UC Santa Barbara

UC Santa Barbara Electronic Theses and Dissertations

Title

Rapid and Spatially Explicit Assessment of Contaminants of Emerging Concern in Data Limited Watersheds

Permalink

https://escholarship.org/uc/item/67b4k478

Author

Parker, Nicol

Publication Date

2023

Peer reviewed|Thesis/dissertation

eScholarship.org Powered by the California Digital Library
University of California

UNIVERSITY OF CALIFORNIA

Santa Barbara

Rapid and Spatially Explicit Assessment of Contaminants of Emerging Concern in Data Limited Watersheds

A dissertation submitted in partial satisfaction of the requirements for the degree Doctor of Philosophy in Environmental Science and Management

by

Nicol A. Parker

Committee in charge:

Professor Arturo Keller, Committee Chair

Professor Ashley Larsen

Professor Patricia Holden

December 2023

The dissertation of Nicol A. Parker is approved.

_____

Ashley Larsen

_____

Patricia Holden

_____

Arturo Keller, Committee Chair

December 2023

Rapid and Spatially Explicit Assessment of Pesticide Risk to Diverse Taxa across Varying Management Scales

Copyright © 2023

by

Nicol A. Parker

ACKNOWLEDGEMENTS

My Ph.D. journey, a rigorous yet fulfilling endeavor that shaped my approach to scientific inquiry, was made possible by a diverse group of mentors and supporters. Their dedication to nurturing my curiosity and well-being is met with my deepest gratitude. Their steadfast guidance and support were pivotal throughout this process. I extend my profound appreciation to Dr. Keller, whose exemplary support and mentorship, coupled with the freedom to innovate, were pivotal. Dr. Keller inspired the integration of mechanistic modeling into my research, advancing our understanding of the complex field of chemical hazards. His guidance refined my scientific writing, and his provision of research opportunities and funding were invaluable. I am particularly thankful for Dr. Keller's assistance in securing the funding that afforded me the liberty to pursue my research interests and gain early publication experience.

I extend my gratitude to Dr. Larsen for her astute guidance and significant impact on the clarity, relevance, and breadth of my research. Her exceptional skill in scientific writing and communication has been both enviable and inspirational. It has been a privilege to grow under her expert guidance and mentorship. Additionally, my sincere thanks go to Dr. Holden for her meticulous critiques and valuable insights. Her feedback was instrumental in elevating the caliber and professionalism of my work. Her rigorous analysis spurred the critical examination of pesticide risk approaches, which were instrumental to my third chapter.

The freedom to engage in scientific inquiry was made feasible by the California Sea Grant – Bay-Delta Science Fellowship's substantial funding. I am grateful to the selection committee and the agency for their crucial support during these pivotal years. Further financial assistance that significantly advanced my research was provided by The Schmidt Family Research Foundation, the Bren School of Environmental Science and Management, and the Chemical Life Cycle Collaborative."

To my family, Ann, Leon, Taylor, Erika, and Oliver Parker. Although too far away in my home state of Michigan, they always provided the foundational love and support that has enabled me to navigate confidently and curiously what many academics find to be one of the most challenging periods of their lives with a well-balanced lifestyle. Their bedrock of support has provided the initiative for my pursuit of academics, and what is best summarized as a fun Ph.D. To Christoph, whose patience for the never-ending Ph.D. and generosity enabled me to maintain and cultivate my curiosity for the world beyond academia, who taught me the love for good food, was the curator and creative behind endless fun in my free time, and who introduced me to too many superb hobbies. Always there for a laugh and cuddle, you made much of the hard easy. To the ocean, a constant source of serenity, inspiration, and risk. Your vastness has provided solace during challenging times and endless opportunities for adventure, whether catching a wave, petting a shark, or slamming beach volleyballs on your shores.

Nicol A. Parker

December 2023

nparker@ucsb.edu | 7336 Freeman Pl, Goleta, CA | 989-640-7156

PROFESSIONAL APPOINTMENTS

2020-2023 California Sea Grant Bay-Delta Science Fellow, UCSB
2019 Schmidt Fellow, UCSB
2016-2018 Environmental Protection Agency STAR Grant Researcher, UCSB
2014-2016 Environmental Engineer, Spicer Group
2013 National Science Foundation Fellow, Virginia Institute of Marine Science

EDUCATION

Ph.D., Environmental Science and Management, Bren School of Environmental Science and Management, University of California Santa Barbara (10/2023)
Cumulative GPA: 3.90
Emphasis: Chemical risk assessment and mitigation, focusing on emerging contaminants and agricultural chemicals.
Scholastic Awards/Honors: **Editor's pick** as one of the top 10% of publications in Environmental Science: Nano
Bachelor of Arts in Chemistry, Bachelor of Arts in Biology, Adrian College, MI (8/2010–5/2014)
Cumulative GPA: 3.79
Scholastic Awards/Honors: **Most Outstanding Freshman in Biology**, Trustee with Distinction Scholarship, NCAA Honor Roll, MIAA Honor Roll, and Dean's List throughout each college semester
Extra-Curricular: NCAA volleyball, basketball, and lacrosse teams

PUBLICATIONS

Parker N., Keller, A.A. Scaling Up the Identification of Pesticide Sources and Risk Reduction Targets for Aquatic Environments (In Preparation)
Parker N., Larsen, A., Banerjee, P. & Keller, A. A. Leveraging high spatiotemporal resolution data of pesticides applied to agricultural fields in California to identify toxicity reduction opportunities. *PLOS Water* 2, e0000124 (2023).
Larsen, A., Quandt, A., Foxfoot, I., **Parker, N.** & Sousa, D. The effect of agricultural land retirement on pesticide use. *Sci. Total Environ.* **896**, 165224 (2023).
Parker, N. & Keller, A. A. Screening ecological risk of pesticides and emerging contaminants under data limited conditions - Case study modeling urban and agricultural watersheds with OrganoFate. *Environ. Pollut.* 288, 117662 (2021).

