWC version 1.59), conduct the Latin Hypercube technique, and assess parameter sensitivity using the partial correlation coefficient statistic (RStudio Team, 2018). The shell wrapper consisted of several R scripts each with a specific and sequential task. The scripts were written to: set up the local environment; parameterize PWC inputs with the Latin Hypercube technique and create 5000 sets of model inputs, load initial PRZM and VVWM input files, insert the Latin Hypercube sampled input parameter values into the PRZM and VVWM input files according to each simulation; execute PWC by executing PRZM and VVWM for each simulation; and write out PWC input/output files for each simulation. PWC output variables from all simulations were consolidated into .RData packages to be used in the subsequent PCC computations and analyses. The results from the probabilistic simulation design are discussed in section \_\_\_.

# Results and Discussion

## Deterministic Findings

### Runoff Evaluation

Researchers have often cited runoff as the main mode of pesticide transport (Wittmer et al., 2011; Weston et al., 2012) in urban areas. One of the factors which influence runoff is precipitation. At the study sites, high annual precipitations of 1304 mm and 1209 mm for 2010 and 2011 respectively; and annual low of 210 mm was recorded for the 2013 period (Fig. 2). Average annual precipitation for the entire study period, 2009-2014, was 934 mm.

The CN, another factor that influence runoff, reflects the impermeability of a given land use based on soil type and hydrologic conditions. For the modeled urban sites in this study, the CN used ranges from 92 to 98 (CALFED Report, 2011) because of the high amount of impervious surfaces (Buildings, pavements, etc.). A higher CN means a higher runoff potential and vice versa.

Fig. 2 and 3 shows a graphical representation of simulated runoff from the Folsom and Roseville study site and the observed runoff at the USGS gauging station at Arcade C NR Del Paso Heights, which are about 10 miles and 16 miles from the Roseville and Folsom sites respectively. Runoff simulated by the PWC accurately tracked the monthly precipitation trends during the study period. The average simulated annual runoff was 614 and 674 mm for Folsom and Roseville sites respectively while the average simulated runoff was 540 mm at the USGS gauging station at Arcade C NR Del Paso Heights. The runoffs from the modeled sites, closely match that of the modeled USGS site in both trend and magnitude. Both closely follows the annual trend in precipitation. The slight variation in the magnitude of runoff at the USGS site compared to that of the study sites may be due to differences in land cover composition of the sites. That is, impervious surface percentage associated with the study sites may be more than impervious surface percentage associated with the USGS site since the study site was found to be made up entirely of urban land use and the USGS site composition is 90% urban and 10% agricultural as stated in the study area description The high amount of runoff from the urban sites may result in high annual flows at the respective storm drain outlets (DPR-FOL002, DPR-FOL003, DPR-PGC010 and DPR-PGC022). With the model simulated runoff of 614 mm and 674 mm for the Folsom and Roseville storm drains respectively, the possibility of pesticides reaching the Sacramento-San Joaquin River, downstream of the modeled sites, is high.

Fig. 2 Total Annual Precipitation and Simulated Runoff at the USGS 11447360, Folsom and Roseville Study Sites

Fig. 3. Monthly Precipitation, Simulated Runoff at USGS 11447360, Roseville and Folsom Sites.

### Bifenthrin Simulation

High bifenthrin concentrations were observed in all the modeled sites. These highs were dominant at the Folsom sites compared to the Roseville sites. That is, from the simulated bifenthrin concentrations, results had some peaks in 2011and 2014 which is a reflection of the high amount of bifenthrin used during those periods (Fig. 4). For example, the predicted peak bifenthrin concentrations of 55.2 ng/L, 41.8 ng/L, and 43.4 ng/L on 11 March, 2011, 10 October 2011, and 3 December, 2014 for DPR-FOL002 storm drain outlet (Fig. 2) reflected individual PUR database entries of about 3.2, 2, and 2.6 kg recorded for the same period. This peak values demonstrate the sensitivity of the PWC model to individual entries in the PUR database. Similar relationship between the simulated peaks of bifenthrin and individual used amount entries was also obtained by Jorgenson et al. (2012).

1. DPR-FOL002
2. DPR-FOL003
3. DPR-PGC010
4. DPR-PGC022

Fig. 4. The observed and simulated daily bifenthrin concentration from 2009 to 2014.

