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A Sensitivity Analysis of Pesticide Concentrations in California Central Valley Vernal Pools

Sumathy Sinnathamby[a], **Jeffrey M. Minucci**[a], **Debra Denton**[b], **Sandy Raimondo**[b], **Leah Oliver**[b], **Yuan Yongping**[b], **Dirk Young**[b], **James Hook**[b], **Ann Pitchford**[b], **Eric Waits**[b], **S. Thomas Purucker**[b]

[a]Oak Ridge Institute for Science and Education (ORISE) Postdoctoral Research Participant at U.S. Environmental Protection Agency, Athens, GA

[b]U.S. Environmental Protection Agency

Abstract

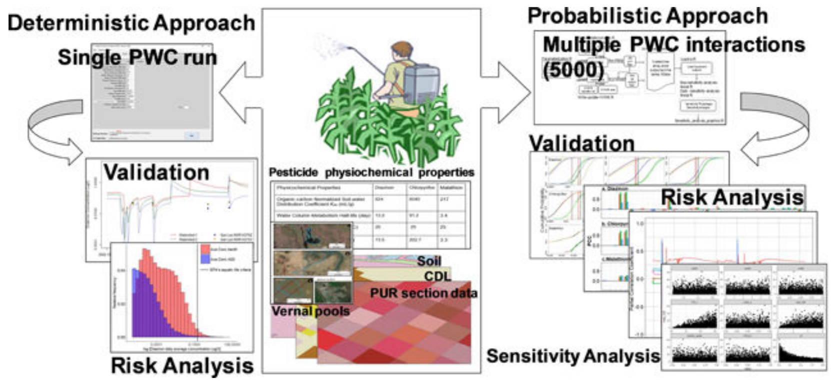
Vernal pools are ephemeral wetlands that provide critical habitat to many listed species. Pesticide fate in vernal pools is poorly understood because of uncertainties in the amount of pesticide entering these ecosystems and their bioavailability throughout cycles of wet and dry periods. The Pesticide Water Calculator (PWC), a model used for the regulation of pesticides in the US, was used to predict surface water and sediment pore water pesticide concentrations in vernal pool habitats. The PWC model (version 1.59) was implemented with deterministic and probabilistic approaches and parameterized for three agricultural vernal pool watersheds located in the San Joaquin River basin in the Central Valley of California. Exposure concentrations for chlorpyrifos, diazinon and malathion were simulated. The deterministic approach used default values and professional judgment to calculate point values of estimated concentrations. In the probabilistic approach, Monte Carlo (MC) simulations were conducted across the full input parameter space with a sensitivity analysis that quantified the parameter contribution to model prediction uncertainty. Partial correlation coefficients were used as the primary sensitivity metric for analyzing model outputs. Conditioned daily sensitivity analysis indicates curve number (CN) and the universal soil loss equation (USLE) parameters as the most important environmental parameters. Therefore, exposure estimation can be improved efficiently by focusing parameterization efforts on these driving processes, and agricultural pesticide inputs in these critical habitats can be reduced by best management practices focused on runoff and sediment reductions.

Graphical abstract

*Corresponding author: Sumathy Sinnathamby; 960 College Station Rd, Athens, GA 30605; 706-355-8174; (sinnathamby.sumathy@epa.gov).

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.



Keywords

pesticides; exposure; vernal pools; sensitivity analysis; agricultural watersheds

1.0 Introduction

Vernal pools are a type of geologically isolated wetlands (Tiner, 2002) characterized as shallow, ephemeral depressions on underlying impervious substrates that fill with winter and spring rains and dry up during summer months (Holland and Jain, 1981). In some years, overland runoff also supports the hydrology of these systems (Keeler-Wolf et al., 1998). Their ephemeral nature limits the establishment of many perennial plants and aquatic predator species, creating a unique refuge for sensitive, endemic species (King et al., 1996; Silveira, 1998). The endemic plants and animals found in vernal pools have specifically adapted to the conditions of these transient aquatic environments.

In the US, California's vernal pools (CVPs) are biologically diverse and are listed as critical habitat for vernal pool fairy shrimp and tadpole shrimp, in addition to providing habitat for a diversity of listed annual plants and species of concern such as migratory birds and amphibians (King et al., 1996; Silveira, 1998). Vernal pool organisms are adapted for completing their life cycle under fluctuating wet and dry conditions. CVPs have three distinct phases (aquatic, terrestrial, and dry) that are determined by the timing and amount of rainfall. And they also have diverse, dynamic water chemistry which varies with water level during the aquatic phase (Keeley and Zedler 1998). Despite this, the size of vernal pool can vary from one square meter to one hectare or more. More detail on CVPs can be found in Supplemental (S) text1.

Besides being physically, biologically, and chemically diverse, CVPs are heavily impacted by agricultural land conversions, mineral extraction, and urban development. Holland (2009) estimated that CVP habitat in 1976–1995 has fallen by 87% due to such land-use conversions. Although physical fragmentation effects have been emphasized for CVPs, water quality and occurrence of pesticides are also thought to impact biodiversity (Johnson 2006). Many remaining CVPs are located in or near agricultural areas, changes in water quality associated with overland runoff, drift, and direct spray are important in determining their risk to pesticide exposure. Some pesticides can also enter vernal pool systems as wet

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deposition via rainfall (Seiber et al., 1993; Domagalski et al., 1997; Bailey et al., 2000), as evidenced by the presence of selected pesticides in vernal pools, even when they are relatively far from any agricultural area (Frank et al 1990; Du Preez et al., 2005; Battaglin et al., 2009). However, the highest concentrations of pesticides typically occur in pools or ponds directly adjacent to agricultural lands (Battaglin et al., 2009). High pesticide loads in surface waters can cause adverse effects on the development and survival of amphibians, which rely on small bodies of water for reproduction (Tavera-Mendoza et al., 2002; Gilbertson et al., 2003; Hayes et al., 2002 a, b; Christin et al., 2004; Howe et al., 2004; Mann et al., 2003; Relyea, 2004, 2005). However, the presence of pesticides and their effects on vernal pool communities are not well-documented.

Although identifying pesticide occurrence in vernal pools and evaluating their potential effects on federally listed species is important, the ephemeral and seasonal nature of these habitats makes field sampling and extrapolation to other seasons difficult. Modeling the fate and transport of pesticides in vernal pools is complex, requiring adequate knowledge of pesticide chemical properties, their degradates, and the physical transport processes. In addition, knowledge of site-specific conditions, such as climate, pest demands, and management practices is necessary to better represent transport processes in modeling. Data available for inputs to pesticide models are typically sparse and variable. Additional uncertainties are associated with an incomplete understanding of key physical processes and complex landscapes features that may influence the likelihood of exposure. Pesticide exposure modeling used to develop Estimated Environmental Concentrations (EECs) plays a key role in regulatory decision making, predicting future risks to listed or vulnerable species, and supporting regulatory standards programs (USEPA, 1989,1992).