Parker, N. and Keller, A. A. 'Variation in regional risk of engineered nanoparticles: nanoTiO_2 as a case study'. January 2019. *Environmental Science: Nano*, 6, 444-455.
Keller, A. & **Parker, N.** Innovation in procedures for human and ecological health risk assessment of engineered nanomaterials. in *Exposure to Engineered Nanomaterials in the Environment* (2019).

GRANTS

2022-2023	California Sea Grant Bay-Delta Science Fellowship
2020-2022	California Sea Grant Bay-Delta Science Fellowship
2019	Schmidt Research Accelerator Fellowship
2013	National Science Foundation Research Fellowship Program

INVITED/HOSTED SEMINARS

2022	Interagency Ecological Program
2022	San Francisco Estuary Institute
2021	California Department of Pesticide Regulation Environmental Monitoring Team
2021	California Department of Water Resources Stormwater Management Team
2021	United States Geological Survey Water National Water Quality Assessment Team
2020	Office of Environmental Health Hazard Assessment
2020	The Freshwater Trust

GRADUATE AND UNDERGRADUATE STUDENT MENTORING

2018-2023	† 60 Undergraduate Engineering Students (UCSB Engineers Without Borders Project Lead and Mentor)
2021-2022	† Priyanka Banerjee (Professional Development/Internship Mentor)
2019-2020	*Cheyenne Coxon (Master's Thesis Mentor)
2019-2020	*Ella Golovey (Master's Thesis Mentor)
2019-2020	*Alexander Stejskal (Master's Thesis Mentor)
2019-2020	*Savannah Tjaden (Master's Thesis Mentor)
2019-2020	† *Tiffany Tran (Master's Thesis Mentor)
2019	† Kristine Nyugen (McNair Scholar Mentor)

* Indicates graduate student and † an underrepresented student

TEACHING

Instructor	Summer Research Academies (2020)
Teaching Assistant Master's Courses	Watershed Management (2018, 2019, 2020), Landscape Ecology (2019 and 2020)
Teaching Assistant Undergraduate Courses	Introduction to Environmental Science (2022), Laboratory for Introduction to Biology (2019)

CONFERENCES

The European Society of Environmental Chemistry and Toxicology, 2023
The SoCal Society of Environmental Chemistry and Toxicology, 2022
The North American Society of Environmental Chemistry and Toxicology, 2017, 2019, 2020
California Water Board Data Symposium, 2019
Western Water Summit, 2019
American Geophysical Union, 2018
Emerging Contaminants Summit, 2018
Sustainable Nanotechnology Organization , 2017
International Society for Industrial Ecology, 2017

SELECTED OUTREACH AND SERVICE

Project Lead Team Lead Panama, Engineer's Without Borders, Santa Barbara, CA (9/2018–2023)
Board Member Society of Environmental Toxicology and Chemistry, Southern California (05/2018-05/2020)
Scientific Advisor Denver Water
Service Graduate Division Community (GDC), University of California Santa Barbara, Santa Barbara, CA (09/2017–09/2019)
Advisor McNair Scholars Program, University of California Santa Barbara, Santa Barbara, CA (05/2018–06/2019)
Service Bren School Sustainability Club, University of California Santa Barbara, Santa Barbara, CA (9/2017-9/2018)
Service Chemistry Club, Adrian College, Adrian, MI (05/2011-05/2014)

ABSTRACT

Rapid and Spatially Explicit Assessment of Contaminants of Emerging Concern in Data Limited Watersheds

By

Nicol A. Parker

Contemporary contaminants of consequence to the health of aquatic ecosystems are dispersed in the environment owing their widespread use. Some are highly toxic yet cannot be monitored at concentrations which induce severe impacts, such as mortality, to aquatic organisms. In this research, the focus is on addressing the pressing need for accessible and practical tools to perform screening-level ecological risk assessments in the face of an increasing number of chemicals used by society. The challenge of obtaining field data for calibration and validation, particularly in data-limited conditions, forms the backdrop of this research.

The first chapter delves into the application and evaluation of OrganoFate, showcasing its effectiveness in making screening-level predictions that align with observed concentrations in surface water. This chapter highlights the model's capability to assess potential aquatic health risks associated with CECs and pesticides.

The second chapter shifts the focus to pesticides, acknowledging their significant impact on aquatic and terrestrial ecosystems. It introduces the Environmental Release Tool, a sub-tool of the Pesticide Mitigation Prioritization Model, designed to address critical challenges in evaluating pesticide toxicity over large extents, tracking spatiotemporal

pesticide use, assessing cumulative toxicity, and identifying the contributions of different pesticide application sites. The chapter reveals key insights into the applied toxicity of pesticides and underscores the importance of considering cumulative applied pesticide toxicity for effective risk assessment.

The third chapter introduces the Environmental Fate Tool (EFT), a novel tool with the unique ability to quantify aquatic risks for numerous pesticides and watersheds across expansive landscapes, pinpoint spatially explicit source contributions, and scale up analyses. This tool represents a significant advancement in identifying and prioritizing strategies to mitigate risks associated with dispersed chemical pollution in surface waters.

Overall, this dissertation offers an exploration of tools and methodologies for ecological risk assessment in the context of a growing and changing chemical landscape. It underscores the importance of modeling approaches to restore and safeguard our water resources and provides valuable insights into the ecological risks posed by emerging contaminants in various aquatic ecosystems.

