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Screening ecological risk of pesticides and emerging contaminants under data limited conditions – Case study modeling urban and agricultural watersheds with OrganoFate

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ABSTRACT

The increasing number of chemicals used by society requires accessible, easy to implement tools to perform screening-level ecological risk assessments. However, field data to calibrate and validate screening tools is challenging to obtain for many watersheds. Thus, the evaluation must be done under data limited conditions. Here we employ a fate and transport model, OrganoFate, to predict environmental concentrations of contaminants of emerging concern (CECs) as well as a number of pesticides. CECs evaluated include antibacterial compounds sulfamethoxazole and triclocarban and a flame-retardant tris(1,3-dichloro-2-propyl)phosphate (TDCPP). We also evaluated widely used pesticides chlorpyrifos, bifenthrin and esfenvalerate. We predict concentrations of the contaminants in high-risk watersheds which were dominated by either urban or agricultural development and have small aquatic compartments. Screening-level predictions were in good agreement with observed concentrations in surface water and sediment. Maximum predicted concentrations were close to the highest observed concentrations for CECs, only ~0.1 μg/L greater for sulfamethoxazole and triclocarban concentrations, and for TDCPP <5 μg/L higher. ChemFate was also employed to screen possible aquatic health impacts. Results demonstrated possible CEC aquatic health risk for TDCPP and triclocarban (risk quotients of 0.9 and 1.1 respectively). For pesticides, exceedance of effect (EC50) and lethal (LC50) endpoints was predicted for various taxonomic groups which include aquatic invertebrates, fish, amphibians, and benthic organisms.

1. Introduction

Each year, hundreds of new chemicals are introduced to the US in consumer products (e.g., pharmaceuticals, food additives, personal care products, paints and coatings). To understand and mitigate risks associated with these chemicals in the US, the United States Environmental Protection Agency (USEPA) is tasked with evaluating human and environmental health risks. To evaluate most chemicals, the Toxic Substances Control Act (TSCA) serves as the primary legal framework (USEPA, 2017; Krimsky, 2017). However, in the first ~30 years of TSCA, less than 10% of the 36,000 chemicals proposed for use were reviewed, and 62,000 chemicals already in use were grandfathered in without review (Wilson and Schwarzman, 2009). In light of the limited number of chemicals assessed for health risks, the enormous quantities of chemicals sold annually, and increasing chemical diversification, concerns for adverse effects of chemicals in use is on the rise (Malaj et al., 2014; Snyder et al., 2003; USEPA; Gogoi et al., 2018).

Models have served as an important complement to observation as an approach for filling in data gaps, extending the available observations, and for pro-active risk assessment. Since the 1980's, fate and transport models have been employed by the USEPA to describe the behavior of crop protection products in the environment (Jones and Mangels, 2002). Today, a suite of models are employed by the USEPA, each targeting different risk factors (e.g. exposure pathways and bioaccumulation) and organisms which include humans, terrestrial and aquatic flora and fauna. For pesticides alone there exist a tool suite of 16 models for predicting environmental exposures. (odels for Pestici) While many fate and transport models have been developed and employed by the USEPA, none are able to simulate radically different chemicals within a single framework (e.g., nanoparticles, ions and organic

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contaminants). A new modeling framework, ChemFate (Tao and Keller, 2020), has been demonstrated to achieve this aim. Here, we evaluate a model within ChemFate, namely OrganoFate, for screening the risk of diverse organic contaminants.

ChemFate is a dynamic, multi-media modeling framework. ChemFate contains a suite of chemical-class specific models, while employing the same watershed compartment characterization and common processes for each chemical class (e.g., atmospheric deposition, soil erosion, deposition and resuspension of suspended sediments) for predicting fate and transport. Collectively these features significantly reduce the user effort to simulate chemicals from different classes. ChemFate includes OrganoFate (non-ionizable organic contaminants), ionOFate (ionizable organic contaminants), MetalFate (metal ions), and nanoFate (nanomaterials). Additionally, to simplify the risk assessment process using ChemFate, more than 20 default environmental scenarios have been developed to represent unique environmental characteristics, including predominantly agricultural (e.g., Central Valley, California and Des Moines, Iowa) or urban (e.g., New York City, San Francisco, Los Angeles, Austin, London, and Zurich) areas. The user can modify all default inputs or develop additional scenarios using data from USGS, USDA and NOAA for the United States, or the approach indicated in previous work (Parker and Keller, 2019) for European regions. For further details, see *Supplementary Information (SI) ChemFate User Guide.*

In previous work, ChemFate has been employed to predict nanoparticle concentrations (Parker and Keller, 2019; Garner et al., 2017) as well as ionizable organics, metal ions, organic compounds (Tao and Keller, 2020). In this investigation, we evaluate the use of OrganoFate for comparing predicting concentrations of diverse organic contaminants of contemporary concern, in monitoring data limited watersheds, which is very common. Chemical classes considered include pesticides, pharmaceuticals, an anti-bacterial agent and a flame retardant. To highlight key module attributes for predicting environmental exposure, we compare OrganoFate to the current model that USEPA uses to screen pesticides during registration, the Pesticides in Water Calculator (PWC) 2.0 model, (USEPA; Xie et al., 2018).

PWC predicts concentrations in soil and surface waters at a daily time-step for organic contaminants. Terrestrial processes accounted for include plant uptake, foliar wash-off, dispersion, diffusion, retardation/sorption, erosion, degradation/transformation, volatilization (as a loss term), runoff, leaching, management operations (timing of pesticide application and irrigation). In the receiving water body, deposition/sedimentation, burial, volatilization, and degradation are accounted for. Although there are many similarities between OrganoFate and PWC in the processes and compartment considered, there are also important differences in terms of compartments, processes and model outputs (see Table 1), and in the some of the algorithms employed to simulate fate and transport. PWC is focused on the interaction between the landscape and its soil with a receiving freshwater stream, while OrganoFate also simulates concentrations in estuarine, coastal water, and atmospheric compartments. They also differ in that the PWC employs Freundlich isotherms as well as boundary conditions to simulate diffusive transport (odels for Pestici; Young and Fry, 2020). OrganoFate employs the fugacity approach with rate-limited mass transfer from one compartment to another (Tao and Keller, 2020).