This study explores deterministic and probabilistic approaches to generate EECs in vernal pool habitats, using selected sites in the California Central Valley (Giesy et al., 1999). The goals were to estimate pesticide concentrations (surface and pore water) and quantify the effects of input variability on site-specific model predictions with the Pesticide Water Calculator (PWC).

2.0 Methods

2.1 Site description

The three vernal pools used in this study are located in the Merced County agricultural area of California's Central Valley, which is one of the most productive agricultural regions in the world (Luo and Zhang, 2009). Merced County is a top-producing agricultural county in central California and continued agricultural land conversion in this county poses a threat to vernal pool habitats (Vollmar et al., 2013). Due to the intensity of agricultural land use, the county also ranks high in pesticide application rate, falling sixth and seventh among 58 counties in California in 2014 and 2015, respectively (CDPR, 2018) based on total pounds of active ingredients applied. Detail pesticide use patterns in Merced County can be found in S2 and Figure S1.

Study sites (Figure 1) were chosen due to their uniqueness in size (Witham et al., 2014), pesticide usage (Figure S2), and their input variability (agricultural acreage, soil group, crop types, application rate, etc.). The watershed areas that drain into each vernal pool were delineated using the ArcGIS Hydrology tool, a component of Spatial Analyst (Clemow et al., 2018). Their drainage areas ranged from 4.5 to 887 square km (Figure 1; Table S1).

Maximum possible extent of vernal pool areas was identified by overlaying the US Fish and Wildlife Service (USFWS) vernal pool mapped area (Witham et al 2014), Soil Survey Geographic (SSURGO) soil layers (USDA-NRCS, 1995), aerial photographs (ESRI, 2018), and Google Earth Imagery (accessed 06/01/2018) (Figure S3). The SSURGO layers identified specific types of soils, geologic formations, and landforms associated with CVPs (Smith and Verrill, 1988).

Following identification of the vernal pools, the surface area and approximate volume of the pools were calculated through 3D Analyst, an ArcGIS Toolbox, using 10 m DEM as the input. Calculated vernal pool surface areas ranged from approximately 5634 m^2 to 8977 m^2. These size distributions were within the ranges reported by Clemow et al. (2018) and King et al. (1996). Possible pool depths and extent were also cross-checked using historical imagery available from 1998 to 2013 (Google Earth, 2018). All selected watersheds have a Mediterranean climate with hot, dry summers and cool, wet winters. Summary of watershed and pool characteristics are given in S3 and Table S1.

2.2 Defining site specific input parameters

Daily rainfall, temperature, wind speed, solar radiation, and evapotranspiration (ET) are the weather inputs required by PWC's hydrologic component. Daily average precipitation and temperature for 1999 through 2014 were obtained from the Global Historical Climatic Network-Daily (GHCN-Daily) database of the National Climate Data Center (NCDC). Other weather inputs were retrieved from the National Center for Environmental Prediction Reanalysis and the NOAA Climate Prediction Center Unified Rain Gauge Analysis at 0.25 × 0.25-degree latitude/ longitude resolution (Fry et al., 2016). After compiling weather inputs, one weather station was assigned to each watershed based on the nearest distance between the station and grid centroid. Other spatial data used included National Elevation Dataset (NED) digital elevation model (DEM; 10m-resolution), National Agricultural Statistics Service (NASS) cropland data layer (30m-resolution), and SSURGO database soil layer (10m-resolution). Soil properties including bulk density (BD), organic carbon content (OC) and Universal Soil Loss Equation (USLE) soil erodibility factor (K) were gathered from the SSURGO database (Table S2). Cropping dates for emergence, maturation, harvest, and other crop parameters for interception storage, maximum coverage, active root depth, aerial coverage, and maximum canopy height were gathered from United States Environmental Protection Agency (USEPA) Standard Tier 2 crop scenarios and Endangered Species Act (ESA) 18(a) scenarios (USEPA, 2016 a, b. c). Irrigation practices and amount were specified based on crop type for the entire growing season. In addition to the calculated values (Table S1), vernal pool depths were adjusted within typical ranges of 0.1 to 1 m (Rains et al. 2006; 2008; Clemow et al., 2018) while simulating Variable Volume Water Model (VVWM) with the variable water volume option in order to produce clear dry and wet phase periods in the water level time series. The final vernal pool depth was set to the average depth for each pool (Table S1) during deterministic simulations.

2.2.1 Agrochemicals—Three organophosphates insecticides were selected for analysis from recent USEPA draft biological evaluations: chlorpyrifos (USEPA 2016a), diazinon (USEPA 2016b), and malathion (USEPA 2016c). These three organophosphates are commonly used in Central Valley (CDPR, 2006) and detected in snow, air and surface waters (Schomburg et al., 1991; McConnell et al., 1998; LeNoir et al., 1999) in Central Valley in the μg/L or mg/L levels (Gruber and Munn, 1998; Brady et al., 2006). Chlorpyrifos and malathion are used on a variety of terrestrial food and feed crops, terrestrial non-food crops, greenhouse food/non-food, and non-agricultural indoor and outdoor sites. Diazinon is mainly used on orchards (almonds, stone fruit and pome fruit), ground fruit and vegetable crops (e.g., lettuce, tomatoes), outdoor nurseries, and cattle ear tags. These pesticides also may be used in urban environments; however, urban uses were not considered in this study. Physiochemical properties used in modeling were obtained from USEPA (2016 a, b, c) and are given in Table S3. In all modeling scenarios, diazinon was applied as a dormant season application, chlorpyrifos was applied as both ground and aerial application based on application date, and malathion was applied aerially. First-order transformation and linear equilibrium sorption in soil were assumed and used as model inputs (Young and Fry, 2016; Young, 2016 b).

2.2.2 Crop scenarios—Crop scenarios were included based on the NASS Cropland Data Layer (CDL) 2007 crop coverages to generate spatially-relevant aquatic exposure concentrations. Crops percent area coverages are given in Table S4.