Table of Contents

Chapter 1. Screening Ecological Risk of Pesticides and Emerging Contaminants under Data Limited Conditions 1

1.1 Introduction 2

1.2 Methods 9

1.2.1 Study Areas 10
1.2.2 Contaminant Loads 11
1.2.3 Simulations 13
1.2.4 Evaluation of PECs 15
1.2.5 Ecological Risk Screening 17

1.3 Results and Discussion 20

1.3.1 Ecotoxicological Thresholds 21
1.3.2 Urban PECs 22
1.3.3 Agricultural PECs 28
1.3.4 Limitations and Significance 32

1.4 Conclusion 34

1.5 References 35

2.1.0 Introduction 40

2.1.1 Scale 41

2.1.2 Sources 42

2.1.3 Cumulative applied toxicity 42

2.1.4 Economic and health scores 43

2.1.5 Toxicity Reduction Targets 44

2.2.0 Methods 45

2.2.1 Scale 46

2.2.2 Sources 46

2.2.3 Cumulative applied toxicity 52

2.2.4 Economic and health scores 53

2.2.5 Toxicity Reduction Targets 54

2.3.0 Results 55

2.3.1 Scale 56

2.3.2 Sources 58

2.3.3 Cumulative applied toxicity 62

2.3.4 Economic and health scores 67

2.3.5 Toxicity Reduction Targets 68

2.4.0 Discussion 69

2.5.0 Conclusion *73*
2.6 References *74*
2.7 Environmental Release Tool User Guide *80*
2.7.1 Environmental Release Tool Methods *81*
2.7.1.1 Pesticide Sources **85**
2.7.1.2 Affected Compartment **87**
2.7.1.3 Applied toxicity **88**
2.7.1.4 Health and Economic Indices **92**
2.7.2 Environmental Release Tool Installation and Operation *94*
2.7.2.1 Installing RStudio **94**
2.2 Installing the Environmental Release Tool **96**
2.7.2.3 Running a Simulation Environmental Release Tool **97**
2.7.3 Parameterization *99*
2.7.3.1 Default Simulations **101**
2.7.3.2 Custom Simulations **101**
2.7.3.2 Simulations **105**
2.7.3.2.1 Simulation Overview 105
2.7.3.2.2 Simulation Parameters 106
2.7.3.3 Watershed Spatial Data **113**
2.7.3.3 Pesticide Autoload Feature **115**
2.7.4 Outputs *116*
2.7.4.1 Graphical Outputs **116**
2.7.4.2 Tabular Outputs **120**
2.7.5 Example Applications – Environmental Release Tool *123*
2.7.5.1 Temporal Trends **123**
2.7.5.2 Chemical Alternatives **124**
2.7.5.3 Prioritizing Monitoring **125**
2.7.5.4 Health and Economic Tradeoffs **125**
2.7.6 Errors and Updates *126*
2.7.7 Acknowledgements *126*
2.7.8 References *126*
Chapter 3. Scaling Up the Identification of Pesticide Sources and Risk Reduction Targets for Aquatic Environments *130*

3.1 Introduction....131

3.2 Methods....137

3.2.1 Sources....137

3.2.2 Irrigation....140

3.2.3 Environmental Compartments and Pesticide Transport....146

3.2.4 Pesticide Phase Distribution....152

3.2.5 Risk....160

3.2.6 Validation....164

3.3.0 Results....169

3.3.1 Predicted Environmental Concentrations – Validation....169

3.3.2 Aquatic Risks and Sources....176

3.3.3 Sources....183

3.4.0 Discussion....187

3.5 Conclusion....191

3.6 References....191

Chapter 1. Screening Ecological Risk of Pesticides and Emerging Contaminants under Data Limited Conditions

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 and evaluate an uncalibrated-mechanistic fate and transport model, OrganoFate, to predict environmental concentrations of contaminants of emerging concern (CECs) and pesticides under data-limited conditions. CECs evaluated include antibacterial compounds sulfamethoxazole and triclocarban and a flame-retardant tris(1,3-dichloro-2-propyl) phosphate (TDCPP). Pesticides evaluated include the widely used insecticides chlorpyrifos, bifenthrin, and esfenvalerate. We predict concentrations of the contaminants in watersheds heavily impacted by either urban or agricultural development and with low-volume aquatic compartments relative to land area. Screening-level predictions were in good agreement with observed concentrations in surface water. For instance, observed concentrations of CECs span orders of magnitude, yet maximum predicted concentrations captured all observed and were within a factor of 2-3 of the highest observed concentrations. OrganoFate was also employed to screen possible aquatic health impacts. Results demonstrated possible CEC aquatic health risks for TDCPP and triclocarban, with risk quotients of 0.92 and 0.88 respectively. For pesticides, exceedance of the United States Environmental Protection Agency Health Benchmarks was predicted and observed for each pesticide for most of the simulation, and taxonomic groups that may

experience adverse effects endpoint include aquatic invertebrates, fish, amphibians, and mollusks.

1.1 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 United States and the 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(1,2). 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(3). 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 are on the rise(4–7).

Models have served as an important complement to observation as an approach for filling in data gaps, extending the available observations, and for proactive risk assessment. Since the 1980s, fate and transport models have been employed by the USEPA to describe the behavior of crop protection products in the environment(8). Today, a suite of models is employed by the USEPA, each targeting different risk factors (e.g., exposure pathways and bioaccumulation) and organisms which include humans, terrestrial, as well as aquatic flora and fauna. For pesticides alone, there exists a tool suite of 16 models for predicting environmental exposures(9). 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 contaminants). A new modeling framework, ChemFate(10), has been demonstrated to achieve this aim. Here, we evaluate a model within ChemFate, OrganoFate, for screening the risk of diverse organic contaminants.

OrganoFate is part of a dynamic, multi-media modeling framework ChemFate. 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(11) (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 United States scientific agencies (i.e., USGS, USDA, and NOAA) or the approach indicated in previous work(12) for European regions.

ChemFate has been employed to predict nano-particle concentrations(11,12) as well as ionizable organics, metal ions, and organic compounds(10). In this investigation, we assess the effectiveness of OrganoFate in predicting concentrations of various contemporary organic contaminants in watersheds with limited monitoring data, a situation frequently

encountered when analyzing CECs. Chemical classes considered include a pharmaceutical, an anti-bacterial agent, a flame retardant, and three pesticides.

