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Methodology for Evaluating Pesticides for Surface Water Protection: PREM version 6 updates

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1 Introduction

In 2010, the Surface Water Protection Program (SWPP) of California Department of Pesticide Regulation (CDPR) incorporated computer modeling into registration evaluation methodology to provide a more consistent and transparent registration process for surface water protection. The evaluation methodology is incorporated into a computer modeling system called Pesticide Registration Evaluation Model (PREM). The first public version of the model (PREM version 2 or PREM2) was released in 2012 (CDPR, 2012). The SWPP continues to support and improve the model through updating modeling approaches and introducing new simulation capabilities for more realistic and California-centric predictions. The latest version of the model, PREM5, was published in 2017 (CDPR, 2017).

The PREM5 established the modeling framework for pesticide risk assessment in aquatic ecosystem. The modeled pesticide use patterns and application methods were applicable to most products in pesticide registration evaluation. During model applications, challenges are mainly observed for the requirements of (1) extended modeling capabilities for additional pesticide use patterns, (2) realistic modeling on pesticide partitioning and transport mechanisms, (3) accurate representation of application scenarios, and (4) considerations of label-required mitigation practices. To address these concerns, the SWPP developed new model functions and options for better simulating pesticide fate and transport under California field conditions (Table 1). This report summarizes the model development after 2017 and incorporation of those new items into the new version, PREM6. Some of the new functions, e.g., modeling scenarios in receiving water body (Xie et al., 2018), pesticide removal in a vegetative filter strip (Luo, 2020), and modeling approach for down-the-drain products (Xie and Luo, 2022), have been presented in other documents. This report will describe their computational implementations with the PREM6. Other components in the evaluation process, such as input data preparation, additional data request, modeling results interpretation, professional judgment, and final reporting with registration recommendation, will be provided in the model user's manual.

Table 1. Overview of model updates in PREM6

New development and integration	Description
Fate modeling and exposure assessment:	
[1] New pesticide simulation models	Coupling with the new models from the Pesticide Water Calculator (PWC) v2.0+ with improved algorithms on runoff generation from treated fields and chemical distribution in receiving water bodies
[2] Modeling scenario for receiving water body	Validation and integration of the U.S. Environmental Protection Agency (USEPA) standard pond scenario for California field conditions
[3] K_d-based partitioning	Pesticide phase partitioning based on K_d values for land, water, and impervious surfaces
[4] Biotic ligand model	Toxicity adjustment for copper in freshwater according to water quality parameters
[5] Volatile compounds	Aquatic exposure assessment for soil fumigants
[6] Chronic risk assessment	Risk characterization based on chronic toxicity test results to aquatic organisms
Use patterns and application methods:	
[7] Percent treated area	Agricultural watershed potentially treated by the pesticide product under evaluation
[8] Advanced options for agricultural uses	Parameters for each individual application
[9] Advanced options for residential uses	Refined landscape characterization for pesticide uses on impervious surfaces in California residential settings
[10] Down-the-drain products	Exposure assessment on pesticide in wastewater treatment plant (WWTP) discharges
[11] Multiple crop seasons	Pesticide applications during successive cropping seasons of vegetables
Mitigation practices:	
[12] Vegetative filter strip (VFS)	Pesticide removal through a VFS
[13] Spray buffer zone	Adjustment on the spray drift fraction according to the required buffer-zone distance for pesticide applications
[14] Application restrictions by rainfall	Application timing algorithm to avoid forecasted rainfall events after applications

2 Pesticide fate modeling and exposure assessment

2.1 New simulation models for pesticides

In the recently updated PWC version 2.0+ (2.0 and 2.001) (USEPA, 2021b), the USEPA released new simulation models for pesticide modeling, including Pesticide Root-Zone Model (PRZM) version 5 revision B and Varying Volume Water Model (VVWM) revision B. The new models have been incorporated into the PREM6.

Compared to the previous version in PWC 1.52 (Young, 2016b), the new simulation models improved the algorithm for unit peak discharge from the treated field (Young, 2020) and initial phase distribution of pesticide entering the receiving water body (Young, 2019) (Table 2). Specifically, the unit peak discharge rate is now calculated with the original coefficients for rainfall distribution generated by U.S. Department of Agriculture (USDA, 1986), compared to the coefficients in previous version modified to represent longer duration precipitation events. This change would generally increase model-predicted soil erosion from pervious surfaces and provide more consistent results with other models using the same USDA rainfall characterization. For the initial pesticide phase distribution in the receiving water body, the new models first establish equilibrium by mixing the incoming pesticide in the water column, and update the distribution factor (PRBEN) for each day of simulation. Compared to the previous versions with a fixed value of PRBEN (0.5 by default) for the whole simulation period, the new modeling approach provides more realistic simulations on pesticide fate and transport in the receiving water body. For hydrophobic compounds, with the new algorithm, more pesticide mass would be distributed to the benthic region, suggesting an effective PRBEN>0.5 as confirmed in the previous modeling studies, such as 0.85 used for pesticides with K_{OC}>100,000 (Hoogeweg et al., 2011).

Table 2. Major revisions applied to the new pesticide simulation models in PWC 2.0+

Revision and effects	Peak discharge rate	Initial phase distribution of incoming pesticide to the receiving water body
Revision A (previous version)	Modified coefficients in the calculation of peak runoff rate (Carsel et al., 1998)	A user-specified fraction (0.5 by default) of incoming eroded pesticide is distributed to the benthic region
Revision B (new version)	Original USDA coefficients (USDA, 1986)	Varying distribution by equilibrium
Effects of the changes	Generally increases predicted soil erosion and associated pesticide runoff	Increase the ratio of pesticide masses in the water column vs. benthic region for water-soluble pesticide, and decrease the ratio for hydrophobic components to better represent chemical partitioning.

Notes: The effects of using the original USDA coefficients on modeling results are derived in this study with crop/weather scenarios in California with a type I rainfall distribution (Central Valley, San Francisco Bay, Central Coast, and Southern California).

In April 2023, USEPA released new modeling scenarios of drinking water assessment ("dw_scenarios_v4"), and made a note that the same scenarios would also be used for ecological risk assessments (USEPA, 2023). SWPP is evaluating the new scenarios and associated weather data. Meanwhile, the existing crop/weather scenarios for ecological risk assessment ("eco_scenarios") used in PREM6, are the same as those in the previous versions of PREM.

2.2 Receiving water body

The USEPA recommends the receiving water modeling with a "standard farm pond" scenario (Table 3) for ecological risk assessment (except for rice pesticides). Since the version 3, the pond scenario has been used by PREM for both agricultural and urban outdoor applications. Although this scenario may not physically represent the site-specific conditions in each application, it is expected to provide reasonable and conservative estimation of pesticide concentrations in surface water of California when compared to monitoring data. This assumption has been validated in a series of CDPR studies.

Table 3. Input parameter values for the USEPA standard farm pond scenario (Young, 2016a)

Parameter	Value
Drainage area normalized to capacity (DANC, m^2/m^3)	5
Water column suspended solids (SS, mg/L)	30
Water column fraction of organic carbon (foc) (-)	0.04
Water column dissolved organic carbon (DOC, mg/L)	5
Water column biomass (mg/L)	0.4
Benthic porosity (-)	0.5
Benthic bulk density (g/cm^3)	1.35
Benthic foc (-)	0.04
Benthic DOC (mg/L)	5
Benthic biomass (g/m^2)	0.006

First, during the development of the California urban/residential scenario in PREM version 3 (Luo, 2014b), model predicted pesticide concentrations with the pond scenario were summarized from USEPA risk assessments for historical urban pesticide uses in California for 11 active ingredients with a wide range of chemical properties (acephate, alachlor, bensulide, bifenthrin, carbaryl, cyfluthrin, beta-cyfluthrin, deltamethrin, lambda-cyhalothrin, malathion, and methomyl) (USEPA, 2013a). The modeling results were compared to the monitoring data in CDPR's surface water database (SURF). The results showed that model predictions with the pond scenario generally overestimated measured peak concentrations within 1 order of magnitude. The only significant under-prediction was observed for bifenthrin for which the monitoring data as whole-water concentration in water column exceeded the water solubility of the chemical used in modeling (i.e., 0.014 ppb). According to the uncertainty analysis by the USEPA (USEPA, 2012b), this may suggest presence of dissolved organic matter or suspended matter in the water that could sorb the chemical and cause it to be present at higher concentrations, although it would not be bioavailable. More detailed model validations were also conducted for residential uses of fipronil (Budd and Luo, 2016) and bifenthrin (Luo, 2017b, c).