Pesticide application rate and timing were inferred based on the Merced County, Public Land Survey System (PLSS) Pesticide Use Reporting (PUR) database from California Department of Pesticide Regulation (CDPR). PLSS data set includes Township, Range, and Section land parcels in State of California. CDPR PUR database annually reports agricultural pesticide use at PLSS one-square mile (mi^2) sections and non-agricultural pesticide use by active ingredient at county level (CDPR, 2018). More detail can be found in the S.5. In some cases, pesticide application methods were not available in PUR database and were inferred using section-level application dates and best professional judgment (CDPR 2018). Application efficiency was set to 99% in all conditions (Young, 2016 a). Spray drift contributions were calculated using the AgDRIFT model (Teske, et al., 2002, Bird et al., 2002), based on the closest crop. Applications occurred from the first year (1999) to the last year (2014) of available precipitation data.

2.3 Pesticide Water Calculator (PWC) Model description

PWC version 1.59 was used to estimate pesticide concentrations in vernal pools. PWC is a USEPA model that simulates surface and groundwater pesticide concentrations resulting from land application (Young, 2016a). PWC is an updated version of the Surface Water Concentration Calculator (SWCC), renamed to better reflect surface and groundwater simulations capabilities. PWC comprises two simulation engines: the Pesticide Root Zone Model (PRZM version 5.02) and the VVWM (version 1.02) (PWC Manual, 2015). PRZM is a one-dimensional hydrologic model that simulates transport of pesticide leachate from the root zone through the soil by considering land phase hydrology and chemical transport (Young and Fry, 2016). VVWM simulates water body processes for the water column and benthic region, and estimates fate, persistence and concentration of the pesticide daily, with runoff, eroded sediment and spray drift fluxes (Young, 2016 b). Detail descriptions on PRZM and VVWM and represented hydrological and chemical process can be found in Young and Fry (2016) and Young (2016 b), respectively.

2.4 Deterministic assessment

Screening level exposure assessments typically implement a deterministic approach using readily available data, professional judgment, and default assumptions to derive an EEC (Young, 2016 a). The output of the deterministic approach consists of a single representative concentration estimate for each space, time, and media combination.

Johnson (2006) study was used to validate PWC simulation. Johnson (2006) is the only study in which pesticide concentrations in vernal pools were measured within 24 hours after major storm events. However, the application rate and application time were not known, and pesticide concentrations were not monitored following application. Johnson (2006) measured diazinon concentration from three vernal pools on the Kesterson National Wildlife Refuge, which were used in the present study to compare diazinon crop scenarios in both deterministic and probabilistic approaches. There were no vernal pool monitoring studies available in San Joaquin Valley for chlorpyrifos or malathion for a similar analysis. Estimated pesticide concentrations were also compared to stream and/or river measurements collected within 20 km from each vernal pool. These data were obtained from CDPR and the National Water-Quality Assessment (NAWQA) and used as a proxy for the occurrence and trends of these pesticides in the environment under existing conditions.

Daily modeling results from the 16 year simulation period are reported as time series peak concentrations at a daily, 21-day, 60-day and annual average EECs. For each of these statistics, 1-in-15 year concentrations, defined as the maximum value that is expected to occur every 15 years, were calculated. To estimate this statistic, the maximum yearly values at each time scale (daily average, 21-day average, 60-day average and annual average EEC) were sorted from high to low. The rank magnitude for a 1-in-15 year concentration was then calculated as follows: $m = (n+1)/T$; where n is the number of data points (16 years in this study) and T is the return period (15 years). This rank magnitude ($m=1.13$) gives the position of the expected maximum yearly value in the ranked list. The exact value was then calculated with linear interpolation (*e.g.*, between the 1^{st} and 2^{nd} ranked concentrations for $m=1.13$). In a typical exposure analysis, the USEPA uses 1-in-10 year EECs to assess risks. The 1-in-15 year EEC was used here to reflect some of the USEPA's recent risk assessments (USEPA, 2016 a, b, c) which match the USEPA's 15-year cycle for pesticide reevaluation.

2.5 Probabilistic approach: Monte Carlo simulation and sensitivity analysis

The probabilistic approach uses the same set of initial data and assumptions as the deterministic assessment, except the probabilistic approaches rely on distributions of input values to propagate variability through the model instead of fixed values for one or more of the inputs. A probabilistic sensitivity analysis (SA) is then performed to identify dominant parameters within a model, support prioritization of efforts for uncertainty reduction, provide a structured framework for quantifying the strength of input-output relationships in assessed models, and determine less influential parameters during calibration (Hamby, 1994). Detail on our implementation can be found in the supplemental text (S.6)

Probabilistic SA was carried out for applications of chlorpyrifos, diazinon and malathion on two major crops (almonds, alfalfa), resulting in six sets of 5000 simulations. During these simulations, 51 input parameters were sampled with Latin Hypercube sampling using the “lhs” R package (Carnell, 2016). These parameters include soil properties, crop conditions, environmental conditions, and pesticide parameters (chemical, application rate, efficiency). A list of inputs sampled, their description, and the range limits of each distribution are given in Table S5. Lower and upper limits were defined according to literature and/or professional judgement. The partial correlation coefficient (PCC) statistic, from the “sensitivity” R package (Pujol et al., 2017), was used as a primary sensitivity metric for analyzing model output. PCC measures the strength of linear associations between the output and each input parameter, after effects of the other parameters are accounted for, on a scale from −1 and +1.

2.6 Risk Assessment

As there are no available data on the effects of pesticides on listed vernal pool species, potential direct effects of studied pesticides to these invertebrates were analyzed using USEPA Office of Pesticide Programs (OPP) aquatic life benchmark values, California Regional Waterboard Aquatic Life Criteria, and predicted values for the vernal pool fairy shrimp (Table 1). For the latter, sensitivity of vernal pool fairy shrimp to each of the pesticides was predicted by entering surrogate species toxicity values into the Web-based Interspecies Correlation Estimation application (Web-ICE; https://www3.epa.gov/ceampubl/fchain/webice/; accessed 10/23/18; Raimondo et al. 2015). Raimondo et al. (2019) demonstrated that protection of the vernal pool fairy shrimp would be protective of the community of listed species occupying the habitat using a weight of evidence approach. Brief description on Web-ICE method is presented in S7.

The Web-ICE predictions were evaluated using the criteria recommended by Willming et al. (2016) and shown in Table 1. In addition, the OPP aquatic life benchmarks were derived by evaluating toxicity data for a pesticide active ingredient or metabolite, and include acute and chronic toxicity values for fish, invertebrates, vascular and nonvascular plants, and other organisms within the aquatic ecosystem to yield a single baseline value applicable across all these organisms (USEPA, 2016a). Throughout this document acute and chronic benchmarks refers to the OPP aquatic life benchmark for invertebrates.