While the PWC has been demonstrated to have general agreement with field observations (Xie et al., 2018), the model has several limitations for screening chemical exposure within the environment relative to OrganoFate. Within the PWC framework, users can only consider non-ionizable organic pesticides. For OrganoFate, the only requirement to simulate different contaminants is to provide contaminant physicochemical properties and use rates. The PWC is also limited in that it cannot account for important pesticide processes (e.g., atmospheric deposition, resuspension of dust to the atmosphere, sediment resuspension in the water column) nor atmospheric concentrations and transport which are an important pathway for pesticide fate and exposure (Zhang et al., 2018; Yao et al., 2008). Moreover, the PWC requires the user to enter pesticide use data manually (e.g. no import function) which is severely limits its use for high resolution pesticide use data available in California (CDPR). Given the sensitivity of pesticide transport to the date of application (Boithias et al., 2014), accurate daily inputs of pesticide use are important in predicting high exposure events.

Table 1
Summary of key similarities and differences in compartments and major processes accounted for in PWC and OrganoFate. X indicates inclusion of a compartment or process.

Compartments/ Advective Processes	PWC Simulation	OrganoFate Simulation	PWC Output	OrganoFate Output
Freshwater	X	X	X	X
Water Column	X	X		X
Suspended Solids	X	X		X
Sediment Pore-Water	X	X	X	X
Sediment Solids	X	X	X	X
Variable Water Volume	X			
Water Column Advection	X	X		X
Sediment Advection		X		X
Estuarine or Coastal Waters		X		X
Suspended Solids		X		X
Sediment Pore-Water		X		X
Sediment Solids		X		X
Water Column Advection		X		X
Sediment Advection		X		X
Land Uses/Crop Types	1	4	0	4
Soil	X	X		X
Soil Horizons	8	2	0	2
Soil Air	X	X		X
Soil Solids	X	X		X
Groundwater	X	X	X	X
Erosion	X	X	X	X
Runoff	X	X	X	X
Leaching	X	X		X
Lateral Flow	X	X		X
Air		X		X
Aerosols		X		X
Air		X		X
Air Advection		X		X
Vegetation	X			

Relative to OrganoFate and the PWC, there are watershed fate and transport models which are can simulate chemical concentrations at multiple catchments within a hydrologic system (e.g., watershed or river basin). Examples include the Soil and Water Assessment Tool (SWAT) (Srinivasan et al., 1998; Arnold et al., 1998; Wang et al., 2019), the Watershed Assessment Risk Management Framework (WARMF) (Zheng and Keller, 2006; Keller et al., 2014) and the Hydrologic Simulation Program Fortran (HSPF) (USEPA; Xie and Lian, 2013; Saleh and Du, 2004). However, there are important tradeoffs to consider when employing watershed models for regulatory risk assessments. Although they can provide model output for multiple catchments, they require higher resolution spatiotemporal data or knowledge of environmental characteristics and chemical use data, which is often unavailable. Moreover, the watershed-scale models require more computational power, user expertise, and often take hundreds of hours to implement and calibrate for a given watershed. Data for calibrating a watershed model at multiple locations for pesticides and other low use (but potentially high toxicity) chemicals is sparse. In addition, these models are also mostly limited to considering only non-ionizable organic pesticides.

Other dynamic multi-media models, similar to OrganoFate, have been employed by government or international agencies for organic chemical risk assessment. Examples include SimpleBox (Hollander et al., 2016) which is employed by the European Chemical Agency, Stochastic Human Exposure and Dose Simulation (SHEDS) (tochastic Human E)

utilized by the USEPA, CalTOX (Mckone et al., 2002) used by the California Department of Toxic Substances Control, and the Berkeley Trent (BETR)-North America (MacLeod et al., 2001) which the Organization for Economic Coordination and Development (OECD) uses to evaluate chemical risk. Most of these models are limited to organic contaminants. Additionally, OrganoFate offers higher spatial resolution via the consideration of more environmental compartments. In total, OrganoFate predicts environmental concentrations in 26 sub-compartments (e.g., aerosols; suspended sediments in freshwater and seawater; soil air, water and solid phases in four different types of land uses).

In this investigation, we explore the use of OrganoFate as a means to accelerate the pace of chemical risk assessment with an advanced prescreening tool. For the study, we evaluate current risks of diverse organic contaminants in the aquatic compartment of regions of California which represent a high degree of urbanization and agricultural activity. Chemicals evaluated include the antibiotic sulfamethoxazole, anti-bacterial agent triclosan, flame retardant tris(1,3-dichloro-2-propyl) phosphate (TDCPP), as well as the insecticides chlorpyrifos (organophosphate), bifenthrin and esfenvalerate (pyrethroids). The CECs were selected due to suspected/known toxicity at environmentally relevant concentrations and due to the need to predict their risks even with limited available monitoring data. Notably, TDCPP is a known animal carcinogen which has been used to replace pentabromodiphenyl ether (PBDE) flame retardants in products such as flexible polyurethane foams, furniture, coatings, bedding products, baby products, and electronic equipment (Wang et al., 2020). The insecticide chlorpyrifos was chosen due to the attention it has drawn in recent years for adverse health effects, principally due to studies demonstrating the impairment of childhood neurological development, which ultimately led to its ban in California as of 2020 (CDRP, 2019; Mohan, 2020). The ban of chlorpyrifos provides an opportune time for predicting the risk of likely chemical alternatives such as bifenthrin and esfenvalerate which have substantially different physicochemical properties. These chemicals were considered likely alternatives due to their use as insecticides on the six crops chlorpyrifos was most widely used to treat in 2005–2014: alfalfa, almonds, corn, cotton, oranges, and walnuts (CDPR). Moreover, for crops such as almonds and walnuts, esfenvalerate and bifenthrin are already employed to treat nearly equal or greater acreage of the crop relative to chlorpyrifos.