Other dynamic multi-media models are existent for the prediction of CECs and have been employed by the government or international agencies for organic chemical risk assessment. Examples include SimpleBox(13) which is employed by the European Chemical Agency, Stochastic Human Exposure and Dose Simulation (SHEDS)(14) utilized by the USEPA, CalTOX(15) used by the California Department of Toxic Substances Control, and the Berkeley Trent (BETR)-North America(16) which the Organization for Economic Coordination and Development (OECD) uses to evaluate chemical risk.

OrganoFate improves upon these tools by offering a 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). Additionally, most available multi-media models are limited to organic contaminants, while OrganoFate is hosted in a platform where parameterization of a study extent can be readily used to evaluate diverse chemical classes.

To evaluate the risks of pesticides in the United States, a key tool used by the Environmental Protection Agency is the Pesticides in Water Calculator (PWC)(9,17). The PWC predicts concentrations in soil and surface waters at a daily time-step for pesticides. Although there are many similarities between mechanistic approaches used in fate and transport models such as OrganoFate and the PWC, there are also important differences.

The primary focus of the PWC is the examination of how the landscape and its soil interact with freshwater bodies in relation to non-ionizable organic pesticides. The PWC

emphasizes edge-of-field scenarios, and while it predicts loss via volatilization, it does not predict atmospheric concentrations of pesticides. OrganoFate expands its scope by simulating concentrations in atmospheric compartments as well as estuarine and coastal waters and is part of a comprehensive risk analysis framework that allows for model parameterization to be used to evaluate various classes of pesticides. The model also accommodates rapid imports of daily time-step pesticide use data in *.csv files, while the PWC requires the user to enter pesticide use data manually, with a maximum of 50 inputs per simulation, which severely limits its use for high-resolution pesticide use data available in California(18). Given the sensitivity of pesticide transport to the date of application(19), accurate daily inputs of pesticide use are important in predicting high-exposure events.

Another key difference is the PWC employs Freundlich isotherms to simulate diffusive transport(9,20). OrganoFate employs the fugacity approach with rate-limited mass transfer from one compartment to another(10), which is advantageous for considering changes to the rate of diffusion with fluxes in chemical concentrations(21). A summary of key differences in compartments, processes, and model outputs are highlighted in **Table 1**.

Table 1. Summary of key similarities and differences in compartments and major processes accounted for in PWC and OrganoFate. X indicates the inclusion of a compartment or process, and numeric values the number of compartments/processes considered.

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
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		

To evaluate human health considerations, the ability of OrganoFate to provide a comprehensive suite for soil, water, and atmospheric concentrations is important for enabling the use of a single tool to explore the risks of contaminants in diverse compartments. For instance, a number of pesticides are volatile, and evaluating their presence in the atmosphere as well as soil and water is critical to understanding exposure(22,23). As a single model for evaluating risks in diverse compartments, OrganoFate may facilitate more rapid risk evaluations of emerging contaminant concerns.

An important limitation of OrganoFate, other multi-media models, and the PWC is their inability to simulate chemical concentrations beyond a single catchment or watershed. However, several watershed fate and transport models, such as the Soil and Water Assessment Tool (SWAT)(24–26), the Watershed Assessment Risk Management Framework (WARMF)(27,28), and the Hydrologic Simulation Program Fortran (HSPF) (29–31), can overcome this limitation by simulating chemical concentrations in multiple catchments within a hydrologic system (e.g., watershed or river basin).

Despite their capability to provide output for multiple catchments, using watershed models for risk assessments comes with important trade-offs. These models require higher-resolution spatiotemporal data and access to environmental characteristics and chemical use

data, which are often not readily available. Additionally, implementing and calibrating watershed-scale models demand more computational power and user expertise. Often, they take hundreds of hours to implement and calibrate for a given watershed making them more challenging and time-consuming than simpler models. The calibration of these models for pesticides and other low-use chemicals with potential high toxicity is particularly problematic due to the sparse availability of relevant data. Furthermore, most watershed models are limited in their scope, primarily considering non-ionizable organic pesticides and not accounting for other types of chemicals.

A key challenge hindering the advancement of our understanding of environmental risks posed by contaminants is the lack of data in certain regions. In this study, we aim to 1) evaluate concentrations in data-limited watersheds by exploring the application of the mechanistic fate and transport model OrganoFate without calibration; 2) explore concentrations of CECs and pesticides in watersheds with intensive urban and agricultural runoff as well as a relatively small water compartment to the land area; and 3) to quantify potential risks for diverse aquatic species. We hypothesize that, in vulnerable waterways with relatively high development intensity and a high drainage area to surface water volume, our approach using the uncalibrated fate OrganoFate model will enable us to provide predictions of environmental hazards that reasonably capture the median and maximum of observed concentrations. By employing this model, we aim to predict concentrations in data-limited watersheds, paving the way for a more comprehensive assessment of environmental risks associated with contaminants in such regions.

1.2 Methods

To conduct this study, we evaluate the current risks associated with various organic contaminants in the aquatic compartment of highly urbanized and agriculturally developed regions in California. Specifically, we focus on 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). These contaminants were chosen due to their suspected or known toxicity at environmentally relevant concentrations.

Sulfamethoxazole and triclosan are anti-bacterial agents that have been demonstrated to significantly contribute to horizontal transfers of antibiotic resistance genes(32). TDCPP is a known animal carcinogen that has been used to replace pentabromodiphenyl ether (PBDE) flame retardants in commonly used products like furniture, coatings, baby products, and electronic equipment(33).

Chlorpyrifos, an insecticide, has attracted attention in recent years for adverse health effects, particularly its impact on childhood neurological development. As a result, chlorpyrifos was banned in California in 2020(34,35). This ban presents an opportunity to predict the risks associated with alternative chemicals such as bifenthrin and esfenvalerate, which have distinct physicochemical properties. These alternatives are commonly used insecticides on crops such as alfalfa, almonds, corn, cotton, oranges, and walnuts(18). Notably, for crops like almonds and walnuts, esfenvalerate and bifenthrin are already employed to treat nearly equal or greater acreage compared to chlorpyrifos.