3.0 Results and Discussion

3.1 Simulated vernal pool depths and hydrology

PWC model was able to represent pool stages, ET and pool phases satisfactorily (S8). Clear vernal pool hydrological phases were observed during the driest year (Figure S5c). As expected, precipitation is a leading indicator for the variation in the change in pool depths, and is a driving force in the model. Similarly, ET was identified as the principal pathway for water loss. ET peaks during May, and exceeds precipitation inputs from mid-June through mid-September. The water deficit period results in a loss of pool depth until a period of vernal pool drying is observed. During drier years, pools dried earlier and stayed longer, with larger cumulative water deficits.

Previous studies used a uniform distribution of three vernal pool depths (0.15 m, 0.575 m, and 1 m) and constant volume estimates based on observed surface areas to model vernal pool exposure using PWC (Clemow et al. 2018). In contrast, we simulated the vernal pool hydrology using the varying volume and flow through option of the model. Our results show that PWC model is capable of simulating dynamic complex vernal pool hydrology. Validation of vernal pool depths with observed data was not possible for the current study due to lack of pool depth data; however, comparison of the model output with field validated depths would help calibrate the vernal pool dynamics of the model and improve concentration predictions.

3.2 Deterministic approach

3.2.1 Modeled pesticide concentrations using PWC—PWC was used to estimate diazinon, chlorpyrifos and malathion concentrations in vernal pool surface water and sediment pore water. Average daily surface water EECs and their 1-in-15 years concentration frequencies were calculated from the PWC results for each watershed, and are summarized in Table S6. The highest diazinon EECs were observed with almond dormant spray application scenarios in all watersheds. Simulated pesticide concentrations in vernal pools tended to be higher than the observed concentrations in streams (Figure S6) and exhibit higher difference for chlorpyrifos. Detailed discussion on stream comparison is provided with Figure S6.

In other hand, predicted diazinon concentrations were closer to those measured by Johnson (2006) and within the 97.5% confidence interval in 3 vernal pool sites (San Luis NWR KST 62, San Luis NWR KST 63 and San Luis NWR KST 70) within the Kesterson National Wildlife Refuge, located approximately 32 km west of the study site (Figure 3). The maximum PWC diazinon concentrations were observed immediately after dormant pesticide applications to almond, especially in January to March. The daily peak simulated malathion concentration was 29.98 ug/L. As a broad comparison, Segawa et al. (1990) found average concentrations as high as 49.4 ug/L malathion in freshwater ponds immediately after aerial malathion application to eradicate the Mediterranean fruit fly in California. Although there are differences in the applications, soil, weather, and other conditions between this study and Segawa et al. (1990), we consider these concentration similarities a rough corroboration of our simulated malathion results.

As expected, runoff and pesticide loading were greatest when applications immediately preceded significant precipitation events, and these high concentrations were usually short lived. Similar results have been reported by many studies (Baker, 1983; Leonard, 1990; Wauchope, 1978; Willis and McDowell, 1982). Although high EECs often were short in duration, they may still have acute adverse effects on aquatic organisms. Results from the PWC model also indicate that a substantial mass of all simulated pesticides applied to these agricultural watersheds were transported to the pools, with runoff being the main mode of transport.

In most cases, PWC simulated total pesticide concentrations (Table S6) that were higher in the Canal Creek tributary watershed and lower in the Middle Mariposa Slough tributary watershed, which are the smallest and largest investigated sites, respectively. Similar negative correlations between aqueous-phase insecticide concentrations and catchment area have been reported by other studies (Schulz,2004; Luo and Zhang, 2009). Higher runoff potential (D), hydrologic soil group and higher slope compared to other watersheds are likely the primary determinants of higher concentrations in the Canal Creek tributary watershed.

3.2.2 Deterministic risk assessments—

The PWC 1-in-15 year simulated 1-day and 21-day EECs averages (Table S6) were used as acute and chronic exposure concentrations, respectively. Modeled chronic and acute concentrations exceeded US EPA aquatic invertebrate benchmark values (Table 1) in all conditions. The site average percentage of days during the study period (1999–2014) above the benchmark values are shown in Table 2. Detailed results are available in Table S7. Chlorpyrifos had the highest exceedance frequency, with acute exposure exceeding the benchmark on 99% of days, averaged across scenarios, compared to 59% for Diazinon and 11% for Malathion. In contrast, using the Web-ICE predicted surrogate values for vernal pool fairy shrimp, exceedance frequencies for chlorpyrifos, diazinon and malathion were 55%, 4%, and 0%, respectively.

3.2.3 Uncertainties and limitations related to PWC simulations—

Pesticide application methods were selected using section-level application dates and best professional judgment (CDPR, 2018). For all the scenarios, diazinon was applied as a dormant season application, chlorpyrifos was applied as both ground and aerial application based on application date, and malathion was applied aerially. The PLSS section-level data has higher resolution than the CDL layer, and in most cases the number of applications is also assumed. When application dates in same section are close (within 7 days), they were combined into a single application. The PWC model does not consider the application of best management practices (BMPs) on site, which may help to mitigate the pesticide mass leaving the fields via runoff. Other model restrictions which may also lead to uncertainties were identified. These include a limit of 50 for the maximum number of applications in graphical user interface (GUI) PWC interface. However, alfalfa has a maximum number of 4 application per year. For the 16-year simulation period, with 4 applications per year, this would result 64 applications and therefore all the applications could not be specified. A restriction for the SA is that PWC root depth needs to be less than soil depth for the purposes of the Monte Carlo simulations. For smaller soil depth, maximum root depth must be effectively equal to the soil depth. In this case, the sensitivity of root depth cannot be evaluated effectively since the input parameters are correlated.

Other limitations include the inability to include interannual changes in cropping area, planting and harvesting dates, and other management practices. In this study, a single crop area was used throughout the simulation period. Also, only one irrigation value can be provided and therefore changes in irrigation as a function of crop growth cannot be specified. The type of irrigation (e.g., flood, sprinkler, furrow irrigation etc.) also cannot be specified. Instead, one irrigation amount, either over or under crops as a maximum rate, can be provided. Another SA restriction is that for current standard water bodies the pH of the entire system (benthic and water column) are held at a constant pH of 7, and therefore that default value was kept throughout the study.

These model limitations are not necessarily weaknesses, but opportunities may exist to make additional model modifications if it were shown to strengthen the model fate and transport behavior. Any such changes would also impact the sensitivity results.