Graphically, the patterns of simulated bifenthrin concentrations were consistent with the observed bifenthrin concentration pattern (Fig. 4). For the four study sites, observed mean and maximum concentrations were between 10.6-12.3 ng/L and 21.4-48.6 ng/L respectively, and the simulated mean and maximum concentrations were between 3.74-13.8 ng/L and 19.3-41.6 ng/L, respectively. With respect to the simulated bifenthrin concentrations, the Pleasant Grove site DPR-PGC022 had a maximum of 33.4 ng/L in comparison to the simulated maximum value of 21.7 ng/L obtained at the DPR-PGC010. The higher concentration at the DPR-PGC022 may be due to the higher bifenthrin use amount associated with higher number of residential units. For the Alder Creek sites in the City of Folsom, the simulated maximum bifenthrin concentration at the DPR-FOL003 outlet was 21.4 ng/L compared to the maximum value of 48.6 ng/L at the DPR-FOL002 outlet. Like the Roseville site, the number of residential units that drain to the DPR-FOL002 is more than that drains into the DPR-FOL003 outlet.

Table 5. Urban Site Observed and Simulated bifenthrin concentration from 2009 to 2014

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | | | **Observed Bifenthrin** | | | **Simulated Bifenthrin** | | | **TTest** |
| **Site** | Monitored Outlets | Number of Observe Data | Mean  Conc. (ng/L) | Median  Conc. (ng/L) | Max.  Conc. (ng/L) | Mean  Conc.  (ng/L) | Median  Conc.  (ng/L) | Max.  Conc.  (ng/L) | p = 0.05 |
| **Pleasant**  **Grove**  **Creek** | DPR-PGC010 | 21 | 5.55 | 3.27 | 21.7 | 3.74 | 0.67 | 23.56 | 0.24 |
| DPR-PGC022 | 11 | 12.27 | 9.60 | 33.4 | 8.81 | 8.64 | 23.37 | 0.15 |
| **Alder**  **Creek** | DPR-FOL002 | 19 | 16.3 | 14.4 | 48.6 | 13.8 | 11.2 | 41.6 | 0.27 |
| DPR-FOL003 | 16 | 10.60 | 11.30 | 21.40 | 9.33 | 8.34 | 19.32 | 0.25 |

In general, the PWC model output performed well in simulating bifenthrin concentration at the four storm drain outlets. The results show a close match between the simulated and observed bifenthrin data (Fig. 4 and Table 5). The slight variability between the simulated and the observed data may be due to expected variability associated with environmental measurements. The statistical evaluation revealed a strong to moderate correlation between the simulated and observed concentrations. This is evident in the R2 values of 0.67, 0.54, 0.85, and 0.70 for the DPR-FOL002, DPR-FOL003, DPR-PGC010, and DPR-PGC022 respectively when the same day observed and simulated bifenthrin concentration values were plotted (Fig. 5). There was not much difference when the means and median of the same day observed and simulated concentrations were plotted (Fig. 6). The T-Tests of equality of means (Table 5) also indicated that no statistically significant difference between the observed and simulated bifenthrin data with *p* =0.37 at DPR-FOL002, *p* = 0.25 at DPR-FOL003, 0.24 at the DPR-PGC022, and 0.15 at the DPR-PGC010 outlets. Overall, the PWC model was able to simulate bifenthrin concentration with reasonable accuracy. This suggests that the PWC model is capable of being used to generate bifenthrin concentration values in areas where there is limited to no data when needed for analysis.

(DPR-FOL002) (DPR-FOL003)

(DPR-PGC010) (DPR-PGC022)

Fig. 5. Scatterplot of observed vs. simulated bifenthrin concentration at the four sites

(DPR-FOL002) (DPR-FOL003)

(DPR-PGC010) (DPR-PGC022)

Fig. 6. The Same day observed vs. simulated bifenthrin mean and median concentration at the four sites