2. Methods

2.1. Study areas

In this investigation, we evaluated OrganoFate for the prediction of organic contaminants in the aquatic compartment of three different watersheds for a 10-year period, 2005–2014. The selected analysis period and sites (watershed) coincide with the time period and watersheds for which monitoring data was available for the contaminants of interest. Sites selected for analysis were highly developed watersheds with a Mediterranean climate. Site #1, the upper Santa Clara River Watershed (~1300 km^2), is located just north of Los Angeles (see Fig. 1). During the analysis period, the site received a mean average annual precipitation of 290 mm, and its flow is dominated by wastewater treatment effluent for most of the year. Developed land in the watershed is ~90% urban and the rest agricultural. The concentrations of sulfamethoxazole, triclocarban, and TDCPP were predicted for Site #1, the only location with available monitoring data.

To evaluate the prediction of the pesticide concentrations, the other sites, #2 and #3, were selected to represent intensive agricultural watersheds in the Central Valley. Site #2 is the Visalia Watershed and Site #3 the San Joaquin River Watershed. Site #2 (~22,000 km^2) is located at the southern end of the Central Valley (see Fig. 1) and had an average annual precipitation of 170 mm for the analysis period. Site #3 (~35,000 km^2) encompasses the entire drainage network upstream of the USGS monitoring site at Vernalis, CA. This area was selected for Site #3 because at the Vernalis monitoring site, many detections of chlorpyrifos have been observed. Located just north of Site #2, Site #3 had a higher mean annual precipitation of 290 mm. Both Site #2 and Site #3 are hydrologically connected to the Sierra Nevada Mountain range from which most of the instream flow is derived. Additionally, the proportion of developed land in both watersheds is ~90% agricultural.

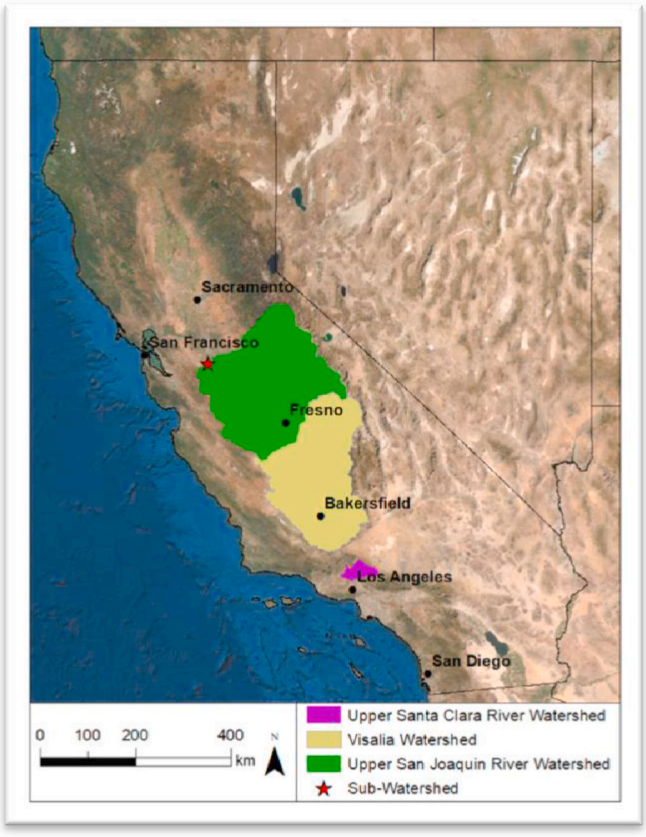

Fig. 1. Watersheds under investigation; note the subwatershed is too small to be visible on the map and is indicated with a star.

For the watersheds considered, area boundaries were delineated utilizing the area of interest as best fitted to watershed boundaries (hydrologic unit codes (HUC) 8 and 12 (USDA, 2011)). Three different land use compartments, with their corresponding soils, were considered for each site. The proportion of urban, agricultural, and natural land uses were obtained from the National Land Cover Data (2016) (Multi--Resolution Land Cha). Soil, climate, and hydrologic data for regions were compiled according to methodologies published in the ChemFate User Guide (Tao and Keller, 2020). All site parameter values employed for these sites can be viewed in *SI* Table S1.

2.3. Generation of PECs

To generate PECs, we developed input files for (1) the physicochemical parameters for each pollutant; (2) watershed characteristics including daily meteorology and streamflow for each site; and (3) daily release rates for each pollutant. To view parameterization employed for all contaminants and physicochemical properties and loads, see *SI* Tables S–1 to S4. OrganoFate then calculates transport (e.g., advection, diffusion/dispersion, mass transfer between phases, runoff transport, erosion and sediment transport, sedimentation within the water column, resuspension of sediments) and fate (i.e., degradation processes) for each compartment indicated in Table 1, at a daily time step. The model was run for the 2005–2014 analysis period. OrganoFate can be run assuming zero background concentrations (i.e., the chemical has never

been used in the region before) or with some initial background concentrations in the case the chemical has been in use for some time before the simulation period. The background concentrations can be based on monitoring data, or in their absence with a "warm-up" run. For Site #1. instead of assuming zero initial concentrations, we opted to run the model one time for 10% of the total simulation time, and then used the predicted concentrations as initial concentrations for the entire analysis period. For Sites 2 and 3, initial pesticide concentrations were predicted by employing pesticide use data from 1995 to 2004 using all other OrganoFate parameterization for the 2005–2014 analysis period. The environmental concentrations observed at the end of the 1995–2004 simulation were used as initial data for the analysis period 2005–2014.