3.3 Probabilistic assessment

3.3.1 Monte Carlo simulation of pesticide concentrations—For the probabilistic assessment, pesticide concentrations were estimated across a wide range of possible model inputs using MC simulations. The MC percentile estimates (25, 50, 75 and 97.5) of the almond diazinon scenario simulations are presented in Figure S7. Observed concentrations (Johnson, 2006) are below the predicted 97.5 percentile of the MC exposure distribution for all three watersheds. Similar comparisons could not be carried out for the other two pesticides since there are no observed vernal pool concentrations for them. However, for chlorpyrifos and malathion, all concentrations predicted by the deterministic assessment were within the simulated range of concentrations produced for both the water column and benthic zone (Figure S8 and S9). Diazinon and chlorpyrifos concentrations estimated by the deterministic model for the Canal Creek tributary watershed were above the 97.5 percentile of simulated concentrations, reflecting the conservatism built into the deterministic parameters.

3.3.2 Probabilistic risk assessments—A considerable amount of the total diazinon and chlorpyrifos simulated concentrations (total of 5000 simulations each containing 5844 daily estimates) were above the acute benchmark values (≈23% and 48%, respectively), compared with only 1% for malathion. Simulated diazinon and chlorpyrifos concentrations also exceeded the Web-ICE predicted surrogate values (≈4% and 14%, respectively). These suggest that diazinon and chlorpyrifos generally pose a greater threat to aquatic organisms than malathion. However, as with the deterministic assessment, it is important to consider that several factors contribute to uncertainty in PWC predictions (e.g., limited application number, constant crop coverage).

3.3.3 Sensitivity analysis—Sensitivity analyses (Table S8 to S10) identified the most influential parameters for determining pesticide concentrations in the PWC model. Figures 4 and Figures S10 to S14 highlight these key parameters for pesticide concentrations in surface runoff, vernal pool water column, and benthic water. A positive PCC value indicates that the model output is positively correlated to the corresponding input parameter, while a negative PCC value indicates an inverse correlation.

Analysis results indicate that the most sensitive parameters for pesticide input to all three watersheds were hydrological and related to the generation of water and sediment runoff (Figure 4 and Figures S10 to S14). The curve number for antecedent moisture condition (CN) was a very important parameter, which characterizes the runoff properties for a soil and land cover based on soil hydrologic group, land use, and hydrologic condition. High CN values cause most of the rainfall to appear as runoff, with minimal absorption to soil, while lower values correspond to an increased ability of the soil to retain rainfall, thus yielding less runoff. The CN for both cropping (CN_c) and fallow (CN_f) periods was identified as important factors in determining pesticide concentration in runoff in almond scenarios (Figure 4). In contrast, CN_f was not sensitive in alfalfa scenarios (Figure S12). CN_f for almonds covers months from mid-September to end of December, whereas alfalfa has a very short follow period from December to January. For almond scenarios, CN_c was the highest ranked sensitive parameter for all pesticide concentrations in runoff, followed by wilting point (WP) and CN_f (Figure 4). For alfalfa scenarios, CN_c, WP and field capacity (fc) were the most sensitive parameters (Figure S12). As discussed in S3, all three watersheds are vulnerable to runoff (C and D soil hydraulic groups), thus yielding high sensitivity indices ($PCC \geq 0.79$) for CN_c and/or CN_f. Dissolved pesticide concentrations in runoff were also sensitive to WP at different soil depths ($PCC \geq 0.35$). When soil water content falls below WP plants can no longer extract water, which alters the available water content at different soil depths, and thus the potential surface runoff for transportation of pesticides. Other significant hydrologic parameters that were sensitive for pesticide concentrations in runoff ($|PCC|>0.10$) included: field capacity (fc), minimum depth from which ET is extracted (ANETD), and pan factor used to estimate daily ET (PFAC) (Figure 4 and S12). This further supports the assumption that the water content available for runoff or subsurface flow across the soil profile plays an important role in driving transport of these chemicals to vernal pools. Overall, the sensitivity of runoff pesticide concentrations to model parameters were similar across all pesticides and for both crops.

Water column and benthic pesticide concentrations were highly sensitive to application rate (app_eff) and efficiency (app_rate) for both crops (Figure S10, S11, S13 and S14). As with runoff, CN_c was also identified as one of the most influential parameters. Pesticide concentrations in the vernal pool water column, and benthic zone were also sensitive to the USLE parameters (Figure S10-S11). These parameters include the USLE management practice factor (uslep), the USLE soil loss cover management factors (uslec), the USLE topographic factor (uslels), and the USLE soil erodibility (uslek), particularly for diazinon and chlorpyrifos in both crops. This indicates that erosion was a substantial driver of pesticide transport. USLE parameters were more important for chlorpyrifos scenarios than for the diazinon scenarios in all media. For malathion, no USLE parameters were identified as important drivers of concentrations in the water column for the almond scenarios. However, some USLE parameters were identified as sensitive parameters for almond scenario benthic pesticide concentrations and for both water column and benthic concentrations from alfalfa. This variation in the importance of the USLE parameters is attributed to differences in almond and alfalfa root depths. The greater sensitivity of chlorpyrifos to erosion may be explained by its much higher sorption coefficient (Koc) value compared with diazinon and malathion. In general, erosion is likely to be a more important transport pathway for chemicals with a large Koc. As expected, variation in Koc led to changes in the partitioning of pesticides within the vernal pools. Koc was negatively correlated with water column and benthic zone concentrations, but positively correlated with sediment concentrations, with stronger correlations overall in the chlorpyrifos scenario. The same parameters were identified in a SA using the Soil and Water Assessment Tool (SWAT) model as key factors controlling diazinon and chlorpyrifos yields from a California agricultural watershed (Luo and Zhang, 2009).

The fraction of organic carbon on sediment in benthic region (FROC2), and the depth of benthic region (benthic_depth) were also identified as sensitive parameters in all scenarios. Higher sensitivity of FROC2 in chlorpyrifos and diazinon scenarios can again explain the most hydrophobic nature of chlorpyrifos than other two pesticides and diazinon’s low solubility and relatively high affinity to organic matter. These parameters influence the pesticide partitioning between water and sediment. In addition, total suspended sediment is held static at 30 mg/l with a constant fraction of the sediment sorbed pesticide inflowing into the benthic compartment (Padilla et al., 2015). These parameters should be carefully considered while using PWC to predict pesticide exposure concentrations for benthic organisms, especially for chemicals with high Koc values (e.g. chlorpyrifos).