For agricultural uses of pesticides, model validation was first conducted for six pyrethroids (bifenthrin, cyfluthrin, lambda-cyhalothrin, cypermethrin, esfenvalerate, and permethrin) with monitoring data in benthic region (Luo, 2017d, 2019), and results suggested prediction/observation ratios ranging from 1.0 to 10.7 with the pond scenario for receiving water modeling. Another study (Xie et al., 2018) selected seven pesticides (chlorpyrifos, diazinon, malathion, simazine, bifenthrin, permethrin, and imidacloprid) for model testing based on the use in California and the availability of aquatic life benchmarks. By comparing with the

measurements in CDPR's SURF, the results suggested that the pond scenario was able to provide a conservative and reasonable estimate of concentrations (i.e., within one order of magnitude greater than the worst-case monitoring data) for the regulatory exposure assessment in California's agricultural settings.

More recently, the pond scenario was validated for down-the-drain products and WWTP discharge (Xie and Luo, 2022). Twelve pesticides that have discharge monitoring data reported in California were tested: acetamiprid, bifenthrin, chlorpyrifos, clothianidin, cyfluthrin, cypermethrin, deltamethrin, esfenvalerate, fipronil, imidacloprid, lambda-cyhalothrin, and permethrin. The 99th percentile of concentrations measured in WWTP discharges, representation the worst-case discharges from WWTPs, are used as model inputs to the receiving water body. Due to insufficient monitoring data immediately downstream of WWTP discharges, the 99th percentile of all monitoring data reported in California surface waterways are compared with the model predictions. For most of the modeled pesticides, the pond scenario conservatively estimates the measurements within 1-2 orders of magnitudes.

Therefore, pesticide simulations in receiving water body are incorporated into PREM6 with the standard farm pond as the default scenario. Receiving water modeling would be used for the evaluation on agricultural, urban, down-the-drain, and aquatic products, but not for rice pesticides. For aquatic uses, the PREM6 provides the option to adjust water depths according to the label information. For down-the-drain products, more information is provided in Section 3.4. For the ecological risk assessment on rice pesticides, exposure is only evaluated in the rice paddy with predicted concentrations that may be released after a specified holding period, thus modeling for a receiving water body is not needed (White et al., 2016b; White et al., 2016a).

The PREM6 generally follows the same modeling procedures for receiving water body as in the PWC (USEPA, 2021b). Except for the evaluation on copper products (Section 2.4), the PREM6 uses the daily *average* concentrations of pesticide predicted in the water column and benthic region of the receiving water body for acute risk characterization. Note that most of the previous ecological risk assessments (ERA) conducted by USEPA were based on the daily *peak* concentrations for acute risk assessment (USEPA, 2017b). Peak concentrations reflect the conditions immediately after pesticide runoff flowing into the receiving water, while daily averages are more appropriate for comparison with the acute toxicity data which are usually reported with a test duration of 48 to 72 hours.

2.3 Solid-water phase partitioning coefficient (K_d)

By default, PREM simulates phase partition of pesticide with a K_{OC}-based approach. User-provided K_{OC} is used to estimate K_d values for modeling simulations in the agricultural field, receiving water body, and impervious surface with the corresponding organic carbon (OC) content. For example, the OC content of 0.04 was predefined in the pond scenario for both suspended and bed sediment. The OC content in soil is dependent on crop scenarios and soil depth, e.g., 0.081 for the top soil layer in the "California almond" scenario (USEPA, 2022). The OC content on impervious surface is set to be zero ("California impervious" scenario), therefore, K_d for impervious is also zero in the K_{OC}-based approach.

The PREM6 provides an option for user to specify K_d value for each environmental compartment of soil, water, and impervious surface. With this option, the PREM6 will ignore OC contents but directly predict pesticide phase partitioning with the given K_d values. This option is recommended for the following conditions:

1) Chemicals for which the K_d approach better represents the mobility than K_{OC}, according to the coefficient of variation (CV) for K_d vs. K_{OC} values from submitted soil adsorption/desorption studies. In addition, a plot of the OC content vs. K_d can be used to further determine whether the K_d is correlated with organic carbon. In the ERA of pyrethroids and pyrethrins (USEPA, 2016c), for example, four of the chemicals were modeled using the K_d approach instead of K_{OC}: bifenthrin, lambda-cyhalothrin, permethrin and pyrethrins.
2) Products for urban outdoor uses with effective K_d on impervious surface. Compared to the default value of zero K_d, the effective K_d estimated from washoff studies more realistically simulate pesticide runoff from impervious surface. A back-calculation method to determine effective K_d was proposed in the previous study, and demonstrated with washoff measurements from CDPR contracted studies for nine pesticides (Luo, 2014a).
3) Metal-containing pesticide products. PREM is not originally designed to model inorganic chemicals; however, the pesticide simulation models PRZM and VVWM integrated in PREM have been used to model the runoff of copper into surface water (USEPA, 2011). For the evaluation of metal-containing products, the PREM6 uses two K_d values (for landscape and in-water simulations, respectively). Recommended K_d values are retrieved from USEPA review of partition coefficients for metals in surface waters and soils (Allison and Allison, 2005). The median of reported K_d values are used, consistent with the input data preparation for PREM (Luo et al., 2019). For copper, a soil-water K_d of 501 L/kg was used to model the partitioning of copper between soil and overland flow and a sediment-water K_d of 15,849 L/kg was used for the receiving water. Note that the PREM6 modeling on copper is developed for agricultural and urban applications, while marine uses of copper-containing pesticides such as anti-fouling paints should be evaluated by the Marine Antifoulant Model to Predict Environmental Concentrations (MAM-PEC) (Zhang and Singhasemanon, 2014).

2.4 Biotic ligand model for copper in freshwater

Copper is a naturally occurring element and becomes toxic to aquatic life at elevated concentrations. The toxicity of copper is evaluated according to its transferability from aquatic system to biochemical receptors on or in the organism. This transfer is not only related to the total concentration, but also the bioavailability of copper in the aquatic system. Once released into a water body, copper exists in various forms and each is associated with different bioavailability. Generally, “free” copper that exists as cupric ion – Cu(II) is more bioavailable than other forms (USEPA, 2007b). Most dissolved copper is bound to various ligands (including dissolved organic compounds, hydroxides, carbonates, and other inorganics).

USEPA (2007b) suggested the use of the biotic ligand model to calculate copper toxicity to aquatic organisms as a function of site-specific chemical constituents that can limit

bioavailability of copper by either complexing or competing with copper. The model inputs are water quality parameters of dissolved organic carbon (DOC), humic acid (HA) fraction of DOC, geochemical ions (GIs, including calcium, magnesium, sodium, potassium, chloride, sulfate, and alkalinity), pH, and water temperature. The model output is a final acute value (FAV), which is derived as the 5th percentile toxicity value for approximately 350 acute freshwater toxicity tests adjusted by the biotic ligand model.

The PREM6 uses the USEPA approved biotic ligand model version to calculate the FAV (HydroQual, 2007; USEPA, 2007b). The model is incorporated in the PREM6 with two simulation options: [1] for USEPA modeling scenarios with regional representative water quality parameters, and [2] for a receiving water body characterized with site-specific water quality parameters.

2.4.1 Representative water quality parameters

Dissolved organic carbon (DOC) and humic acid (HA) fraction of DOC

DOC values are retrieved from the receiving water scenario for the standard farm pond (Table 3, 5 mg/L for both water column and benthic region). The HA fraction is set to a default value of 10% (Windward, 2019).

Geochemical ions

Similar to the crop modeling scenarios with prescribed soil and canopy parameter values, the water quality parameters for the biotic ligand model could be summarized from measurements. GI (Ca, Mg, Cl, Na, K, and SO_4) and alkalinity are taken from the USEPA recommended estimates (USEPA, 2016a). The estimation was based on surface water monitoring data for rivers and streams between 1984 and 2009 from United States Geological Survey (USGS) National Water Information System (NWIS). Geostatistical analysis was conducted to estimate GI parameters based on the 10th percentile of conductivity data. Results were summarized by Level III ecoregions and presented in two formats: estimates for the whole ecoregion or separated by Strahler stream orders. The PREM6 uses the ecoregion-wide statistics for registration evaluation. Most of the agricultural and urban areas of California are enclosed by the four Level III ecoregions, including ecoregion 6 (Southern and Central California Chaparral and Oak Woodlands), 7 (Central California Valley), 8 (Southern California Mountains), and 85 (Southern California/Northern Baja Coast) (Figure 1). The USEPA provided GI estimates for the three regions of 6, 7 and 8 (Table 4), but no data for #85 which leaves a significant portion of the Los Angeles Region without default values. Los Angeles Regional Water Quality Control Board has proposed the development of monitoring studies and water quality databases for this area (LARWQCB, 2019).