### Bifenthrin Application Mass Loss

Results from the PWC model shows that a substantial mass of the bifenthrin applied at the urban sites were transported to the water bodies with runoff being the main mode of transport in comparison to drift, the other modes of transport (Table 6). At the Folsom sites, a mass of 0.84% (232kg) and 0.78% (310kg) of the total applied bifenthrin were transported by combined effects runoff and drift to the urban creek at the DPR-FOL002 and DPR-FOL003 sites respectively for the entire simulation period (Table 6). Out of these, runoff alone accounted for 76% (176 kg) at the DPR-FOL002 and 60% (186 kg) at the DPR-FOL003 site. For the urban sites in Roseville, 1% (72kg) and 0.56% (72kg) of total bifenthrin applied were transported to the urban creek at DPR-PGC010 and DPR-PGC022 with runoff alone accounting for 85% and 92% of the mass loss at the respective sites. In the study area, the dominant land use is impervious surfaces and lawns which generate a substantial amount of runoff during storm events and results in washing off the applied bifenthrin to the urban creeks. While the total mass of bifenthrin lost are greatest at the Folsom sites than at the Roseville sites, the mass loss is a proportional representation of the mass applied in both counties. This outcome indicates that, the total amount of bifenthrin loss by transport is substantial enough to increase surface water pollution and its associated toxicity to aquatic species in the urban creeks and the receiving Sacramento-San Joaquin River Delta downstream of the urban sites.

Table 6. Mode of Relative Transport of Pesticide Mass

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | County | Sacramento | | Placer | |
|  | Urban Storm drain outlets | DPR-FOL002 | DPR-FOL003 | DPR-PGC010 | DPR-PGC022 |
| Bifenthrin | Percentage of runoff as main mode of transport | 76 | 60 | 85 | 92 |
| Percentage of drift as transport mechanism (%) | 24 | 40 | 15 | 8 |
| Percentage of mass transported to the urban creek by Runoff +Drift (%) | 0.84 | 0.76 | 1 | 0.56 |
| Mass applied transported to the urban creeks by Runoff +Drift (kg) | 232 | 310 | 72 | 72 |
| Mass applied transported by Runoff (kg) | 176 | 186 | 61 | 66 |
| Mass applied transported by Drift (kg) | 56 | 124 | 11 | 6 |

### Predicted Bifenthrin Toxicity in the Water Column

Bifenthrin is toxic to aquatic species at even low concentrations (Solomon et al., 2001; Feo et al., 2010). The State Water Resources Control Board has numerous water bodies in the State that are listed as being impaired by the presence of pyrethroids. This leads to the development of water body specific program plans to mitigate these impairments. At the study sites, the daily mean concentrations of bifenthrin during the simulation period were between 0.66 ng/L to 17.0 ng/L at DPR-FOL002 and between 0.41 ng/L to 9.18 ng/L at DPR-FOL003. At the Roseville area, mean bifenthrin concentration at DPR-PGC010 ranged from 0.25 ng/L to 6.44 ng/L and that at DPR-PGC022 ranged from 0.10 ng/L to 12.27 ng/L. Maximum concentrations of bifenthrin were recorded at all the urban sites for the 2011 period (Table 7) which is also the year of maximum bifenthrin application for both Sacramento and Placer County.

Table 7. Daily Mean and Maximum Urban Creek Concentration in ng/L Predicted by the PWC Model

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Site | Outlets | DPR-FOL002 | | | | | | DPR-FOL003 | | | | | |
| FOLSOM | **Year** | 2009 | 2010 | 2011 | 2012 | 2013 | 2014 | 2009 | 2010 | 2011 | 2012 | 2013 | 2014 |
| **Mean** | 1.1 | 9.54 | 17.0 | 4.69 | 2.95 | 0.66 | 0.98 | 4.95 | 9.18 | 3.51 | 2.83 | 0.41 |
| **Max** | 7.32 | 53.1 | 55.2 | 20.3 | 19.8 | 44.1 | 5.2 | 28.9 | 25.2 | 10.8 | 24 | 26.1 |
|  |  |  |  |  |  |  |  |  |  |  |  |  |
| ROSEVILLE | **Outlets** | **DPR-PGC010** | | | | | | **DPR-PGC022** | | | | | |
| **Year** | 2009 | 2010 | 2011 | 2012 | 2013 | 2014 | 2009 | 2010 | 2011 | 2012 | 2013 | 2014 |
| **Mean** | 0.39 | 3.36 | 6.44 | 1.35 | 0.54 | 0.25 | 0.54 | 6.48 | 12.27 | 2.29 | 0.10 | 0.44 |
| **Max** | 3.58 | 19 | 21.9 | 7.9 | 5.74 | 20.8 | 6.86 | 32.4 | 44.8 | 16 | 0.58 | 29.2 |
|  |  |  |  |  |  |  |  |  |  |  |  |  |

Simulated daily bifenthrin concentrations show that high peak values mainly occur during the wet season (October to April) (Fig. 4). These increased peaks may be due to the washing of accumulated bifenthrin that was applied during the dry season, in addition to flow and low dilution capacity. This is in line with urban surface water pyrethroid concentration observed by Jorgenson et al. (2012).