Overall, these results show that chemical concentrations in CVPs are sensitive to watershed, crop type, and pesticide parameters. Therefore, careful selection of pesticides, watershed characteristics and model parameters are recommended before any probabilistic assessment. The daily time series of sensitivity values can be used to examine how the relationships between model parameters and pesticide concentrations change through time (Figure S15). The highest PCC values were observed immediately after applications in mid-February. App_ rate, app_ efficiency, CN_c and fc had a positive PCC with a peak immediately after application and pulses with precipitation. This shows that higher values used for these parameters leads to increasing modeled pesticide concentration in the water column. Application rate, application efficiency, and CN had a more significant rise in PCC after precipitation events compared with other parameters, as they have a direct impact on changing the predicted pesticide concentrations. High pesticide concentrations associated with precipitation events were also reported by Hong and Purucker (2018). They also found a positive relationship between the magnitude of vertical pesticide concentration movement and precipitation. This helps to explain the peak pesticide concentrations following pesticide application and precipitation events and the drops in concentrations with no new applications or rainfall events observed in the current study.

In contrast, FROC2, bulk density of 1st soil horizon (bd1), bulk density of benthic region (bulk density), and WP had negative PCC values. This demonstrates that higher soil organic carbon in the benthic region, reduction in soil compaction, and low porosity reduce the pesticide concentration in water column. A negative correlation between pesticide concentration and bd1 and changes in PCC for the bd of other soil compartments were also observed by Hong and Purucker (2018).

4.0 Conclusion

Pesticide fate and transport in three agriculturally dominated vernal pool watersheds was evaluated by deterministic PWC modeling and probabilistic MC modeling with three widely used organophosphate pesticides. Model simulations were based on pesticide use and weather measured from 1999–2014. The PWC model produced simulation results for vernal pool hydrology and pesticide concentrations (diazinon, chlorpyrifos and malathion) in the vernal pool water column and benthic zone that were consistent with observed field data. In most cases, deterministic exposure concentrations were within 2.5 and 97.5 percentiles of MC exposure distributions. Both PWC exposure and MC assessments emphasize that vernal pools are subject to pesticide input from nearby agricultural applications and are under high risk.

Conditioned daily sensitivity analysis indicates curve number for antecedent moisture condition (CN), application rate, application efficiency, plant wilting point and field capacity as important parameters in the simulation of pesticide concentration in the vernal pool water column. The four-universal soil loss equation (USLE) parameters (K, LS, P, C) were also identified as key parameters for water column and benthic zone pesticide concentration, especially for diazinon and chlorpyrifos. These findings indicate that runoff and soil erosion may be the governing processes for these pesticides. A focus on improving estimates for these sensitive parameters can improve model accuracy and potentially reduce model output-based decision errors. Sensitivity of CN and the four USLE parameters also indicate that these parameters are important drivers of runoff yield of these pesticides. BMPs that reduce runoff and sediment loading would be expected to reduce potential for pesticide loading in the CVPs.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Highlights:

- PWC estimates closely match available field data.
- Modeled and observed pesticide concentrations agreement suggest that the same conditions may be found in other California Central Valley vernal pools.
- The curve number (runoff) and universal soil loss equation (soil erosion) parameters are sensitive inputs for pesticide transport.

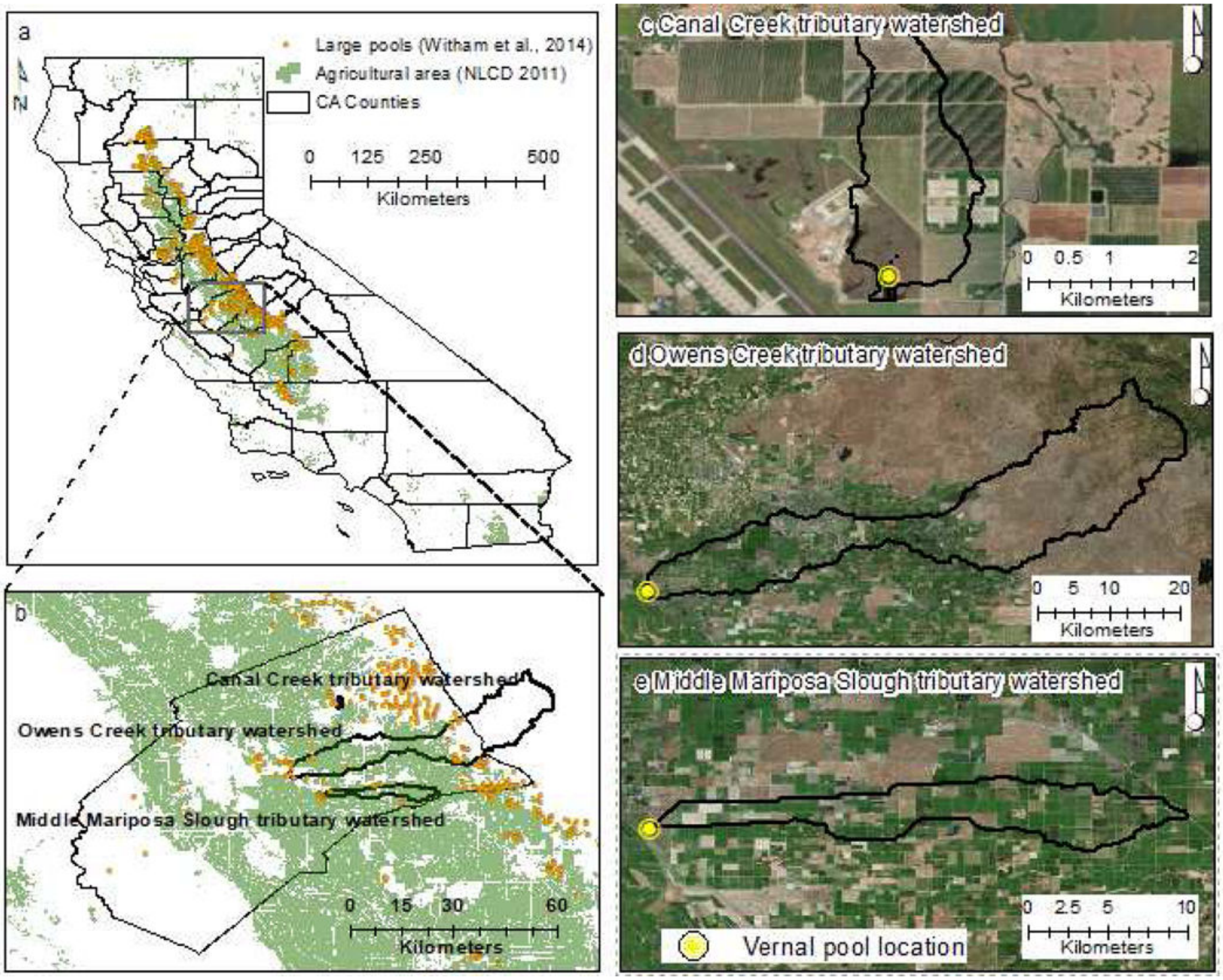

Figure 1.

a) Map of the State and spatial location of CVPs, b) location of study area in Merced County along with agricultural area and other large vernal pools, c) Canal Creek tributary watershed, d) Owens Creek tributary watershed, and e) Middle Mariposa Slough tributary watershed. Vernal pool location within watersheds are marked in yellow.