Figure 1. Level III ecoregions in California. Highlighted are the three ecoregions with USEPA recommended inputs for the biotic ligand model

Table 4. Recommended 10th percentile concentrations for geochemical ions and alkalinity (mg/L) in the Level III ecoregions in Mediterranean California (USEPA, 2016a)

Ecoregion	Ca	Mg	Na	K	SO_4	Cl	Alkalinity
6 (Southern and Central California Chaparral and Oak Woodlands)	42	24	48	2.5	136	56	124
7 (Central California Valley)	21	16	25	1.7	58	21	91
8 (Southern California Mountains)	63	25	63	3.8	171	54	150
85 (Southern California/Northern Baja Coast)	63	25	63	3.8	171	54	150

Note: No statistics were provided for the ecoregion 85. In the PREM6, this region is currently modeled with the default values derived for the ecoregion 8.

Pesticide uses patterns are assigned to Level III ecoregions according to the local of weather station used in the corresponding Tier-2 modeling scenario (USEPA, 2022) (Table 5). For example, the use pattern of "California almond" in the PREM is modeled with the weather data from the NOAA station at Sacramento Airport (WBAN23232), and thus will be modeled with the GI parameters summarized from the ecoregion 7 (Central California Valley). Outdoor nursery is the only use pattern modeled in the ecoregion of 85 where the USEPA-recommended GI parameters are not available. For this use pattern, parameter values from the ecoregion 8 (Table 4) are currently used in the PREM6 for the biotic ligand model and will be updated once the data for the ecoregion 85 become available.

Table 5. Level III ecoregion for each modeling scenario according to the location of weather station

Weather station (WBAN ID)	Station location	Represented regions	Example crop modeling scenarios	Ecoregion
23155	Bakersfield	Southern San Joaquin Valley	Citrus	7
23188	San Diego	Southern California	Outdoor nursery	85
23232	Sacramento	Stanislaus / San Joaquin Counties	Almond, corn	7
23234	San Francisco	Central California Coast, San Francisco Bay area	Urban uses, turf	6
23273	Santa Maria	Salinas area	Lettuce	6
93193	Fresno	Southern San Joaquin Valley	Cotton, tomato	7

Note: WBAN = Weather-Bureau-Army-Navy. WBAN is a five-digit station identifier used at NOAA for digital data storage and general station identification purposes

pH value

The USEPA does not provide representative values for pH. In the PREM6, a default value for pH is derived for California via a method similar to that used in generating values for GIs. Measurements for pH are downloaded from NWIS for the monitoring site types of "Lake" and "Stream" in California collected during 1984-2009. The default pH value is set to 7.45 as the 10^{th} percentile of all pH measurements.

Water temperature

Daily water temperature is calculated as the average air temperature for the previous 30 days. The same approach is used in VVWM, which estimates water temperature for adjusting the aerobic metabolism rates. Air temperatures are taken from the same meteorological data used in the tier-2 modeling scenarios (Table 5) (USEPA, 2006).

Figure 2 shows an example of predicted FAVs based on the recommended GI inputs for the Level III ecoregion #6 (Southern and Central California Chaparral and Oak Woodlands) and the

weather station WBAN23234 (SFO international airport) are used. The measured air temperature ranges between 0 to 28.5°C, and predicted water temperature 5.3-19.4°C. Predicted FAVs generally increase with water temperature (e.g., FAV = 44.73 ppb at water temperature of 5°C, FAV = 45.45 ppb at 10°C, and FAV = 47.98 ppb at 20°C), with an average of 46 ppb. The predicted FAVs for copper in freshwater are much higher than the lowest measured LC50 in freshwater of 4.8 ppb for *Daphnia magna* (USEPA, 2007b).

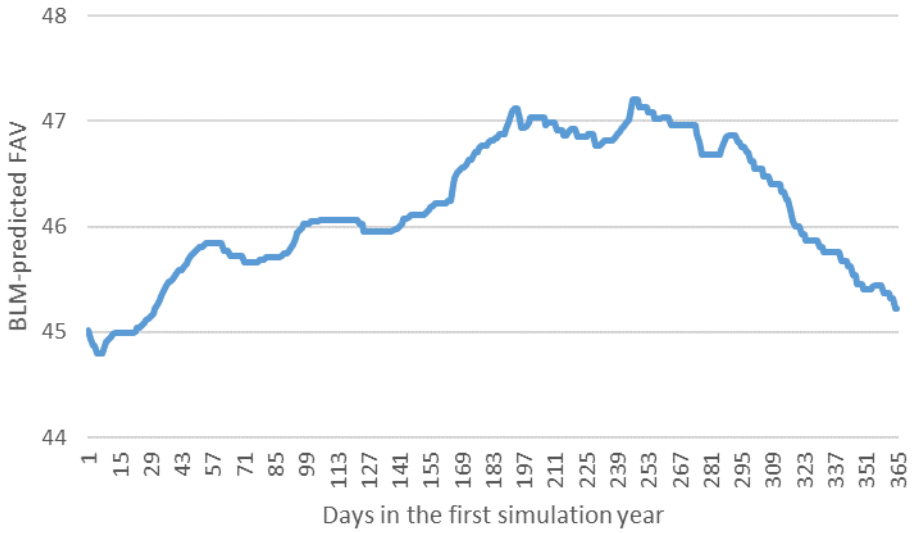

Figure 2. Predicted final acute values (FAVs, ppb) varying with daily water temperature, showing the first simulation year for demonstration

Risk characterization

The biotic ligand model is integrated into the PREM6 and its predicted FAV according to water quality parameters in the receiving water body is used for risk assessment. Similar to other pesticides, the risk quotient (RQ) for copper in freshwater is calculated as the ratio between the estimated environmental concentration (EEC) and the toxicity value (TOX),

$$RQ = \frac{EEC}{TOX}$$

Specifically for copper evaluation, the EEC is estimated by the PREM6 and the TOX value is set to FAV from biotic ligand model (Table 6). As above-mentioned, the toxicity value for copper evaluation is based on the daily FAVs predicted by the biotic ligand model. For the EEC, the USEPA has concluded that the acute criteria duration of 1-hour is appropriate for acute criteria calculations for copper (USEPA, 2017c). The VVWM does not predict hourly concentrations (in the water column and benthic zone of the receiving water), but reports "daily peak" and "daily average" values for each simulation day. The PREM6 uses the daily peaks as the EEC for copper evaluation. Once daily risk quotients are calculated, the 90th percentile of annual maximums over the 30-year simulation period (i.e., "1-in-10-year" risk quotient) is compared with the level of

concern (LOC) for risk assessment in aquatic system as a part of the decision-making processes (Luo, 2017a).

Table 6. Proposed PREM6 modeling approach for copper evaluation in freshwater

Variables	Standard PREM approach	Proposed approach for copper evaluation in freshwater
Partitioning in a receiving water	K_{OC}-based approach	K_d-based approach (see Section 2.3)
Toxicity value (TOX)	The lowest measured LC50 or EC50, a fixed value	Final acute values (FAVs) from the biotic ligand model as a function of water quality parameters
Estimated environmental concentration (EEC)	Predicted daily average concentrations	Predicted daily peak concentrations
Daily risk quotient (RQ)	EEC/TOX	Same
RQ for risk assessment	1-in-10-year RQs	Same

2.4.2 Site-specific water quality parameters

Some registration submissions, such as those for the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) section 24(c) special local needs, may come with measured site-specific chemistry data in the proposed receiving water body. In this case, the PREM6 provides a function to predict the FAV using the biotic ligand model with the provided input parameters (Figure 3). For the humic acid (HA) fraction of DOC and sulfide concentration, if measurements are not available, default values can be used: 10% for HA and a near-zero value such as 1.0E-10 mg/L for sulfide (Windward, 2019). The target concentration is an optional input used to calculate the risk quotient as the ratio between the target concentration and FAV.