### Comparison between Simulated Bifenthrin EEC and CALFED 2011 Values

The CALFED 2011 reported acute and chronic Threatened and Endangered Species benchmarks for bifenthrin are: 7.5ng/L, and 1.3ng/L respectively. The acute benchmarks are equivalent to 1/10th the lowest acute USEPA benchmark for bifenthrin (CALFED, 2011). The USEPA benchmarks, developed by the OPP, are derived from the evaluation of toxicity data for a pesticide active ingredient (A.I.) or metabolite and include acute and chronic toxicity values for fish, invertebrates, vascular and nonvascular plants and other organisms within the aquatic ecosystem (USEPA, 2016a).

To be consistent with the CALFED 2011 report benchmark, the PWC derived 1-day and 4-day EECs averages, were used as the acute and chronic bifenthrin concentrations to determine the toxicity level in the urban creeks. We used these averages because it is the standard employed in laboratory testing of bifenthrin and other pyrethroid toxicity (Weston and Lydy, 2012). The duration appears environmentally relevant given the persistence of the pyrethroids and its toxicity in rivers and lakes (Weston and Lydy, 2012).

For the four storm drain outlets modeled, result from DPR-FOL002 and DPR-FOL003 (Table 8) shows that the Alder Creek, presents the greatest risks to aquatic Threatened and Endangered Species with acute EEC values between 29 ng/L and 55 ng/L compared to the 7.5 ng/L benchmark reported in the CALFED report (2011). This was expected because of the high amount of pesticides usage in Sacramento County as reported in the PUR database during the 2009 to 2014 period. This is not to say the Pleasant Grove Creek sites, DPR-PGC010 and DPR-PGC022, are safe for aquatic species existence since their 1-day average EECs are also higher (22 ng/L to 43 ng/L) than the CALFED (2011) benchmark.

The model predicted result shows that, bifenthrin EEC in the urban creeks far exceeded the reported benchmark in the CALFED 2011 report. This is of major concern at the Folsom and Roseville area since concentrations of this magnitude threaten not only the mostly examined species organism, *H. azteca*, but also a wide variety of macro benthic taxa.

Table 8. EEC of Bifenthrin in ng/L

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| City of Folsom | | | City of Roseville | | |
| Outlets | **EECs** | **EEC** | **Outlets** | **EECs** | **EEC** |
| DPR-FOL002 | Acute | 55 | **DPR-PGC010** | Acute | 22 |
| Chronic | 51 | Chronic | 20 |
| DPR-FOL003 | Acute | 29 | **DPR-PGC022** | Acute | 43 |
| Chronic | 25 | Chronic | 39 |

Though the urban creek runoffs contained a high level of bifenthrin concentration, representing a threat to aquatic species, the threat is not centered at the Pleasant Grove Creek and Alder Creek but can also affect rivers and lakes such as the Sacramento-Joaquin River Delta, which is the main receiving river downstream of these urban creeks. The predicted EECs of bifenthrin, obtained in this study, can also be compared to that seen in other urban rivers and streams in northern California (Weston and Lydy, 2012; Weston et al., 2014).

## Probabilistic Findings

### Monte Carlo simulations of pesticide concentrations

Bifenthrin concentrations were estimated from 2009 to 2014 using a range of possible input values as enabled by the Monte Carlo simulations. The percentile estimates (25, 50, 75, 97.7) of bifenthrin concentration for each study site are shown in Figure \_\_\_\_. As you can see……yada yada yada….

### Sensitivity Analysis

Sensitivity analysis highlighted critical input parameters on the model output as measured by the partial correlation coefficient statistic (Table \_\_ and \_\_\_\_). Visual PCC analyses for bifenthrin concentrations in surface runoff, vernal pool water column, and benthic water are provided in Figures \_\_\_ - \_\_\_\_. Input parameters with PCC values near ±1 can be said to have a strong linear relationship with the model output than input parameters with a PCC near 0. A positive PCC value denotes a positive correlation between the input parameter and model output whereas a negative PCC value denotes an inverse correlation between the input parameter and model output.