1.2.1 Study Areas

To evaluate OrganoFate for the prediction of organic contaminants as an uncalibrated model for data-limited watersheds, we predict concentrations in surface water of three different watersheds for a 10-year period, 2005-2014. The selected analysis period and watersheds coincide with where monitoring data were available for the contaminants of interest. Sites selected for analysis were three highly developed watersheds with a Mediterranean climate in California. The first site, the upper Santa Clara River Watershed (~1,300 km^2), is located just north of Los Angeles, see **Figure 1**. Throughout the analysis period, the site experienced an average annual precipitation of 290 mm. The flow of water in the area is predominantly influenced by wastewater treatment effluent for the majority of the year. In terms of land use, approximately 90% of the watershed consists of urban development, while the remaining portion is dedicated to agriculture.

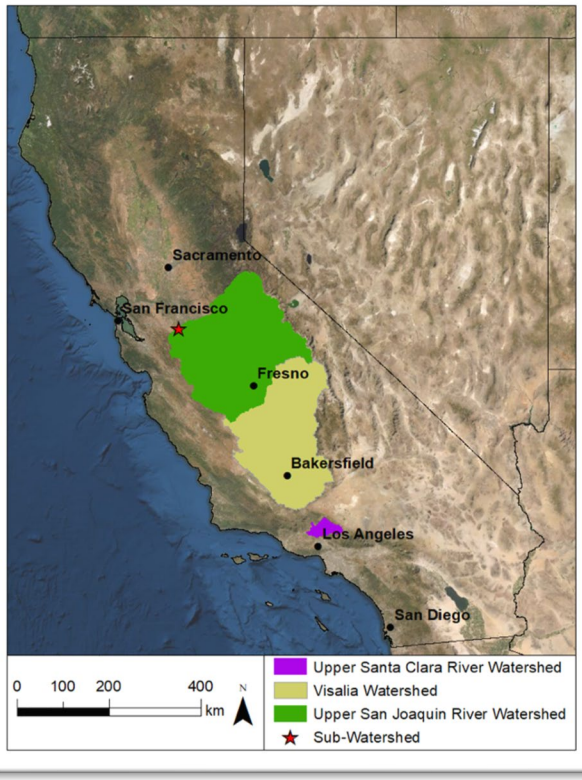


Figure 1. Watersheds under investigation; note the subwatershed is too small to be visible on the map and is indicated with a star.

To assess the accuracy of pesticide concentration predictions, two additional sites were chosen to represent intensive agricultural watersheds in the Central Valley. The second site is the Visalia Watershed and the third the San Joaquin River Watershed. The Visalia Watershed (~22,000 km^2) is located at the southern end of the Central Valley. During the analysis period, the site

had an average annual precipitation of 170 mm.

The San Joaquin River Watershed (~35,000 km^2) encompasses the entire drainage network upstream of a monitoring site for diverse pesticides in Vernalis, CA. Located just north of the Visalia Watershed, it had a higher mean annual precipitation of 290 mm. Both the Visalia and San Joaquin River Watersheds are hydrologically connected to the Sierra Nevada Mountain range from which most of the instream flow is derived, and the proportion of developed land is ~90% agricultural.

To define the boundaries of the considered watersheds, the areas of interest were delineated to align with the Watershed Boundary Dataset(36). Each watershed's soil compartment was divided into three land use compartments: urban, agricultural, and natural. The proportions of land uses were obtained from the National Land Cover Data 2016, which provides comprehensive information on land cover across the country(37). Soil, climate, and hydrologic data for regions were compiled according to methodologies published in the ChemFate User Guide(38).

1.2.2 Contaminant Loads

To assess the presence of contaminants of emerging concern (CECs) in the urban watershed, we focused on sulfamethoxazole, triclocarban, and TDCPP. Our approach involved simulating the loads of these chemicals by determining their mass in the effluent of wastewater treatment plants (WWTPs) during the monitoring period. These monitoring activities were conducted by the Southern California Coastal Water Research Program (SCCWRP) just downstream of the uppermost WWTP on the river. We used measurements

conducted during dry, low-flow conditions when the primary flow consisted of WWTP discharge.

As over 90% of the developed land upstream of the WWTP is urban, we made the assumption that all CEC loads originated from these WWTPs, rather than from other sources like antibiotic loads in runoff from livestock paddocks. To estimate the loads, we calculated the product of the observed concentrations of the contaminants and the daily discharge of the two WWTPs within the study area.

In the investigation of agricultural risks, we focused on evaluating the widely used insecticides chlorpyrifos, bifenthrin, and esfenvalerate To simulate the release of these chemicals, we relied on pesticide use reports obtained from the California Department of Pesticides Regulation(18). The reports provide detailed pesticide application data for the agricultural sector, with applications reported at the daily time step and 2.6 km^2 resolution by application site type.

It's important to highlight that pesticide use also occurs in urban areas of the agricultural watersheds, which was not accounted for in this simulation. Although pesticide use reports are also provided for urban applications, reports only cover professional pesticide applications. Urban use reports have much lower resolution. They are reported at the county level and monthly time-step and do not include residential applications. Given the low resolution of urban pesticide use data and that more than 90% of the developed land in the Visalia and San Joaquin River Watersheds is dedicated to agriculture, our analysis focused solely on employing agricultural pesticide use data.

1.2.3 Simulations

To predict environmental concentrations (PECs), OrganoFate was employed. Inputs required by the model include 1) the physicochemical parameters for each pollutant; 2) watershed characteristics (e.g., environmental compartment characteristics, daily meteorology, and streamflow); and 3) daily release rates for each pollutant. In the remainder of this section, we highlight features of OrganoFate used to predict contaminant concentrations.