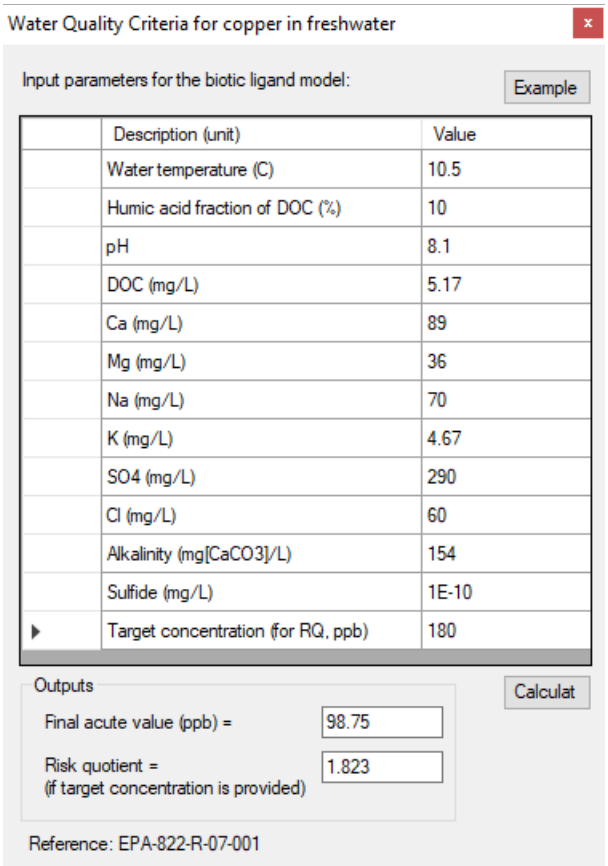

Figure 3. PREM6 function to predict the final acute value for copper in freshwater by the biotic ligand model with site-specific water quality parameters

2.5 Volatile pesticides

The PREM6 uses vapor pressure (VP, torr), commonly available chemistry values submitted by registrants, to classify the volatility of the pesticide under evaluation. Following the thresholds established for environmental fate data interpretation in Pesticide Properties Database (IUPAC, 2023), a pesticide with VP $\geq$ 3.75 torr is moderately to highly volatile and required to be evaluated in the PREM6 with additional input parameters for refined simulations on volatilization.

The required parameters include Henry's law constant (HLC, dimensionless), air diffusivity (DAIR, cm^2/day), and heat of Henry (or enthalpy of vaporization, ENPY, J/mol). Note that HLC may be provided in other units, which should be converted to dimensionless value before use in PREM6. USEPA on-line tools for site assessment calculation include a webpage for HLC conversions (USEPA, 2001). If the HLC data is not submitted for evaluation, it can be estimated as a function of vapor pressure (VP, torr), water solubility (SOL, mg/L), and molecular weight (MWT, mol/g),

$$HLC = \frac{VP \cdot MWT}{760 \cdot R \cdot SOL \cdot T}$$

where T is temperature (K) set as 298K assuming that the vapor pressure is reported at 25ºC, R is the universal gas constant (8.206×10^{-5} atm·m^3/mol/K), and 760 is a constant for unit conversion.

USEPA recommends the following equations to estimate DAIR (Rothman et al., 2015),

$$DAIR = \frac{10^{-3} T^{1.75} M_r^{1/2}}{P(V_A^{1/3} + V_B^{1/3})^2} \times 3600 \times 24$$

$$M_r = \frac{M_A + M_B}{M_A M_B}$$

$$V_B = \frac{M_B}{\rho_B}$$

where T is temperature (K), M_A is the molecular weight of air (approximately 29 g/mol) and M_B is the molecular weight of the chemical, P is the pressure in atm (default of 1 atm), V_A is the molar volume of air (approximately 20.1 cm^3/mol) and V_B is the molar volume of the chemical, and ρ_B is the density of chemical (g/cm^3). The equations were originally developed in the Handbook for Chemical Property Estimation Method published by American Chemistry Society (ACS, 1981), and also implemented in the USEPA online tools for site assessment calculation (USEPA, 2001).

At 298K or 25ºC, the above equation is simplified as,

$$DAIR = \frac{1.847\times10^6 (\frac{1}{M_B} + \frac{1}{29})^{1/2}}{[2.719 + (\frac{M_B}{\rho_B})^{1/3}]^2}$$

As recommended by USEPA (Rothman et al., 2015; Young, 2016c), the heat of Henry (ENPY) for a pesticide could be estimated via the Estimation Program Interface (EPI) Suite (USEPA, 2012a).

For soil injection of volatile pesticides, the initial mass distribution of volatile pesticide in soil is modeled in a linearly increasing fashion from the surface to the user-specified depth of injection. If tarps are applied after application, the PREM6 function for rainfall/runoff restriction can be used to avoid runoff generation from the treated field for the period between application and tarp cutting. See section 4.3 for more information.

2.6 Chronic risk assessment

Previous to the PREM6, the SWPP methodology has evaluated ecological risks and makes registration recommendations based on acute risk quotient (RQ). The acute RQ is calculated as the ratio between the 1-in-10-year daily average EEC and the acute toxicity value (reported as 48-hour EC_{50} or 96-hour LC_{50}) to the most sensitive species of fish or invertebrates. The PREM6 provides a new function for exposure assessment and risk characterization in the receiving water

body based on chronic toxicity values compared to a moving average EEC calculated for the duration of comparable chronic test. The new function is developed for all pesticide use patterns modeled in the PREM6.

For chronic risk assessment, the required model inputs are the chronic toxicity value and associated toxicity test duration, e.g., NOEC (No Observed Effects Concentration) over a 21-d period. The PREM6 calculates the moving averages of predicted daily concentrations according to the toxicity test duration as the averaging time period. Chronic risk quotient is calculated by dividing the predicted moving average concentration by the chronic toxicity value. Consistent with acute risk assessment, the resulting chronic RQ is further compared with the corresponding level of concern (LOC) for risk characterization. The LOC = 0.5 for acute risk assessment and 1.0 for chronic risk assessment (USEPA, 2017a).

The chronic risk assessment in the PREM6 is developed as a post-processing function, and does not affect the main modeling processes for acute risk assessment. Similar to the previous versions, the PREM6 recommendations are based on acute RQ values. However, this new chronic functionality expands existing modeling capabilities; chronic RQ values can be calculated as additional supporting information for SWPP scientists to provide justification for their recommendation.

The new function for chronic risk assessment has been back-tested for all pesticide products (about 120 products, excluding rice pesticides) previously evaluated by SWPP with PREM from 2011 – 2020. The resulting chronic RQs are compared with the previous PREM-based registration recommendations with acute evaluation. Preliminary results show that, for most of the products, the consideration of chronic risk assessment does not change the previous registration recommendations. Only five products (containing four active ingredients of afidopyropen, imidacloprid, fipronil, and flupyradifurone) are predicted with chronic RQ values (relative to LOC) significantly higher than the corresponding acute values. For afidopyropen, its chronic toxicity value (to the most sensitive species, 0.0071 ppb) are lower than the acute value (2170 ppb) by 30,000 times, resulting in much higher chronic RQ values. For other three pesticides, their chronic toxicity values are also significantly lower than the acute values (20 – 4000 times). Based on the testing results, chronic risk assessment is suggested for the following two conditions: (1) the ratio between the acute and chronic toxicity values (to the most sensitive species) is larger than 100, or (2) the ratio is larger than 10 and the acute RQ values between 0.1 and 0.5 (i.e., model-based recommendation of conditional registration). With the available toxicity data in the Aquatic Life Benchmarks (USEPA, 2021a) and the Pesticide Properties Database (IUPAC, 2023), about 10% of all pesticides have an acute/chronic ratio larger than 100.

3 Options for pesticide use patterns and application methods

3.1 Percent treated area

Percent treated area (PTA) represents the fraction of potentially treated area in the drainage area modeled as a 10-ha agricultural or urban catchment. PTA=1 indicates that the entire drainage area could be treated by the pesticide product under evaluation, so all runoff contributing into the receiving water body is associated with the pesticide. For registration evaluation, the PTA is

essentially a parameter for dilution. With PTA<1, a certain portion of the drainage area would not be treated, thus the runoff from untreated areas would mitigate the pesticide exposure in the receiving water body.

Many pesticide products for agricultural uses, such as neonicotinoids, organophosphates, and pyrethroids, are labelled for a wide variety of crops. In a small agricultural watershed, most of the crops could be potentially treated. During the summer dry season in California, in addition, surface water body in an agricultural watershed could be dominated by agricultural runoff as irrigation return flow. Therefore, PTA=1 is used as a conservative estimation in PREM for registration evaluation on pesticide products for statewide agricultural uses. This assumption has been validated by Xie et al. (2018) for agricultural receiving water in California.