2.2. Contaminant loads

At Site #1, the CECs sulfamethoxazole, triclocarban, and TDCPP loads were simulated by calculating the mass of chemical present in wastewater treatment plant effluent during monitoring. Monitoring was conducted by the Southern California Coastal Water Research Program (SCCWRP) immediately downstream of the upper most wastewater treatment plant on the river during dry, low flow conditions when flow is predominantly wastewater treatment plants (WWTP) discharge (Maruya et al., 2016). Given that upstream of the WWTP over 90% of developed land is urban, we assumed that all CEC loads were from WWTPs (e.g., no antibiotic loads in runoff from livestock paddocks). Loads were estimated by calculating the product of observed concentrations and the daily discharge of the two WWTP in the study area. Given that only two sample event dates were available, one on July 27 and October 15 of 2013, and that the flow was lowest on the July sample date, concentrations observed for the July sample event were employed to estimate the daily release rates of the contaminants.

In this investigation, pesticides were evaluated at Site #2 and Site #3. For chlorpyrifos, bifenthrin, and esfenvalerate, we employed pesticide use reports to simulate chemical release. The pesticide use reports are required and collated by the California Department of Pesticides Regulation (CDPR). From the use reports, agricultural pesticide application data is available at the daily time-step and 2.6 km^2 resolution. However, professional pesticide use is only reported at the county level and no residential pesticide use is recorded. Since 90% of developed land at Site #2 and Site #3 was agriculture, where the majority of pesticide use occurs, and given the low resolution of pesticide applications in urban areas, only agricultural pesticide use data was employed. The pesticide load data employed was the mass of active ingredient applied.

2.4. Evaluation of PECs

Predicted environmental concentrations (PECs) for all contaminants and sites were compared to environmental monitoring concentration data from SCCRWP (SCCWRP, 2015) and the CDPR Surface Water Monitoring Program (Surface Water Datab). When evaluating PECs relative to observed, it is important to consider that monitoring campaigns can only reliably capture contaminant concentrations above the limit of quantification (LOQ), yet concentrations can be predicted below the LOQ. The LOQ is the lowest concentration from which quantification with accuracy can be determined. Due to the inability to compare PECs to concentrations below detection limits, only sample detect data were employed to evaluate OrganoFate predictions.

When validating fate and transport models, it is common practice to calibrate the model and analyze the residuals of variance between monitoring and predicted concentrations (Moriasi et al., 2007). In this study, given the limited monitoring data we employed OrganoFate without calibration (i.e., no adjustment to the initial model parameterization) to predict contaminant concentrations. To evaluate the model, a comparative analysis of observed and predicted chemical concentrations was performed for the range and median values. This method was employed rather than analyzing the variance of residuals because of the inability for monitoring data to capture concentrations below the LOQ and the highly limited spatiotemporal resolution of the data. For CECs, monitoring data was only available on 2 different dates (at 5 different sites for each date). For pesticides at Site #2 and #3, the comparative analysis was performed because the watersheds encompass over 20,000 km^2 and a number of rivers/streams. Across such a large extent, the timing of precipitation will vary widely, although the climate data employed from weather stations within the watershed may be representative of climate conditions across the watershed. Our aim was to predict the range of concentrations within the sites surface water, not the timing of the rain event. A comparative analysis rather than residual variance on the days for which monitoring data was available was therefore better suited to the aim of this investigation, a screening-level risk assessment.

Observed surface water CEC concentrations at the various sites varied by orders of magnitude. To accommodate the wide range of observations for which extreme observations are of environmental significance, boxplots of the respective concentrations were compared whereby the inter-percentile range considered was the 90th percentile of concentrations, whiskers 99th percentile, and outliers all values greater than the 99th percentile. To compare median values, the quotient of predicted values with respect to observed values was calculated (QPEC). Since the QPECs can span multiple orders of magnitude, the QPECs were logarithmically transformed to $\log_{10}$ (QPEC) (denominated pQPEC from here on, for brevity) and to improve interpretability.

2.5. Ecological risk screening

The ecological health risk of chemicals in this investigation was predicted for aquatic organisms by comparing predicted concentrations to observed ecotoxicological endpoints. For pesticides, aquatic health benchmarks were obtained from the USEPA Office of Pesticide Protection and California State Water Resources Control Board (SWRCB). USEPA water quality criteria adopted here reflect the maximum concentration at which chemicals may occur prior to causing adverse health impacts; these criteria are used during the pesticide registration process for risk assessment. Two databases were considered since the USEPA criteria are used for developing pesticide labels for the United States (USEPA, 2017), while the SWRCB (sub-entity of California Environmental Protection Agency) criteria are more sensitive and were developed by the agency in consideration of adverse aquatic health impacts observed in California's waterways. For bifenthrin and esfenvalerate, SWRCB ecotoxicological endpoints were adopted from the water quality control plan for pyrethroid pesticide discharges in the Central Valley, which was published in 2017 (Regional Water Quality Co, 2017). For chlorpyrifos, the endpoint was adopted from water quality goals of the SWRCB, published in 2016 (Marshack, 2016).

To explore the accuracy of predictions, it was important to consider the LOQ of monitoring data. For pesticides the LOQ was often above aquatic effect thresholds and OrganoFate can predict concentrations below the LOQ of observed data. The consequence is that many samples for which monitoring data indicated a non-detect, the concentration of the contaminant may have been above an aquatic health criterion. Moreover, the median observed concentration is dependent on the LOQ of the analyses. Thus, the median LOQ of each pesticide's samples were calculated and compared to aquatic health benchmarks and PECs.