OrganoFate(38) is a multimedia and discretized model that calculates chemical concentrations based on a mass balance approach in diverse environmental compartments (**Table 1**). The tool predicts concentrations within each compartment (e.g., air, soil, water, and sediment), degradation, and transfer between compartments. Key transport processes considered include advection, diffusion/dispersion, mass transfer between phases, runoff, erosion, particle settling, and resuspension.

OrganoFate is among the tools which employ the fugacity approach(39,40). The fugacity concept is based upon thermodynamic principles of partitioning whereby the chemical potential (Gibbs free energy) of a compartment will tend toward a lower energy state. The fugacity approach is advantageous in that the method accounts for phase-specific effects in the environment while other available multimedia and discretized models calculate chemical distribution as a single coefficient (e.g., partition coefficients) which can mask important factors in pesticide distribution(41). For instance, fugacity accounts for the effects of variable concentrations on the inter-phase transport potential of a compartment(42). This is advantageous for chemicals such as pesticides which can exist in high concentrations in the

environment due to direct release to the environment, improper disposal (e.g. in sewers (43,44)), or accidental spills.

In data-limited watersheds, OrganoFate and multi-media models offer a valuable advantage by providing concentrations or loads of pesticides in various environmental media for the entire study area. This feature presents a straightforward representation of pesticide distribution in the environment, making it useful for users seeking to perform a screening-level risk analysis.

To perform simulations of fate and transport accurately, it is important to consider the release points of chemicals and their background concentrations in the environment. OrganoFate facilitates these simulations by allowing users to model chemical release in four distinct soil types and directly into air, freshwater, and seawater. Background concentrations can be specified for bulk compartments (e.g., soil) as well as specific phases (e.g., soil air). These background concentrations can be based on actual monitoring data, or, in the absence of such data, a "warm-up" run can be performed to estimate them.

For the analysis of contaminants of emerging concern (CECs) at the urban site, rather than assuming zero initial concentrations, we opted to run the model one time for 10% of the total simulation time to represent background concentrations. We then used the predicted concentrations as initial concentrations for the entire analysis period. This method helps to incorporate realistic initial conditions and provides more accurate results for the full simulation period.

On the other hand, when studying pesticides at agricultural sites, we determined initial pesticide concentrations using pesticide use data from the period 1995-2004. The parameterization for all other aspects of OrganoFate was set for the analysis period 2005-

2014. The environmental concentrations observed at the end of the 1995-2004 simulation were then used as initial data for the analysis period of 2005-2014. By adopting this approach, we ensured that the model started with appropriate pesticide concentrations in different compartments, enhancing the reliability of the results.

1.2.4 Evaluation of PECs

To assess the accuracy of the predicted environmental concentrations (PECs) obtained from OrganoFate, we compared them to the environmental monitoring concentration data collected by SCCRWP(45) and the CDPR Surface Water Monitoring Program(46). However, when performing this evaluation, it's important to consider the limitations of monitoring campaigns.

Monitoring campaigns are typically designed to capture contaminant concentrations above the limit of quantification (LOQ), which is the lowest concentration that can be reliably measured with accuracy. As a result, concentrations below the LOQ may not be captured in the monitoring data. In contrast, OrganoFate can predict concentrations both above and below the LOQ, but we are only able to compare to sample analyses where contaminants are detected.

When using and validating fate and transport models, it is common practice to calibrate the model with monitoring data and to refine parameters to minimize the residuals of variance (e.g., NSE(47)) between observed and predicted concentrations. In this study evaluating the predictive capabilities of OrganoFate in data-limited watersheds, we opted to employ the model without calibration.

To evaluate the model, a comparative analysis of predicted and observed ranges, rather than a residual variance analysis based on the limited monitoring data, was deemed more suitable for the screening-level risk assessment conducted in this investigation. We opted to use this approach provided limitations in the monitoring data's spatiotemporal coverage and ability to capture concentrations below the LOQ.

The comparative analysis quantified OrganoFate's ability to predict median and maximum concentrations of contaminants. Median value analyses demonstrate a model's ability to predict typical concentrations while evaluating maximum predictions explore a model's ability to predict the full range of environmental concentrations. Demonstrating the model is able to capture observed maxima is important to risk assessment where events with high concentrations can introduce the greatest impact on aquatic organisms.

To evaluate median predictions, we calculated the quotient of predicted values relative to observed values, known as the QPEC (Quotient of Predicted Environmental Concentrations). Since concentrations can span multiple orders of magnitude, we logarithmically transformed the QPEC values using a base 10 (referred to as pQPEC for brevity) to enhance interpretability. Positive pQPEC values indicate that predicted concentrations are conservative, exceeding the observed values. Conversely, negative values suggest that the model fails to capture all the observed concentrations. Values between -1 and 1 indicate that predictions are within the same order of magnitude as the observed concentrations, which are considered reasonable by the USEPA(48).

The accuracy of predicted maximum concentrations was assessed through numerical and graphical comparisons. Numerical differences were quantified as concentration values, allowing for direct measurement. Additionally, graphical exploration of predictions utilized

boxplots to accommodate the wide range of observations with environmental significance. Boxplots represent the inter-percentile range of the 95th percentile of concentrations, with whiskers extending up to the 99th percentile. Outliers, depicted as individual points beyond the 99th percentile, highlight extreme values in the dataset.

1.2.5 Ecological Risk Screening

To assess the ecological health risk of chemicals on aquatic organisms, we compiled data from various sources to establish both singular aquatic health benchmarks published by regulatory agencies and effect thresholds available in peer-reviewed literature. The benchmarks established by regulatory agencies provide thresholds for individual chemicals based on conservative analyses of species commonly observed to be most sensitive to chemicals. Data from the literature were also considered provided regulatory ecotoxicological benchmarks for aquatic risks were unavailable for CECs and may not reflect emerging evidence available for chemicals investigated.