The option of PTA<1 is used in the PREM6 for the following three types of registration evaluations: (1) urban outdoor uses, (2) down-the-drain products, and (3) special local needs (SLN) products for certain crops under restricted application conditions. For urban outdoor uses, the treated areas are calculated based on the SWPP urban/residential scenario and the application method (Luo, 2014b, 2017a). Evaluation on down-the-drain products will be described later in section 3.4.

For SLN products, PTA should be determined based on the label-specified commodities and environmental conditions for applications. For example, a series of SLN fungicides is labelled for orchards with standing water during the winter rain season in California. The fractional areas of orchards by watershed at HUC12 level in California are determined based on the cropland data layer (CDL) (USDA, 2020). The highest percent crop area of orchards is 0.64 (observed in a watershed in Tulare Basin), and the 90th percentile is about 0.50 (Figure 4).

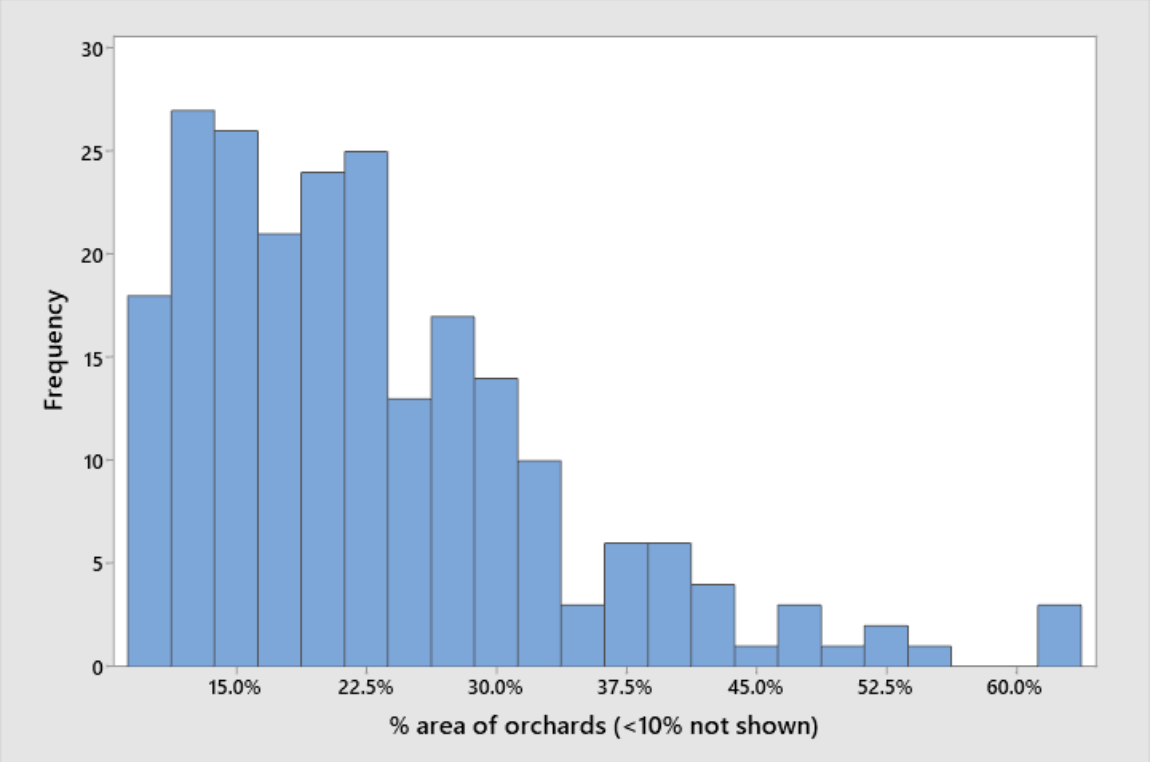

Figure 4. Histogram of cropping areas by HUC12 in California, orchards as an example

A new function in the PREM6 is developed for user-specified PTA for agricultural uses of pesticides. The 90th percentile of land use fraction (e.g., 0.5 for orchards as demonstrated above) is recommended for PTA in the registration evaluations of SLN products.

3.2 Advanced options for agricultural applications

Multiple applications of a pesticide product are modeled in the previous PREM by repeating one prescribed application over a year according to the user-specified interval and number of applications. For example, an aerial application of a pesticide at a rate of 0.1121 kg/ha could be modeled 5 times at an interval of 7 days. An advanced modeling option is provided in the PREM6 which allows users to specify parameters for each individual application. This new function was developed to evaluate more complex scenarios of agricultural applications in product labels. For example, imidacloprid uses on lettuce could be modeled as one application as soil incorporation at a rate of 0.296 kg/ha, followed by five foliar applications at a rate of 0.053 kg/ha and an interval of 5 days, as summarized in the USEPA (2016b) ERA.

In the advanced modeling option, each application is characterized by application date, rate, method, incorporated depth, efficiency, and drift fraction. Application date is specified as the relative days ("Rday" in the PREM6) to the user-provided reference date (usually set as the date of first application or date of crop emergence). For example, Rday = 0, 14, 28 (Figure 5) indicates three applications at 0, 14, and 28 days after the reference date. By default, the reference date for agricultural pesticide uses is set as the date of crop emergence. Therefore, a negative value of the relative days represents a pesticide application before emergence, such as planting of pesticide-treated seeds.

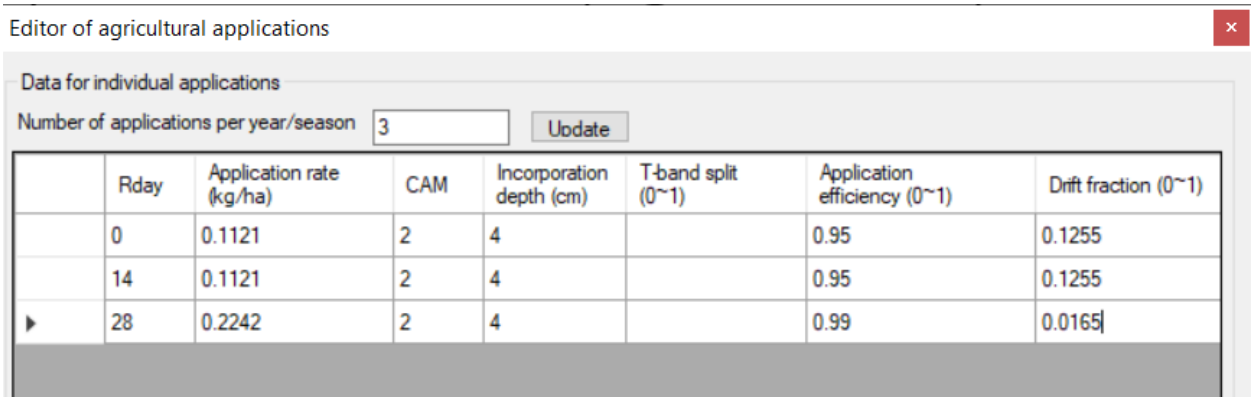

Figure 5. PREM6 advanced modeling option for agricultural applications

Pesticide incorporation in the soil is modeled follows the definition of "chemical application method (CAM)" by USEPA (Young, 2020) (Table 7). For the application methods of CAM≥4, the input value of incorporation depth (cm) is required in the model. In addition, a user-defined split fraction (0 – 1) is also needed for t-band applications. Spray methods (aerial, air-blast, or ground applications) are characterized by the two input parameters of application efficiency and drift fraction. According to the USEPA guidance, the application efficiency is modeled as 0.85

for aerial spray and 0.99 for ground spray and orchard air-blast, and drift fraction as 0.05 for aerial spray, 0.03 for orchard air-blast, and 0.01 for ground spray (USEPA, 2004). Those default values could be refined with label language of the pesticide product such as the requirement of spray buffer zone. See section 4.2 for more information.

Table 7. Definition of Chemical Application Method (CAM) (Young, 2020)

CAM	Description
1	below crop, linearly decreasing incorporation to a soil depth of 4cm
2	above crop (linear interception), linearly decreasing incorporation to 4cm
3	above crop (exponential interception), linear decreasing incorporation to 4cm
4	below crop, uniform incorporation to a user-specified soil depth (DEPI)
5	below crop, linearly increasing incorporation to DEPI
6	below crop, linearly decreasing incorporation to DEPI
7	T-band: below crop, user-defined fraction in the top 2cm, and maximum depth DEPI
8	below crop, application at DEPI
9	similar to CAM=2, but incorporation to DEPI

The PREM6 also provides an option to skip pesticide applications for some years. The default modeling process assumes that the proposed applications will be repeated every year during the 30-year modeling period of 1961-1990. The new option in PREM6 allows users to evaluate pesticide applications on a certain number (N) of years as required in the product label. For example, “applications every other calendar year” is modeled with N=2. In this case, the PREM6 will model applications in 1961, *no application in 1962*, applications in 1963, and so on.