To evaluate aquatic risks for the CECs, for which there are no established regulatory criteria, toxicological data compiled from the USEPA database ECOTOX was employed. (USEPA) The database was thus used to provide an aquatic health benchmark for CECs and to evaluate health risks across a broad range of taxa for all chemicals in this investigation. The ECOTOX database contains ~50,000 toxicological studies for ~12,000 chemicals and ~1,000,000 toxicological endpoints. (X. at < https) Ecotoxicological data for each chemical was compiled for freshwater organisms belonging to *Animalia*, which are more sensitive to

the mode of action of the chemicals evaluated than other taxa belonging to the domain Eukarya. The one exception was ecotoxicological data for the half maximal effect concentration for triclocarban, for which seawater organisms were included as a proxy for freshwater organisms due to limited freshwater test data (n = 1). Data for the following ecotoxicological thresholds was compiled: half maximal effect concentrations (EC50), half maximal lethal concentrations (LC50), and for chemicals with no EC50 data available, the no observable effect concentration (NOEC).

To calculate aquatic benchmarks for CECs, Species Sensitivity Distribution (SSD) curves were constructed using EC50 data for a minimum of eight species, from which the HC5 (i.e., the he hazardous concentration for 5 percent of species) could be determined. SSDs are cumulative probability density functions describing the likely fraction of species for which adverse effects are expected at a given contaminant concentration (Wheeler et al., 2002; Kooijman, 1987). SSDs were generated for acute (≤4 day) and chronic (>4 days) ecotoxicological data using the fitdistr function in the MASS package for the data analysis software R, and were modified such that all available effect data were used. For instance, if two endpoints existed for the same species, all values were used to generate the sensitivity curve. If the number of species studied for a particular chemical and ecotoxicological endpoints were fewer than eight, no SSDs were generated. Instead, the lowest ecotoxicological endpoint was considered.

3. Results and discussion

3.1. Urban PECs –site #1

For sulfamethoxazole, triclocarban, and TDCPP, OrganoFate predicted concentrations in the freshwater column were within the range of monitoring data (see Fig. 2 as well as *SI* Table S5 and Figure S10). The median modeled and observed concentrations also exhibited reasonable agreement with the quotient of predicted and observed concentrations (log transformed); the pQPEC, of each CEC was less than 0.4.

For sulfamethoxazole, no observed or predicted concentrations exceeded the HC5. For TDCPP, insufficient data was available to calculate the HC5 (n = 4), but the chronic NOEC for the fish *Danio rerio* (6.4 μg/L) was not exceeded for either the maximum observed (1.4 μg/L) or predicted concentrations (5.8 μg/L). *Danio rerio* was the only

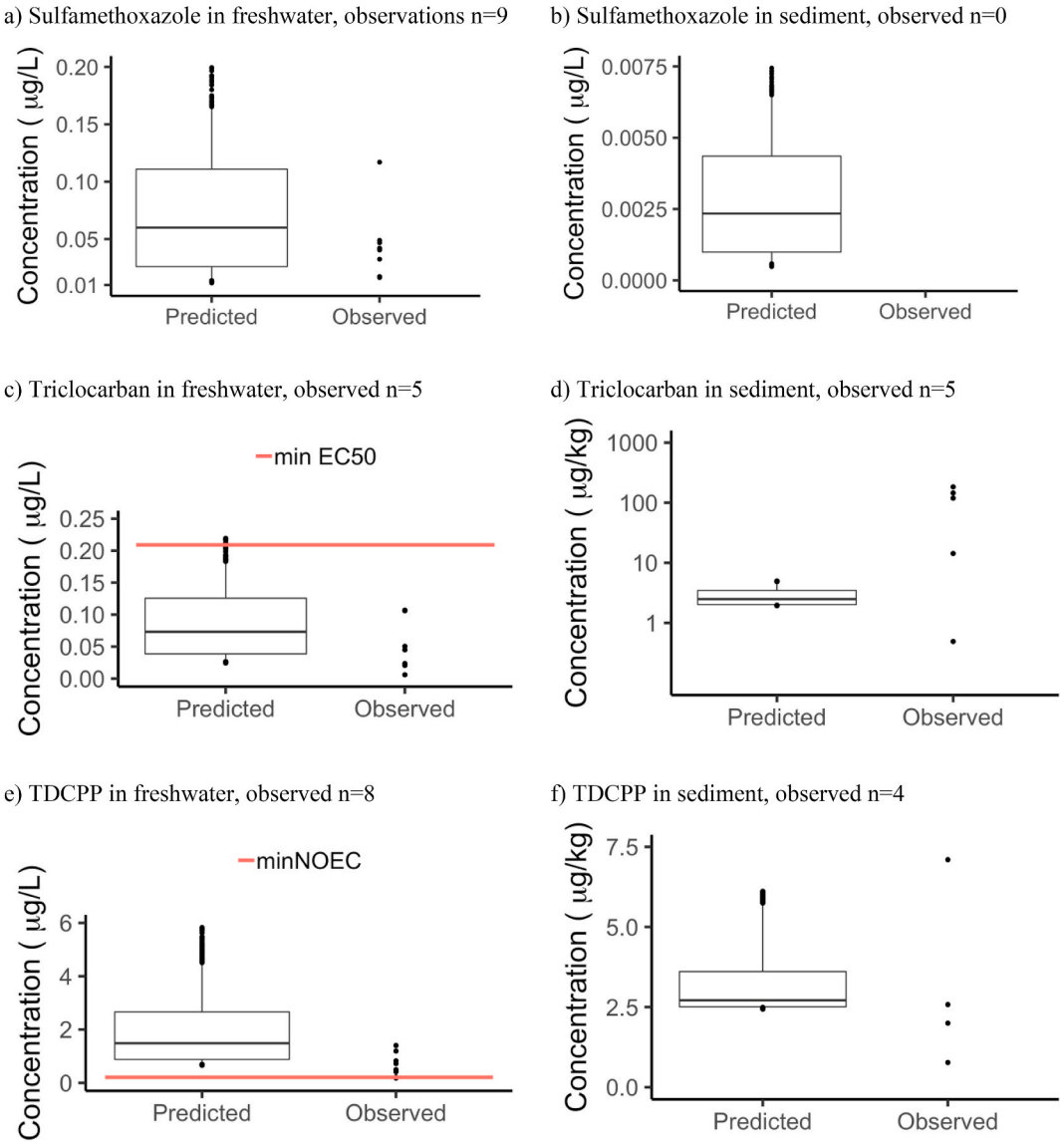

Fig. 2. Predicted and observed freshwater column and sediment concentrations of triclocarban, sulfamethoxazole, TDCPP, and bifenthrin. Boxplot interquartile ranges reflect the 90th percentile of predictions. Aquatic health criteria for the water column are also depicted if they were within the range of observed or predicted concentrations.