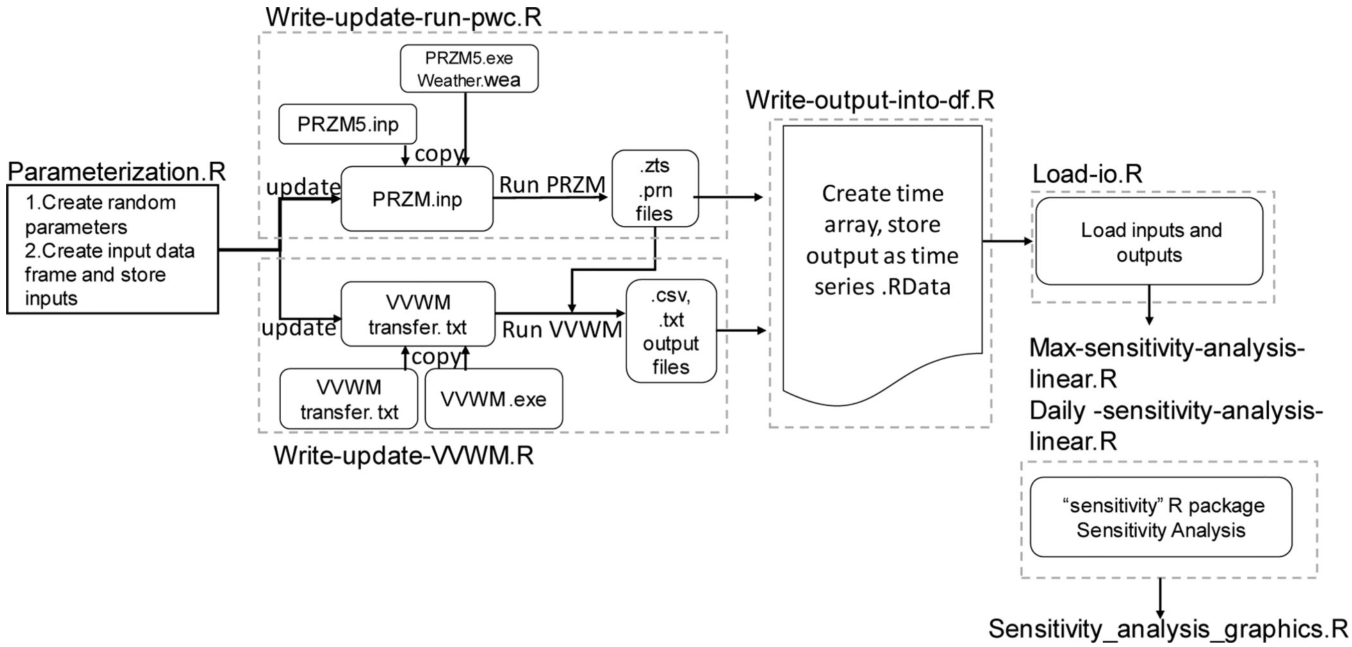

Figure 2:

PWC R script structure. Figure describes the different scripts and their roles used in the R wrapper for PWC.

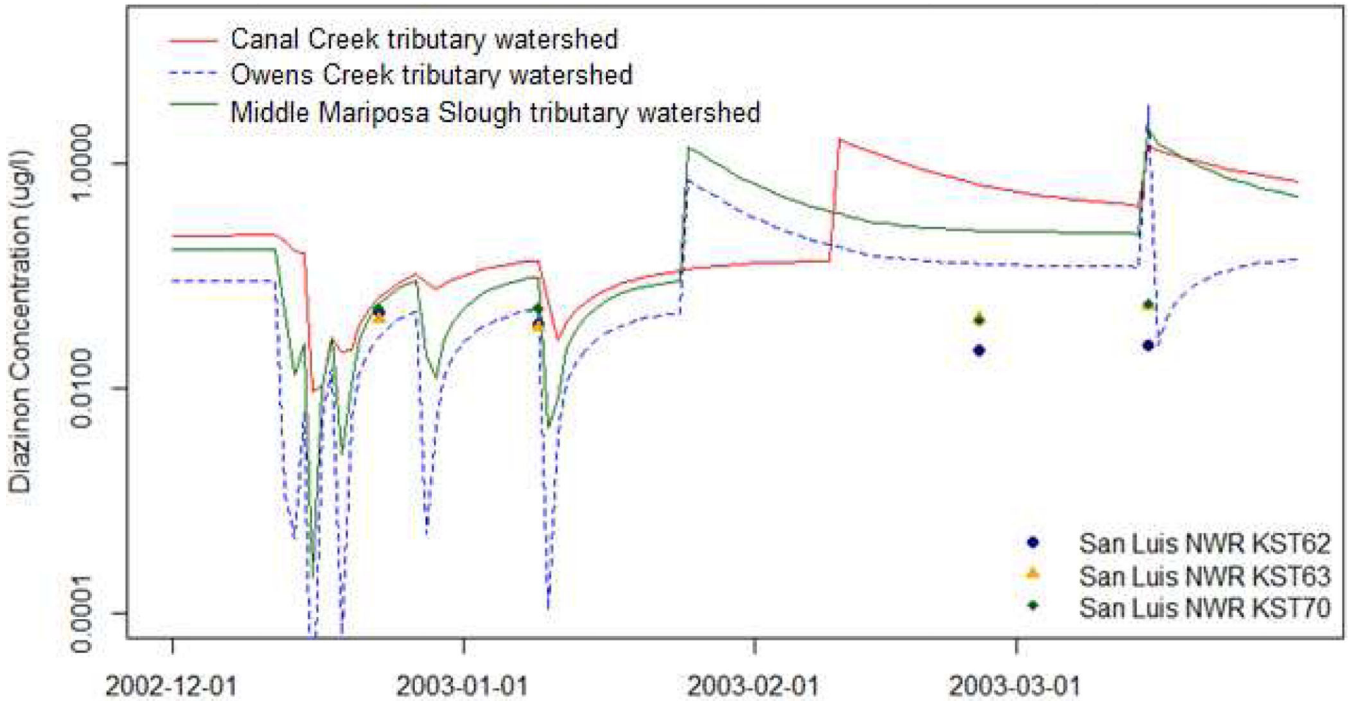

Figure 3:
Diazinon concentration in vernal pool surface water based on PWC simulations and Johnson (2006) observed measurements during 2002–2003. Johnson (2006) has measurements from three sites: San Luis NWR KST 62, San Luis NWR KST 63 and San Luis NWR KST 70