3.3 Advanced options for residential uses

In the initial development of urban/residential module (Luo, 2014b), the landscape in urban areas is modeled as four surface types aggregated by permeability (pervious or impervious) and water sources (with or without dry-weather runoff). During the version 5 updates (Luo, 2017a), hydrological connectivity was considered for residential uses of pesticides. Some of the impervious areas that drain to adjacent pervious surfaces are separated as a new surface type for modeling.

The PREM6 further refines the residential landscape description and provides advanced options to represent alternative application methods for mitigating pesticide uses in residential settings. The mitigation practices are usually associated with restrictions on pesticide applications over impervious surfaces such as driveways and foundation perimeters. Therefore, the new modeling function allows users to specify application methods on each residential landscape component (Figure 6).

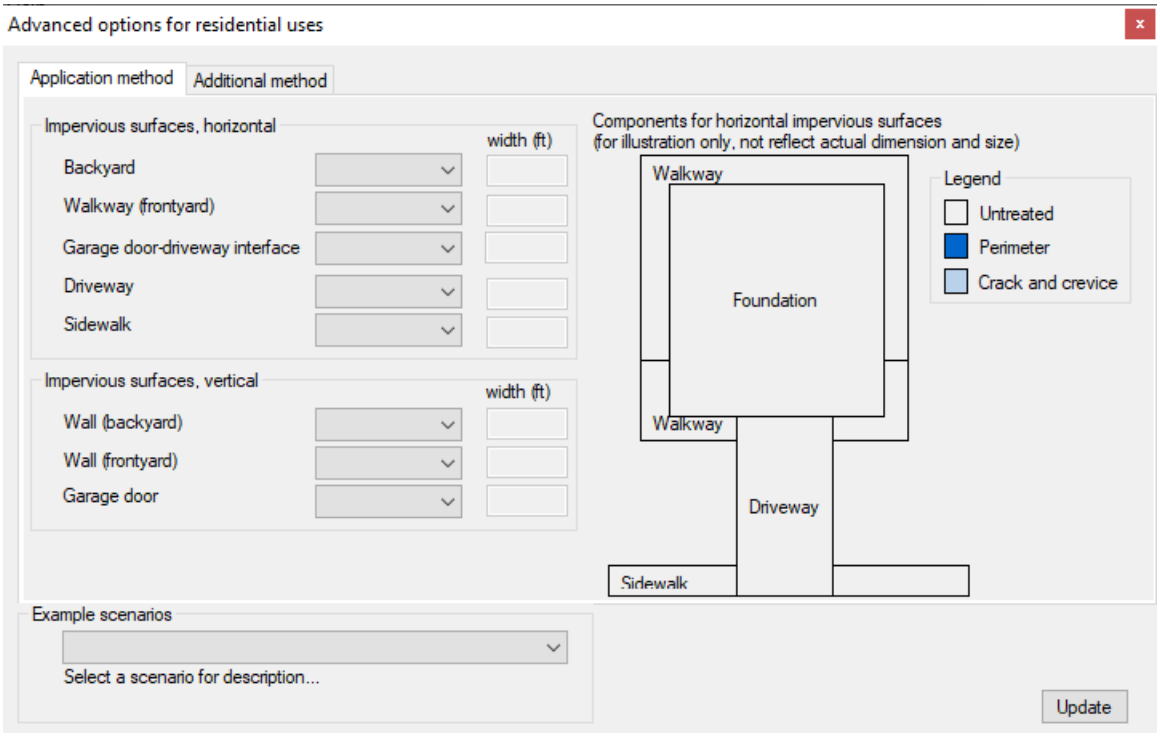

Figure 6. PREM6 advanced modeling options for residential uses

The impervious surfaces commonly treated by pesticide around a house lot are modeled as 7 landscape components (Table 8). The garage door - driveway interface is the upper portion of a driveway connected to a garage door. It is not physically characterized but defined according to mitigation practices. For example, pinstream perimeter treatment was proposed for this area (Davidson et al., 2014; USEPA, 2016c). Application methods can be modeled as no treatment, perimeter treatment, or crack and crevice treatment (Table 8). If a perimeter treatment is selected, users are also asked to specify the application width (ft). Note that the surface components and application methods in the advanced options are provided for evaluating mitigation practices. For general application methods without additional restrictions (such as broadcast on lawns and paved areas), the basic modeling functions should be used.

Table 8. Modeled landscape components and application methods in PREM6 for residential uses

Landscape components	Treatment option 0	Treatment option 1	Treatment option 2
Walkway (backyard)	Not treated	Perimeter	Crack & crevice
Walkway (front yard)	Not treated	Perimeter	Crack & crevice
Garage door - driveway interface	Not treated	Perimeter	-
Driveway	Not treated	-	Crack & crevice
Sidewalk	Not treated	-	Crack & crevice
Wall (backyard)	Not treated	Perimeter	-
Wall (front yard)	Not treated	Perimeter	-
Garage door	Not treated	Perimeter	-

3.4 Down-the-drain products

The PREM6 provides a new pesticide use pattern for down-the-drain (DtD) products. The new modeling capability is to evaluate the ecological risks of indoor uses of pesticides, which are disposed down the drain, transported through the sewer system and WWTP, and released with WWTP discharges into surface water. The DtD products to be modeled include [1] pet products (e.g., spot-on and shampoo), [2] treated articles (e.g., impregnated fabrics and fibers, pesticide preserved garments and apparels), [3] floor drain treatment, [4] general indoor pest control on high-risk sites (e.g., foggers and sprays that are applied to pet and human beddings, floors, carpets, rugs, and upholsteries). These use patterns have been shown in multiple studies to pose a high potential of transporting pesticides down the drain via washing and cleaning (Keenan et al., 2009; Keenan et al., 2010; Moran and TenBrook, 2014; USEPA, 2016c; Teerlink et al., 2017; Sutton et al., 2019; Dery et al., 2022; Budd et al., 2023; Perkins et al., 2024). In addition, the DtD modeling is also applied to other products that are routed to SWPP on a case-by-case basis for special DtD use patterns, depending on the request from outside stakeholders or at the discretion of CDPR Pesticide Registration Branch.

The DtD modeling approach has been developed under the CDPR study 315 (Xie, 2018) and documented in the study report (Xie and Luo, 2022). The approach is implemented in the PREM6 with a two-step procedure. First, the total concentration of pesticide in WWTP discharge is estimated based on the maximum daily release rate of the DtD product and a set of coefficients representing the dilution and removal through the sewer system and wastewater treatment facility. The maximum release rate (μg[AI]/person/day) could be estimated from application rate, minimum application interval, and wash-off coefficient. The coefficients include the use extent of the product in the sewershed (f_1), the delivery factor in the sewer collection system (f_2), the delivery factor during the wastewater treatment processes (f_3), and the dilution factor in the receiving water body to which the WWTP discharges (f_4). The delivery factors are calculated as one minus the removal fraction. If the removal efficiency for a pesticide through a WWTP is 20%, for example, the corresponding delivery factor is 1-20%=80% or 0.8. The derivation of daily loadings from product labels and parameterization of the dilution/removal coefficients have been introduced in the technical report for model development (Xie and Luo, 2022). Specifically, the default values of f_1 and wash-off coefficient are summarized by the category of DtD products (e.g., treatment on dogs, cats, or floor drains) from open literature, if it is not provided in registrant-submitted data. For conservative estimation of pesticide loading to wastewater influent, it is assumed that pesticides are persistent in the wastewater collection system, i.e., f_2 = 1, unless additional studies show that the assumption does not hold for the product under review. The removal efficacy of pesticide in a WWTP could be calculated from measured values in registrant-submitted data or open literatures. If there is no reported value, it can be estimated using the Estimation Program Interface (EPI) Suite (USEPA, 2012a).