organism for which data was available, and the predicted risk quotient with respect to the most sensitive endpoint (PEC/NOEC) was 0.9. For triclocarban, the maximum observed concentration (0.11 μg/L) was near the most sensitive chronic EC50 endpoint (0.21 μg/L), and the maximum predicted concentration of triclocarban (0.22 μg/L) slightly exceeded the endpoint. The predicted risk quotient for triclocarban was 1.1. Thus, OrganoFate was able to predict that TDCPP and triclocarban may pose a hazard at Site #1, even without adjusting parameter values. This demonstrates the value of the model for screening risk assessment.

For concentrations in freshwater sediment, observed data were only available for triclocarban and TDCPP. The predicted concentrations were within the observed range, but unlike predictions in surface water, there were observations higher than the predicted range. While the range of predicted concentrations were still similar to observed for TDCPP, the maximum observed triclocarban concentration was substantially higher than the maximum PEC (see Fig. 1(d)). This discrepancy, which also was observed for triclocarban, may be attributable to the representation of the stream bed organic carbon as homogenous throughout the site, even though a high degree of heterogeneity of organic carbon may exist in these stream beds (Angradi, 1996; Hill and Sanmugadas, 1985). Organic contaminants sorb more readily to high organic carbon content sediment, especially triclocarban owing to its high organic carbon partitioning coefficient (~17,000 L/kg). To more accurately model the concentrations of triclocarban in the vicinity of the WWTP, the analysis region could be reduced to closer proximity to the WWTP, as demonstrated in previous work (Parker and Keller, 2019). An evaluation of concentrations immediately downstream of the WWTP was not conducted here due to the absence of instream flow data near the WWTP.

3.2. Agricultural PECs– sites #2 and #3

In the agricultural Site #2, while observed bifenthrin and esfenvalerate concentrations were within the range of predicted concentrations (Fig. 3 as well as *SI* Table S6 and Figure S11), the observed values were all greater than the 99th percentile of predicted concentrations. This is likely attributable to the high LOQ of samples, for which the median LOQ was greater than the 95th percentile of predicted concentrations. Notably, the median LOQ was also higher than the USEPA and SWRCB health benchmarks, which demonstrates the analytical capabilities for