Regulatory thresholds were retrieved from multiple sources, the USEPA Office of Pesticide Protection(49) and the California State Water Resources Control Board (SWRCB)(50,51). The inclusion of databases from both agencies was driven by the fact that USEPA criteria are used for developing pesticide labels and conducting post-registration monitoring evaluations. Meanwhile, the SWRCB, as a sub-entity of the California Environmental Protection Agency, has developed criteria that specifically account for adverse aquatic health impacts observed in California's waterways.

The USEPA Aquatic Life Benchmarks are criteria derived for registered pesticides in the United States. Benchmarks are based on toxicological investigations of fish,

invertebrates, and plants the USEPA conducted to support pesticide registration or review(49). We compiled the most sensitive criterion for invertebrates for acute and chronic investigations as they are the organisms most sensitive to investigated pesticides. Acute benchmarks are derived from the lowest 48-96 h half-maximal effect concentrations (EC50) or half-maximal lethal concentrations (LC50) and typically are representative of the most sensitive taxa investigated. To obtain a final benchmark for invertebrates, the USEPA multiplies toxicity thresholds by a safety factor of 0.5.

SWRCB ecotoxicological thresholds for bifenthrin and esfenvalerate were retrieved from the water quality control plan for pyrethroid pesticide discharges in the Central Valley(51). This plan provides comprehensive guidelines for managing the impact of pyrethroid pesticides on water quality in the Central Valley region. For chlorpyrifos, the SWRCB endpoint was derived from the agency's water quality goals(50). By incorporating national standards and region-specific considerations, this approach provided a more comprehensive understanding of potential risks from pesticides.

To evaluate ecotoxicological thresholds available in peer-reviewed literature for pesticides and CECs, we compiled thresholds published in the USEPA database ECOTOX(52). This comprehensive database comprises approximately 50,000 toxicological studies, covering around 12,000 chemicals and 1,000,000 toxicological thresholds. For freshwater organisms in the *Animalia* kingdom, we consider acute (<4 days) as well as sub-chronic and chronic (> 4 days) toxicity thresholds for reported EC50s. Where only one endpoint was available for the acute or chronic EC50 of a chemical, we retrieved data for the no observable effect concentration (NOEC).

These organisms were selected because they are more sensitive to the mode of action of the evaluated chemicals compared to other taxa within the *Eukarya* domain. Effect thresholds considered include development, growth, morphology, mortality, injury, immunological, intoxication, physiology, and reproduction. While other thresholds such as genetic or avoidance behavior exist, we sought to leverage data available where a clear, adverse outcome occurred to the sample population.

Data published in the peer-reviewed literature may be subject to less scrutiny than aquatic benchmarks published by regulatory agencies. To evaluate potential effects based on available data while mitigating the effects of outliers which may be erroneous, we calculated Species Sensitivity Distributions (SSDs). SSDs offer a probabilistic assessment of the potential adverse effects across a range of species(53,54).

Typically, for the acute or chronic EC50 of an investigated chemical, data for four species was available. SSDs were generated for chemicals with four or greater species effect thresholds, otherwise, the most sensitive endpoint was adopted. Where data for greater than four taxonomic groups were available, the most sensitive species endpoint for the species group rather than individual species was employed, as characterized by the ECOTOX dataset (e.g., fish, crustaceans, insects). This approach was adapted provided that when more data is available for species of the same group, the data skews the analysis of effect concentrations for organisms towards a particular group with greater available toxicity studies rather than providing a more realistic distribution of effects to diverse taxa.

SSDs are calculable using a number of distributions, among the most common are lognormal and log-logistic(55). Due to the limited toxicity thresholds available for some chemicals to evaluate the best-fit distribution, we opted for a lognormal distribution, which

has fewer heavy tails compared to log-logistic, reducing over-conservative estimates for small ecotoxicity datasets. To evaluate the goodness-of-fit of the distribution, we conducted an Anderson-Darling test ($\propto$=0.05).

Using the SSDs, we determined the probable health effect thresholds using the hazardous fifth percentile (HC5). Leveraging the fifth percentile of ecotoxicological thresholds as an effect index is valuable for exploring potential adverse environmental impacts and is utilized by the United States and European Environmental Protection Agencies(55,56). To enhance the robustness of the estimated HC5, we bootstrapped the dataset (n=1000) to the fitted SSD and calculated the 95th percentile confidence limits.

To illustrate instances where observed concentrations are near to or surpass an aquatic health benchmark, where able, a risk quotient, RQ, was calculated. RQs are calculated from the environmental concentration of a chemical, C, and the concentration at which toxicity has been observed, T:

$$RQ = \frac{C}{T} \qquad \textit{Equation (1)}$$

For T, the USEPA Aquatic Life Benchmarks and median bootstrapped HC5s were employed for investigated chemicals. The RQs were calculated for acute and chronic toxicological thresholds relative to both observed and predicted concentrations. Where the RQ is greater than or equal to unity, the concentration of the contaminant may introduce adverse effects.

1.3 Results and Discussion

We present the results of our investigation on leveraging OrganoFate to predict chemical concentrations in watersheds with limited data. The study focused on the simulation period from 2005 to 2014. Our objective was to explore potential adverse health effects on

unique aquatic taxa and identify contemporary concerns for aquatic ecosystem health in urban and agricultural watersheds in California.

1.3.1 Ecotoxicological Thresholds

In this study, various benchmarks were explored to assess the effects of pesticides on aquatic life. Specifically, the USEPA Aquatic Life Benchmarks, SWRCB water quality criteria, and HC5 calculated from the USPEA ECOTOX database were considered as the effect thresholds.

During the review of available regulatory health benchmarks for pesticides and the calculated HC5, it was found that the USEPA benchmarks were the most conservative, and they were considered to evaluate acute and chronic risks. However, before a major update in 2021, regional recommendations for pesticides (SWRCB criteria) provided even more conservative effect thresholds, differing by 1-2 orders of magnitude. This highlights the importance of considering multiple ecotoxicological effect databases as knowledge continues to evolve, especially given that registered pesticides in the United States are only required to be reviewed once every fifteen years.