With the estimated pesticide concentrations in the WWTP discharge, the next step is to calculate EECs of pesticide in the surface water body the WWTP discharges to. For conservative estimation, it is assumed for DtD product evaluation that the WWTP discharge is the dominant source of the receiving water body (Xie and Luo, 2022). The assumption is also supported by a study by Rice and Westerhoff (2017) and the refinement of the study for California field conditions at the University of North Carolina - Charlotte via a research contract with CDPR

(2019). The contract developed a database of WWTPs in California and calculated the dilution factors for 165 surface water discharging WWTPs. Under low-flow conditions modeled as the 7-day average streamflow with a 10-year recurrence interval (7Q10), the median dilution factor across the sites was estimated to be slightly above 1 (1.01). This finding indicates that, for most of WWTPs in California, the receiving streamflow is significantly lower than the corresponding WWTP design flow under low-flow events. Therefore, dilution of pesticide in the receiving water body is not modeled for DtD products (i.e., $f_4 = 1$), and the initial concentration of pesticide in the water body is set to the above predicted concentration in the WWTP discharge. This approach is similar to that used in the PREM evaluation on aquatic pesticides (Luo, 2017a). The USEPA pond scenario is used for the receiving water modeling for DtD products.

As a part of the model development (Xie and Luo, 2022), the modeling approach has been validated for 12 pesticides with wastewater and surface water monitoring data available in California. In addition, the model was also validated with the previous registration evaluations for seven indoor products routed to SWPP. The modeling results generated the same registration recommendations as those from the previous case-by-case evaluations. SWPP will further test and evolve the modeling capability for DtD product as we have more data.

Degradate evaluation in the DtD modeling is only available for the degradation products formed in the receiving water body. Degradation and formation in the sewer system and during wastewater treatment are not modeled due to the lack of travel time and half-lives in wastewater.

3.5 Multiple crop seasons

The previous versions of the PREM simulate only one crop season in a calendar year. The PREM6 is updated with the modeling capability to predict the exposure from pesticide uses on vegetables sown multiple times per year. For registration evaluation, the PREM6 only models a simple scenario with two seasons of the same crop grown in sequence in the same field. This does not require any changes on the weather data, crop parameters, and soil properties pre-defined in the USEPA crop scenarios. In addition, the same set of application data can be applied to all growing cycles, either presented as repeated applications or individual applications (see section 3.2). The new function currently does not model two different crops, such as wheat production followed by a valuable crop planted as a rational crop.

Two crop groups are modeled in the PREM6 for succession planting: [1] leafy vegetables (crop group 4 in the 40 CFR §180.40, e.g., lettuce) with the USEPA crop scenario "CAlettuceSTD") and [2] brassica (cole) leafy vegetables (crop group 5, e.g., broccoli) with "CAColeCropRLF_V2". Hydrological and pesticide simulations for each crop cycle are based on input parameters in the crop calendar (dates of emergence, mature, and harvest) and soil surface characteristics (runoff curve number, soil loss cover management factor, and Manning's roughness coefficient). Inputs for the first crop cycle are taken from the corresponding USEPA crop scenario. For example, California lettuce scenario is modeled with a prescribed time series of surface characteristics during Feb 16 (emergence) to May 12 (harvest). The second crop cycle is modeled by duplicating all soil and canopy parameters of the first cycle to a later stage of the same year. The emergence date of the second crop cycle is determined relative to that of the first cycle. The time offset should be larger than the length of the crop cycle (from emergence to

harvest), i.e., about 90 and 60 days for cole crops and lettuce, respectively, according to the USEPA crop scenarios. Therefore, a 120-d offset (between the first and second emergences) is assumed in the PREM6 for simulating pesticide applications in multiple crop seasons. In summary, the two crop seasons share the same crop calendar, soil properties, and pesticide applications organized by relative days to their corresponding dates of emergence in each season. The only difference between the two cycles for modeling is the weather data which is assigned by calendar days.

For modeling multiple crop seasons, users are only required to specify pesticide use data for the first season, in the same format as that for single-season modeling. The PREM6 will repeat the same set of applications for the second season. First, the relative days between the user-specified applications and the emergence date of the first season are calculated. The resulting intervals are used to schedule the applications for the second season. For example, if the first application for the first season is made 10 days after the emergence date of the first season, the first application for the second season will be modeled 10 days after the emergence date of the second season. Other input data including application method, incorporation depth, application efficiency, and drift fraction are shared by each pair of applications, e.g., the first applications for the first and second crop seasons.

In addition to the single application rate, product labels may also limit the maximum allowed total rate per year. For the evaluation of multiple crop seasons, the input parameters for pesticide applications should be checked before model simulation to make sure the total application rate accumulated for the two crop cycles do not exceed the limits in the product label.

Compared to one crop season, modeling for multiple crop seasons will increase the total pesticide mass applied per year. However, the actual change of EEC is dependent on pesticide properties and crop scenarios. Compared to the original settings with a single crop season in the USEPA modeling scenarios, the introduction of a second crop season equivalently converts soil surface characteristics from a fallow condition to cultivated condition. Cultivated soils are represented with lower runoff curve numbers (CNs) thus less runoff potential compared to fallow soils. For example, the CN values in the "California lettuce" scenario is 89 for the growing season and 94 for fallow season. The reduced runoff potential acts as a conservation practice for the pesticide residues from the first crop season and the additional applications during the second season. It is theoretically possible that, for certain pesticides and crop scenarios, the predicted EEC with multiple crop seasons could be even lower than that with single crop season. Therefore, the PREM6 modeling for multiple crop seasons should be accompanied by a model run with the same input parameters but for single crop season. The higher EEC will be used for registration evaluation.

4 Evaluation on mitigation practices

4.1 Vegetative filter strip (VFS)

VFS modeling in the PREM6 includes two components of hydrological and pesticide simulations. VFSMOD (Muñoz-Carpena and Parsons, 2020) version 4.5.2 is used for hydrological simulations to determine the removal of runoff and sediment through a VFS. A mechanistic model has been developed by CDPR (Luo, 2020) for pesticide fate and transport in a

VFS. Compared to the previous regression equations (Webster and Shaw, 1996; Cole et al., 1997; Neitsch et al., 2005; Sabbagh et al., 2009; Chen et al., 2016; Reichenberger et al., 2019) and semi-mechanistic approaches (Neitsch et al., 2009; Luo, 2017d; Reichenberger et al., 2019) for pesticide removal, the mechanistic model formulates individual physical processes in the soil-water interaction by following the same variables and terminology in the USEPA's PWC model for landscape simulations. The model has been validated with 4 pesticides (bifenthrin, chlorpyrifos, imidacloprid, and permethrin) and 14 crop scenarios in California (Luo, 2020).

The primary input for modeling VFS in the PREM6 is the label-required width of VFS (ft, in the flow direction). For example, the labels of pyrethroid agricultural use products require a 10-ft VFS (USEPA, 2008), so the model input value of the VFS width is 10 ft. Weather data and soil properties for the VFS are taken from the crop scenario selected for registration evaluation. In addition, a set of default values are prescribed in the PREM6 to represent an average conditions of model input parameters for surface characteristics in a VFS (Table 9).

Table 9. Default values of input parameters for VFS modeling in the PREM6

Parameters	Value	Notes
Width of VFS (m, perpendicular to flow direction)	316.2	Assume a square source field of 10 ha (=316.2 × 316.2 m^2), and set the VFS width = field width
Filter mean Manning's coefficient (m $s^{-1/3}$)	0.45	Value for bluegrass sod, recommended in the VFSMOD user's manual (Muñoz-Carpena and Parsons, 2020)
Spacing of filter media (cm)	2.15	Value for grass mixture, recommended in the VFSMOD user's manual
Filter media (grass) Manning's coefficient (cm $s^{-1/3}$)	0.012	See above
Filter media height (cm)	18	See above
Rainfall intensity (mm/h)	2	Intensity at 24-hour period, 1-year recurrence interval observed in Sacramento area (Luo, 2019)

The rainfall intensity is used to estimate the storm duration and further calculate the peak runoff flow rate (Fox et al., 2010). The default value of 2 mm/h is tested with daily precipitation data for average storm duration. For the precipitation data at station WBAN23232 (Sacramento) as an example, the storm duration is calculated to be 3.9 hours as annual average and 2.2 hours for summer months of June to September. The results are generally consistent with the USEPA recommended representative regional values for California (3.6 and 2.6 hours for annual and summer periods, respectively) (Carsel et al., 1998).

With the option for VFS modeling, the PREM6 predicts the mitigation effects as reductions of runoff water, suspended solids, and pesticide mass through the VFS, and adjusts the incoming pesticide loadings towards the receiving water body. Finally, the PREM6 reports the RQs in the water body for registration evaluation.