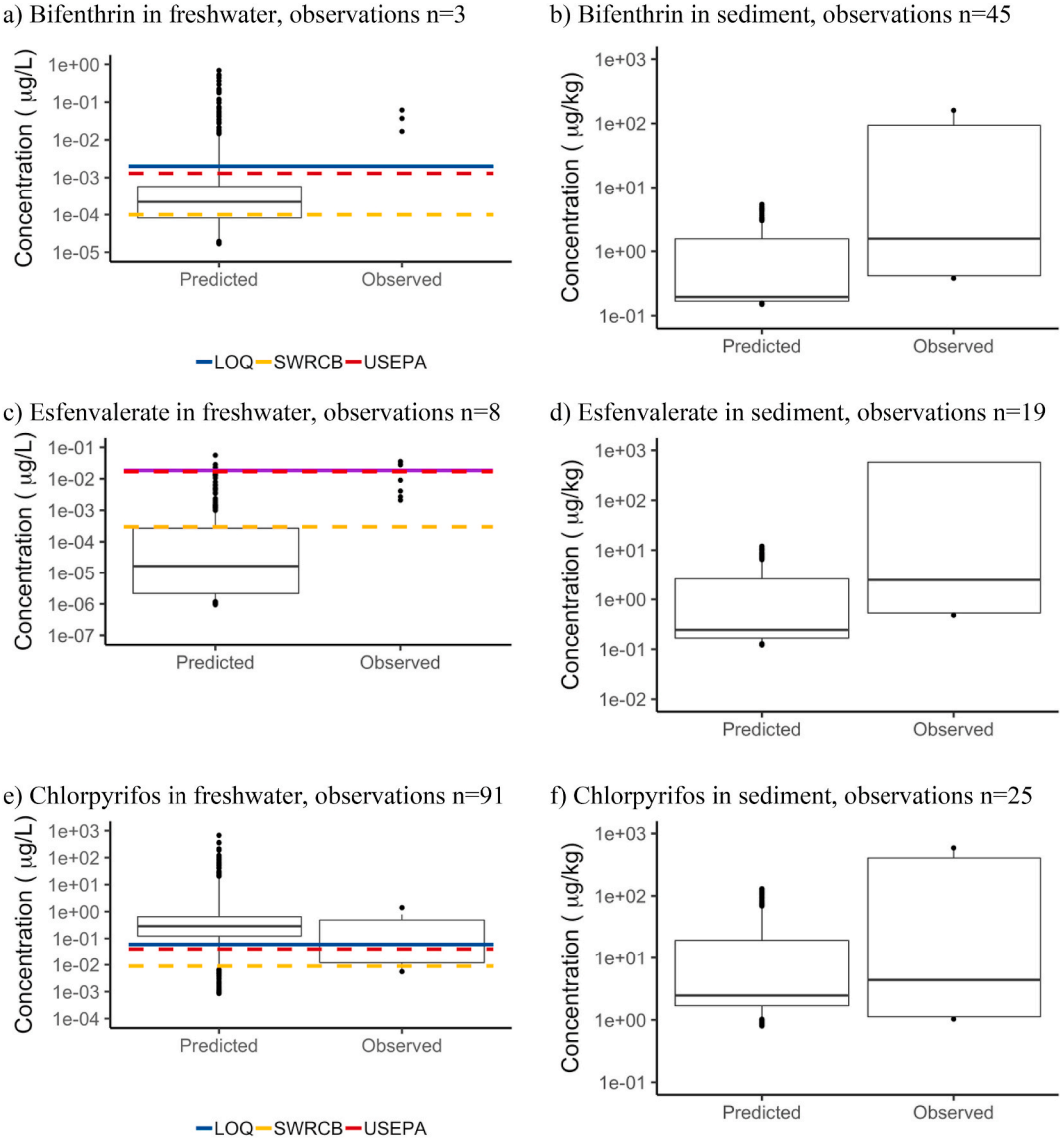

Fig. 3. Predicted and observed concentrations of chlorpyrifos, bifenthrin, and esfenvalerate in the freshwater column of Site #2. Also displayed is the median LOQ of observed concentrations, the SWRCB water quality indices and USEPA aquatic health benchmarks. The boxplot range reflects the 90th percentile of observations, the whiskers the 99th percentile, and outliers the remaining values.

the majority of samples collected in monitoring campaigns were not sensitive enough to capture concentrations of concern to aquatic organisms. Thus, while there were few positive detections at Site #2 for each compound in the CDPR SURF database (detection frequency of ~2% for each), the actual concentrations may frequently exceed aquatic health benchmarks. Moreover, the observed concentrations exceeded at least one aquatic health benchmark at the site.

Chlorpyrifos PECs at Site #2 were also within the observed range for the freshwater column and encompassed all observed concentrations. With the higher number of observations and median LOQ similar to the median predicted and observed concentrations, predictions of OrganoFate were close to observed concentrations, with a pQPEC of 0.68. The results demonstrate good agreement between PECs generated by OrganoFate and observed concentrations. With respect to aquatic health benchmarks, chlorpyrifos was in exceedance for at least one of the criteria set forth by the SWRCB and USEPA for nearly 100% of predicted and observed concentrations. Within the analysis period for pesticides at Site #2, OrganoFate predicted that SWRCB criteria would be exceeded for chlorpyrifos, bifenthrin, and esfenvalerate 363 days, 356 days, and 183 days out of 365 days, respectively. Predicted days of exceedance of USEPA criteria for chlorpyrifos, bifenthrin, and esfenvalerate are 356 days, 9 days, and 2 days, respectively. Collectively, observed and predicted concentrations provide strong supporting evidence that protection goals for aquatic fauna are not achieved with current pesticide use regimes at Site #2.

The accuracy of predictions for chlorpyrifos in the freshwater compartment at Site #3 were similar to Site #2, with an observed pQPEC of 0.4 and the range of predicted values encompassing all observations (*SI* Table S7, Figure S12, and Figure S13). For Site #3, the upper 95th percentile of observed chlorpyrifos concentrations and upper 50th percentile of predicted concentrations exceeded the SWRCB criteria. Unlike Visalia, there were no observed exceedances of the USEPA aquatic life benchmark, only for predicted concentrations in the >95th percentile.

In sediment, similar to the water column, the predicted and observed concentrations of chlorpyrifos were in close agreement. For Sites #2 and #3, a difference in the predicted and observed median concentrations was <2 μg/kg. Similar ranges between PECs and monitoring data were also observed. However, the range of predicted concentrations did not encompass all sample data. After review of monitoring site locations (see *SI* Figure S3), this may reflect that many observations were for small tributaries. For bifenthrin and esfenvalerate, the sediment median PECs were within about an order of magnitude of observed values. However, the maximum observed concentrations were orders of magnitude greater than predicted. The disparity between predicted and observed sediment concentrations of bifenthrin and esfenvalerate may, like for chlorpyrifos, be attributable to monitoring on small tributaries. Another factor is the more localized use of the chemicals (see *SI* Figure S3-Figure S5). Additionally, it is likely attributable to heterogeneity of organic carbon in the sediment discussed for Site #1 and the high sorption tendency of the pesticides. The organic partitioning coefficient of bifenthrin and esfenvalerate are 236,600 L/kg and esfenvalerate 341,000 L/kg, respectively, while that of chlorpyrifos is substantially lower (5460 L/kg).

3.3. Ecological risk screening

Given the paucity of CEC toxicological data, species specific hazards are only discussed for pesticides. The acute and chronic HC5, based on the EC50, were exceeded for all three pesticides, for the observed data