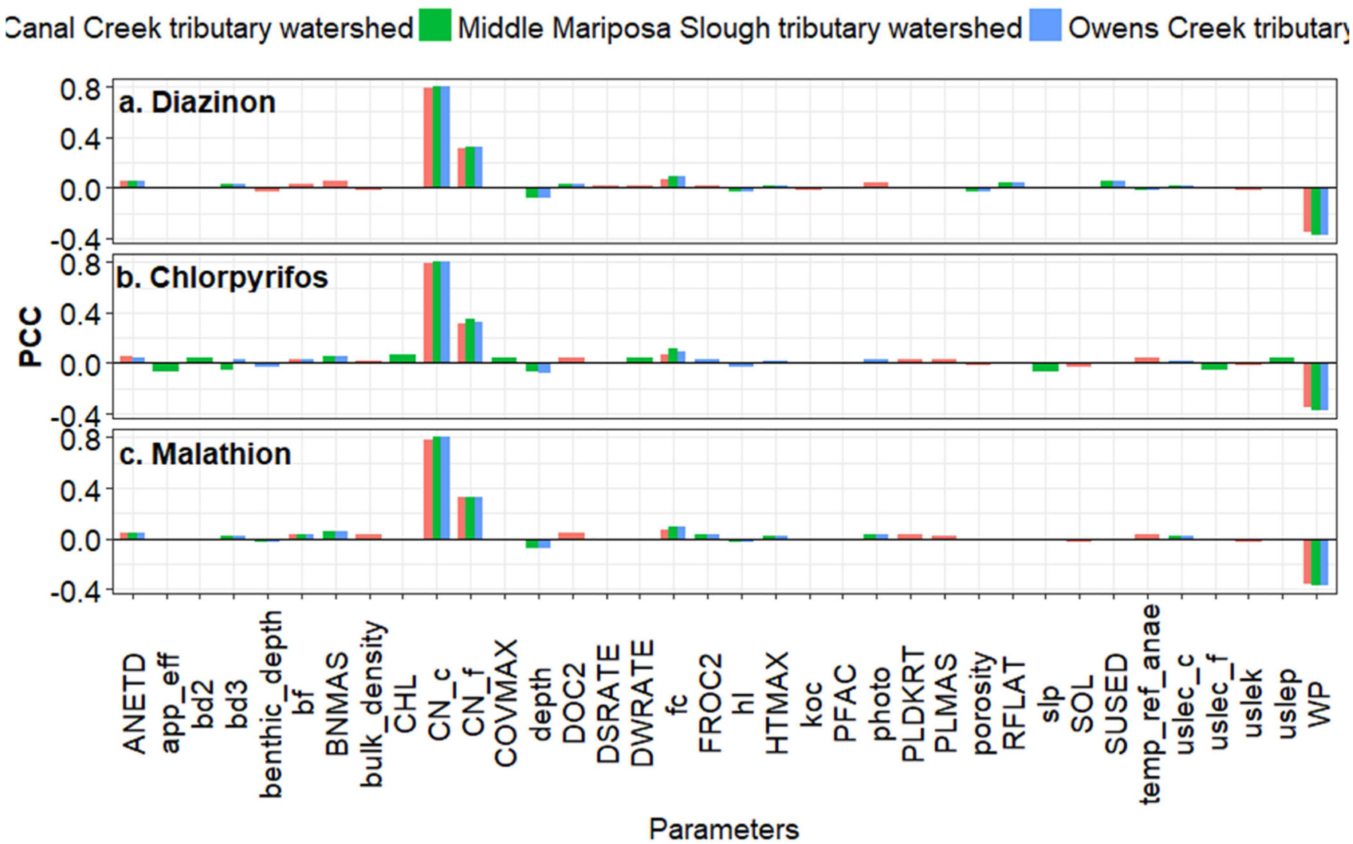

Figure 4:

First fifteen sensitivity PWC parameters for maximum daily a) diazinon, b) chlorpyrifos and c) malathion concentrations in runoff. Concentrations were developed using the almond MC scenario. Different bar colors represent watersheds.

Table 1

Pesticide threshold concentrations for aquatic invertebrates

	Threshold Concentration (ppb)		
	Chlorpyrifos	**Diazinon**	**Malathion**
USEPA OPP aquatic life bench marks			
Acute[a]	0.05	0.17 (0.16 [b])	0.3
Chronic[a]	0.04	0.11 (0.10 [b])	0.035
California Regional Waterboard Aquatic Life Criteria[b]			
Acute	0.025	0.083	0.17
Chronic	0.015	0.072	0.028
Web-ICE predictions for vernal pool fairy shrimp (confidence intervals)	1.29 (0.227 – 7.40)[c]	3.64 (0.95 – 14.02)[d]	6.64 (1.87 – 23.52)[e]

[a]USEPA OPP aquatic life bench marks (USEPA, 2017)

[b]California Regional Water BoardWater Quality Criteria (https://www.waterboards.ca.gov/centralvalley/water_issues/tmdl/central_valley_project s/san_joaquin_op_pesticide/index.html)

[c]Surrogate species = *Thamnocehphalis platyurus* (0.52 μg/L)

[d]Surrogate species = *Daphnia magna* (1.9 μg/L)

[e]Surrogate species = *Daphnia magna* (3.7 μg/L)

Table 2:

Percentage of days exceeded USEPA aquatic invertebrate benchmark values for pool surface water during study period (1999–2014). EECs were simulated based on PWC deterministic simulations

Pesticide	Maximum EECs (ug/l)	Percent of days exceeded %				
		USEPA OPP aquatic life bench marks		California Regional Waterboard Aquatic Life Criteria		Fairy shrimp values
		Acute	Chronic	Acute	Chronic	Acute
Diazinon Sites average	48.58	59.0	72.0	75.0	81.0	04.0
Chlorpyrifos Sites average	10.08	99.7	99.7	99.8	99.7	55.0
Malathion sites average	30.42	11.0	32.0	15.0	38.0	00.0