4.2 Mitigation effects by spray buffer zone

The previous version of the PREM uses USEPA-recommended default values for spray drift fraction, i.e., 0.05 for aerial applications, 0.03 for air-blast applications, and 0.01 for ground applications (USEPA, 2009). In 2013, USEPA proposed a guidance on modeling offsite deposition of pesticides via spray drift from agricultural applications for ecological risk assessment (USEPA, 2013b). AgDRIFT Tier I analysis was used to determine the spray drift fractions to the USEPA pond with a downwind width of 63.61 m. Drift fraction values were pre-calculated for various application methods (aerial, air-blast, and ground applications) and associated options (such as boom heights for ground applications, and types of orchards for air-blast applications), distances (from edge of field to the pond), and drop size distribution. The provided values are incorporated into the PREM6 (Figure 7). This new function is used to evaluate the mitigation effects of spray buffer zone distances if required in the product label for pesticide applications.

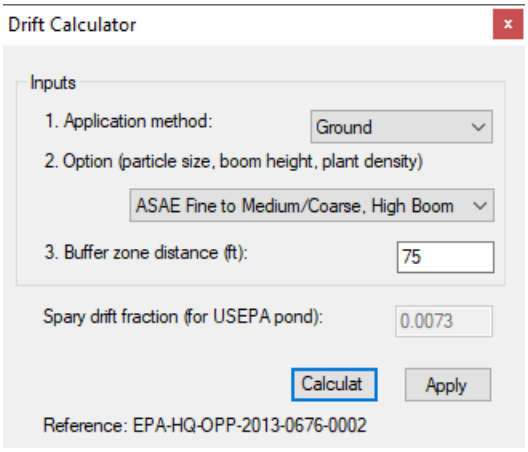

Figure 7. PREM6 function for estimating draft fraction with a buffer zone distance

Note that the higher tier analysis of AgDRIFT or AGDISP is not included in the PREM6. For evaluating advanced options in spray drift control (e.g., meteorological conditions), separate modeling with AgDRIFT is needed and the resulting drift fraction values can be used as input data for the PREM. See the ecological risk assessments for pyrethroids (USEPA, 2016c) for examples of the Agricultural Dispersal (AGDISP) modeling with considerations of wind speed, wind direction, spray volume, and spray material according to the updated spray drift language for all pyrethroid products used on agricultural crops (USEPA, 2008).

4.3 Application restrictions by rainfall/runoff

This function is developed in the PREM6 to evaluate the restrictions in the label for pesticide applications according to soil moisture and weather conditions. As a mitigation practice, some product labels prohibit applications before rainfall or runoff events, for example, "*no application shall occur if … a storm event, forecasted by NOAA or NWS, is to occur within 48 hours following applications; or a storm event is like to produce runoff from the treated area is forecasted by NOAA/NWS to occur within 48 hours following the application*." Similar

mitigation strategies have been required for the use of dormant spray insecticides in California (CDPR, 2005).

In the new version of USEPA's Pesticide Root-Zone Model version 5B (Young, 2020), there is a modeling option for application timing algorithm with respect to rainfall. However, the technical details and computer implementation of the algorithm were not documented. In addition, the modeling option was not integrated in the PWC interface (USEPA, 2011). Therefore, it's not clear whether the same algorithm is also applied to adjust application timing for pesticide inputs to the receiving water body by spray drift.

A CDPR's algorithm is developed and integrated in the PREM6 for pesticide application timing related to rainfall. Similar to the USEPA algorithm, the application restrictions are mathematically represented by rescheduling pesticide applications to avoid rainfall events. With this option on, the user-proposed application dates will be checked forward for forecasted rainfall events. If rainfall events are forecasted within a certain period, the corresponding application will be postponed to the next day and rechecked for rainfall events based on the new application date. Daily rainfall data are taken from the standard meteorological data for exposure modeling (USEPA, 2007a), the same data used for all hydrological and pesticide simulations.

Two windows, in the unit of day, are used in the application timing algorithm: the intolerable window for rainfall events and the acceptable window for an optimum application. The intolerable window for rainfall is given by the product label, for example, the label language "*no application shall occur if … a storm event, forecasted by NOAA or NWS, is to occur within 48 hours following applications*" suggesting a window of 2 days. According to the pesticide transport algorithm in the soils (Young, 2020), a pesticide application is modeled at the first time step of the scheduled date of application. Following the same assumption, the intolerable window is modeled in the PREM6 on the day of the proposed application and days after that. For example, a 2-day intolerable window suggests an investigation on forecasted rainfall events for 2 days of today and tomorrow. For receiving water modeling, the dates for pesticide spray drift are also changed according to the rescheduled application timing.

The application window is the maximum acceptable days for postponing an application from its initially proposed date. With an acceptable window of 7 days, for example, the PREM6 will search from day 0 (i.e., the originally proposed application date), day 1 (the day after the original proposed application date) … to day 7, and stop the search once an optimum date is detected. The optimum date of application is determined by summarizing the total rainfall amount over the intolerable window of rainfall. The first day in the acceptable window with no forecasted rainfall is set to be the optimum date. If all days in the acceptable window are associated with forecasted rainfall events, otherwise, the day associated with the minimum total amount of rainfall is used as the optimum date.

Note that the application timing algorithm does not change the minimum interval between applications as specified in the label as model inputs. That means, if the first application is postponed by N days, the next application (if applicable) will be also postponed for at least N days and subject to its own data check for forecasted rainfall. Generally, a short application window is more practical to make sure that the pesticide would be applied at the desired stage of

crop growth, such as pre-emergent applications. If the application window is too large, the modeled temporal pattern of applications could be significantly deviated from that proposed in the product label. For example, the first application could be postponed to the date or even after the date originally proposed for the second application. To avoid this, the acceptable application window in PREM6 is determined based on the user-specified intolerable window for rainfall events: [application window]=floor(2.5×[intolerable window]), where the "floor()" function gives the greatest integer less than or equal to the input value. For example, if the intolerable window is specified as two days, the application window will be modeled as five days.

The application algorithm in the PREM6 is demonstrated with a case study (Figure 8). The input data include: daily rainfall data (based on the station WBAN23232 in Sacramento, showing February of the first data year), originally proposed two applications on 2/1 and 2/15 with a 14-d interval, and the intolerable rainfall window of two days. For the first application, the PREM6 calculates the total rainfall amounts for two days (today and tomorrow) as 1.65 cm (for 2/1), 1.6 cm (2/2), and 0 (2/3). Therefore, the optimum date of application is detected on the third day in the acceptable window, and the first application is rescheduled to 2/3, i.e., postponed 2 days after the originally proposed date. For the second application, it is first rescheduled to 2/17 according to the minimum interval of 14 days, and 2/17 is also an optimum date for application (the total rainfall was zero on 2/17 and 2/18). In each year of simulation, the initial dates of applications are reset to the user-specified ones, and the actual dates of applications are determined based on the above-mentioned process.

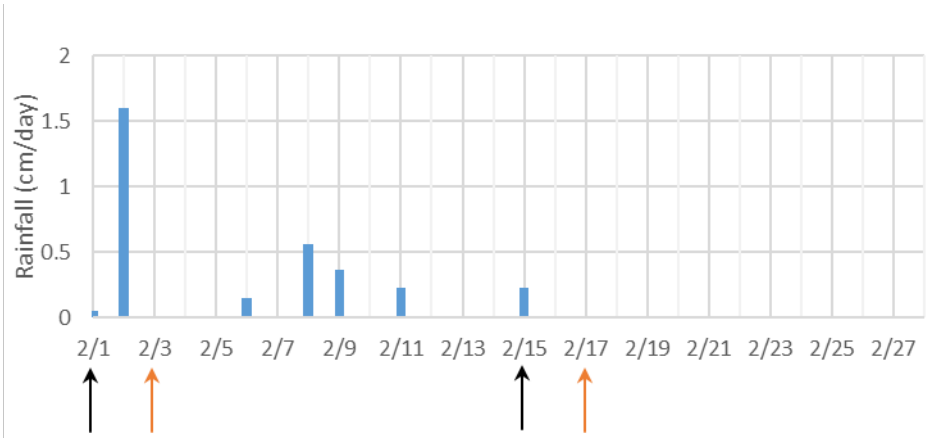

Figure 8. Demonstration of the PREM6 algorithm for pesticide application timing (blue bars for daily rainfall amounts, black arrows for originally proposed dates of two applications on 2/1 and 2/15, and orange arrows for rescheduled dates of 2/3 and 2/17 with respect to forecasted rainfall events).

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