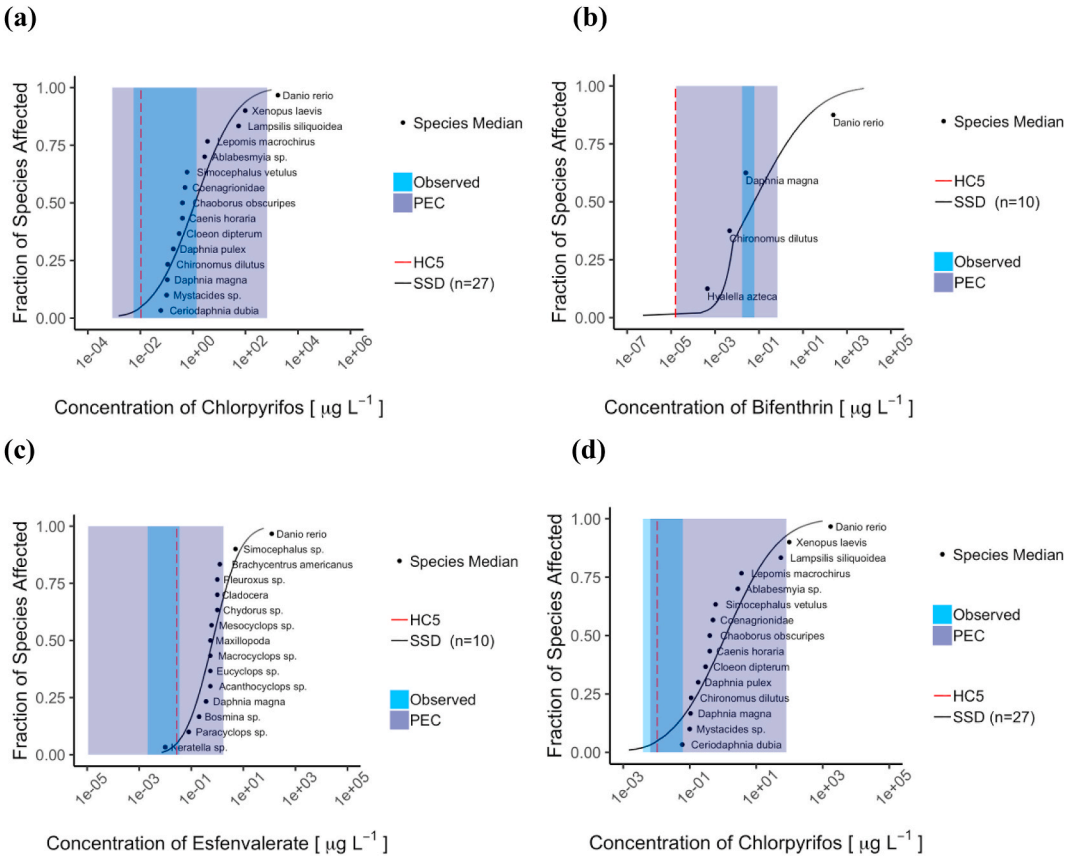

Fig. 4. (a–d). Observed and predicted concentrations (PEC) relative to species sensitivity distribution models derived for the half maximal effect concentration (EC50) in studies with the duration of observation greater than 96 h (sub-chronic to chronic). Depicted for the Site #2 are **(a)** chlorpyrifos, **(b)** bifenthrin, and **(c)** esfenvalerate. Chlorpyrifos within the San Joaquin Watershed is depicted in **(d)**.

and PECs (Fig. 4). Exceedances of the EC50 for several species were also observed for each pesticide. For Site #2, chlorpyrifos, observed and predicted concentrations exceeded the EC50 for water fleas, aquatic flies (e.g., caddis flies, mayflies, damsel flies), mosquitos, pigmy backswimmers, crustaceans, and fish. Predicted chlorpyrifos concentrations also exceeded the EC50 for mussels and frogs. For bifenthrin, the EC50 for water fleas, aquatic flies, and fish were exceeded by observed and predicted concentrations. Observed Esfenvalerate concentrations exceeded EC50 for rotifers, water fleas, and aquatic flies, while PECs exceeded EC50 for water flea, aquatic flies, aquatic beetles, crustaceans, and fish.

3.4. Significance and limitations

This investigation demonstrated that parameterization of OrganoFate based strictly on data available in easily accessible databases can predict environmental concentrations of diverse organic contaminants generally within the observed range. The model parameters were not adjusted, yet the model was able to provide reasonably accurate PECs and important insights with regards to current chemical hazards in the environment. A notable observation from this investigation is that the pesticides bifenthrin and esfenvalerate, which have displaced chlorpyrifos and other earlier generations of pesticides, are likely to be of substantial concern to biodiversity in the surface waters of the agricultural watersheds of this investigation. While this is only a screening level analysis, it is an important concern, identified by OrganoFate, which warrants further investigation with more frequent observations and lower LOQs. The advantage of employing OrganoFate for this analysis is that it is a part of ChemFate, a tool able to predict concentrations for diverse chemical classes, including pesticides based on ionizable organics, metal ions or nanomaterials, which cover a wide range of commercial products. It is advantageous for users to be able to employ the same tool for these analyses as it requires considerable effort to parameterize models as well as for a user to familiarize themselves with tools necessary to conduct analyses for current use chemicals. ChemFate provides a unique environment within which users can quickly screen risks for unique compounds and environmental hazards.

In all environmental models, including multimedia and watershed scale models, environmental media are represented by homogenous compartments at some scale. Yet, there is often significant variability in properties, such as the organic carbon in soils and sediments, as well as concentrations, due to incomplete mixing. In surface water, small streams and creeks may have concentrations which are significantly higher than in larger rivers, since there is less dilution in smaller water bodies compared to larger ones (Schulz, 2004). Distinguishing fate in different areas of the bulk water compartment is also important because small waterbodies have been demonstrated to not only have higher concentrations, but greater biodiversity (Lorenz et al., 2017). A limitation of OrganoFate with respect to watershed scale models is the contiguous representation of compartments which simulates a lower resolution of concentration gradients in the landscape. Though compartment representation is subject to more simplification than other tools, this mitigates over parameterization in data limited regions, reduces model complexity, and offers greater efficiency. While predictive tools such as OrganoFate do not displace the need for monitoring, they can be leveraged to provide important insight with regards to PECs and ecological risks at a higher spatiotemporal resolution than is typically achievable with monitoring data.

4. Conclusions

Chemical use will continue to increase for the foreseeable future as we seek to improve living conditions and sustain a growing population. Our evaluation of OrganoFate for the prediction of the concentration of organic CECs and pesticides within aquatic environments demonstrated the model to predict concentrations within the range of available monitoring data. Moreover, we were able to employ the tool to evaluate probable adverse aquatic health impacts for chemicals with very limited monitoring data (the CECs) and of chemicals for which monitoring analyses often do not capture concentrations that are hazardous to fauna (bifenthrin and esfenvalerate). These results are of import to the broader field of chemical risk assessment in that it validates an important submodule of the tool ChemFate which can provide these types of analyses for an even broader class of contaminants with limited monitoring data such as ionized organics, metals, and nanomaterials.

Authorship statement

Nicol Parker: Conceptualization, Data curation, Formal analysis, study design, Methodology, Validation, Visualization, Writing – original draft, review/editing. Arturo Keller: Conceptualization, study design, Methodology, review/editing

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Declaration of competing interest

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.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2021.117662.

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