The sensitivity analysis identifies \_\_\_\_\_ were highly sensitive parameters …. yada, yada, yada….

# Conclusion

We used the PWC environmental fate and transport model to predict the surface water concentration of bifenthrin in the Alder and Pleasant Grove Creeks in The City of Folsom, Sacramento County and the City of Roseville, Placer County respectively. Results show that the model predicted an acceptable level of same day concentration in comparison to same observed concentration at the four urban study sites. Predicted acute and chronic EEC for the modeled pesticides in the urban creeks were higher than the derived CALFED benchmark for aquatic Threatened and Endangered Species (invertebrates and fish).

These findings suggest that bifenthrin may indeed be a problem at the sites modeled and may also indicate a major issue throughout major cities in the United States where intensive lawn maintenance and pest control practices are common. Furthermore, the results strengthen concerns that bifenthrin poses a significant environmental risk since it is obvious that current use patterns and practices allow bifenthrin, applied to urban landscape and structures, to be carried off-site in urban runoffs and contaminating rivers downstream (e.g. The Sacramento-San Joaquin River Delta)

Bifenthrin is commonly used in treating outside areas of buildings in California for the control of pest, mainly ants and rodents. Its application is either done by homeowners, who gets the products from retail stores, or by professional pest controllers who have a maintenance contract with residents for regular treatment of their property (Weston et al., 2008). Because the study area is an urban environment, it is assumed concentration of bifenthrin occurred as a result of homeowner usage and professional pest control applications. Hence, an inference can be made from the usage application. Survey carried out by TDC Environmental (2010) on homeowner and professional applicators usage, reported in the CALFED Report (2011) gives us an insight into the origin of these pesticides in the urban waters. It was assumed that professional applicators use of bifenthrin in residential areas for the control of pest was 80% with homeowner use of bifenthrin estimated at 25% of professional use (20/80=0.25). In most situations, liquid bifenthrin is used as barrier treatments around the perimeter of structures through spraying and solid granulated bifenthrin is broadcasted on lawns and similar features throughout the year. In 2014, out of the 78379 kg and 18605 kg of pyrethroids active ingredients used in Sacramento County and Placer County for structural pest control and landscape maintenance, bifenthrin accounted for about 9263(12%) and 1297kg (7%) consequently was used (CDPR Database, 2014).

The increased presence of bifenthrin in urban waters, particularly in Folsom, Sacramento, can be attributed to (1) its increased used amount compared to other pyrethroids as exhibited by the CDPR PUR data and (2) its increased perseverance in sediments, and soils than other pesticides (Laskowski, 2002). With the increase perseverance and toxicity of this pyrethroid in urban runoffs shown in this study, and other parts of California (Amweg et al., 2006), it can be concluded that the issue is not linked to only one particular location. For aquatic risk assessment, it is suggested that regular temporal monitoring of pesticides, not only their concentrations and potential replacement active ingredients in ambient surface water, but also detailed market trends in pesticide use needs to be carried out to aid in urban pesticides analysis. Where monitoring becomes a problem due to accessibility, lack of personnel or is expensive, modeling such as the one used in this study will go a long way in providing the needed information on the EECs to aid in assessing the fate of pesticides in urban waters.

Some main assumption made during the modeling is that applications were done outside of buildings and are aboveground, with regards to structural pest-control and landscape maintenance which are mainly due to homeowners and professional pesticide applicators. To effectively reduce the increased presence of bifenthrin in urban runoffs, protocol modifications may have to focus on professional applicators since they account for about 80% of the bifenthrin applications in the study area. A citizen-science initiative could also be put in place to involve homeowners in tracking their use of pesticide to obtain more information about pesticide types and frequency of use to refine the modeling effort. Also, application amounts could be reduced in rainy conditions and lawn watering would need to be integrated into the overall timing if pesticides are used on grass and shrubs. Additionally, future analysis of seasonal variation in precipitation (dry versus wet conditions) and timing of pesticide applications may show preferred time intervals for applications such as; dry conditions in forecast, to allow more time for degradation before runoff occurs. In general summary, the PWC modeling system, used in this study, holds a great promise as an analytical tool for bifenthrin concentration estimation in providing an evaluation of pesticide fate and transport in an urban setting.

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