For CECs with no available regulatory benchmarks in the United States, where 4 or more unique species data were available, the HC5 was predicted from fitted SSDs and employed to calculate risk quotients. Where data for fewer than 3 species were available, the minimum observed effect endpoint was considered. In addition to using HC5s and SSDs for CECs with no regulatory criteria, we employed this approach for pesticides to provide information about specific taxonomic group risks, see **Table 2**.

Table 2. Summary of the USEPA Aquatic Life Benchmarks calculated HC5s, or minimum effect thresholds for chemicals with data for fewer than 3 species. The HC5s were calculated

from Species Sensitivity Distributions which employed a lognormal distribution, results of the Anderson-Darling goodness-of-fit test are also included (null hypothesis lognormal distribution, $\propto = 0.05$).

Chemical	Type	Endpoint	USEPA Benchmark (ppb)	HC5 (ppb)	Stanadard Deviation	Confidence Interval (5%)	Confidence Interval (5%)	n	Test Statistic	p-value
Chlorpyrifos	Acute	EC50	0.005	4.89E-02	1.35E+01	3.24E-02	3.94E+01	42	0.51	0.23
Chlorpyrifos	Chronic	EC50	0.076584	7.66E-02	3.91E+00	6.82E-02	9.88E+00	7	0.36	0.53
Sulfamethoxazole	Acute	EC50	NA	1.79E+04	1.71E+04	1.55E+04	7.78E+04	6	0.29	0.54
Sulfamethoxazole	Chronic	NOEC	NA	2.65E+01	8.34E+01	1.00E+01	3.00E+02	4	0.31	0.81
TDCPP	Acute	Minimum NOEC	NA	0.00E+00	0.00E+00	0.00E+00	0.00E+00	2	0.00	0.00
TDCPP	Chronic	NOEC	NA	6.25E+00	5.04E+01	4.00E+00	1.81E+02	4	0.27	0.83
Triclocarban	Acute	NOEC	NA	5.76E-01	4.39E+00	4.60E-01	1.45E+01	8	0.38	0.31
Triclocarban	Chronic	NOEC	NA	4.04E-01	6.80E+00	2.50E-01	1.98E+01	4	0.38	0.75
Bifenthrin	Acute	Minimum EC50	5.00E-05	NA	NA	NA	NA	3	NA	NA
Bifenthrin	Chronic	Minimum EC50	4.00E-04	NA	NA	NA	NA	3	NA	NA
Chlorpyrifos	Acute	EC50	0.005	4.89E-02	1.80E+01	3.24E-02	9.01E+01	42	0.51	0.23
Chlorpyrifos	Chronic	EC50	0.076584	7.66E-02	4.60E+00	6.82E-02	9.88E+00	7	0.36	0.53
Esfenvalerate	Acute	EC50	3.09E-05	3.00E-02	1.86E-01	2.00E-02	4.24E-01	24	0.26	0.68
Esfenvalerate	Chronic	Minimum EC50	0.2	NA	NA	NA	NA	2	NA	NA

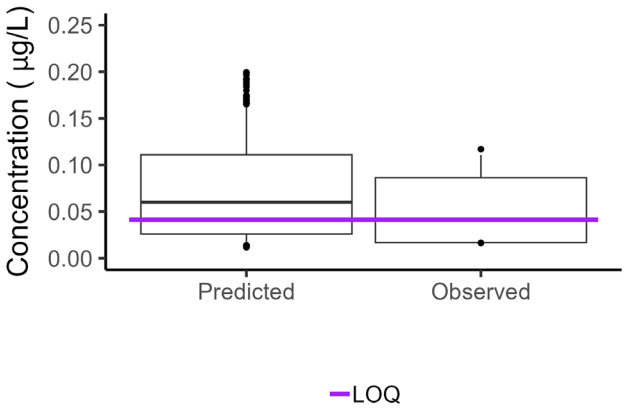
To test the goodness-of-fit of lognormal SSDs for available effect data, we conducted an Anderson-Darling test. The test evaluates whether sample distributions were significantly different from a lognormal distribution (null hypothesis lognormal distribution, $\propto = 0.05$), and for the HC5s, confidence intervals based on boot-strapped sampling were calculated. All fitted distributions for evaluated chemicals were insignificantly different from a lognormal distribution. Results from the goodness-of-fit test and predicted HC5s can be viewed in **Table 2**.

1.3.2 Urban PECs

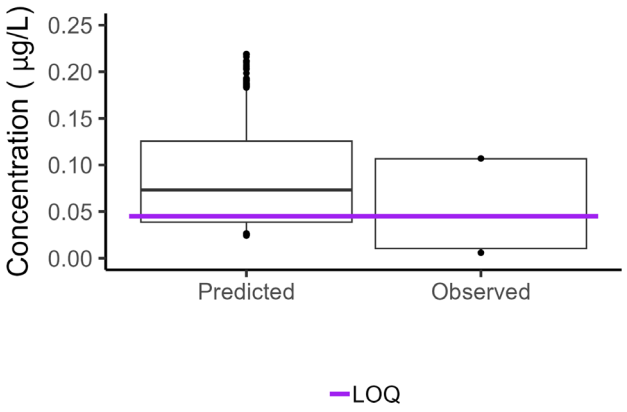
The evaluation of OrganoFate's prediction accuracy for CECs and potential risks in urban environments focused on the upper urban watershed of the Santa Clara River. We simulated the concentrations and risks of three chemicals with available monitoring data in surface water: sulfamethoxazole, triclocarban, and TDCPP (**Figure 2**). Notably, the freshwater observed concentrations of the CECs (and pesticides) were commonly near or

below the median limit of quantification (LOQ) of monitoring analyses. Provided many monitoring analyses will not capture concentrations below the LOQ, we included the median LOQ of observed data in **Figure 2** to illustrate a common lower bound of observed data.

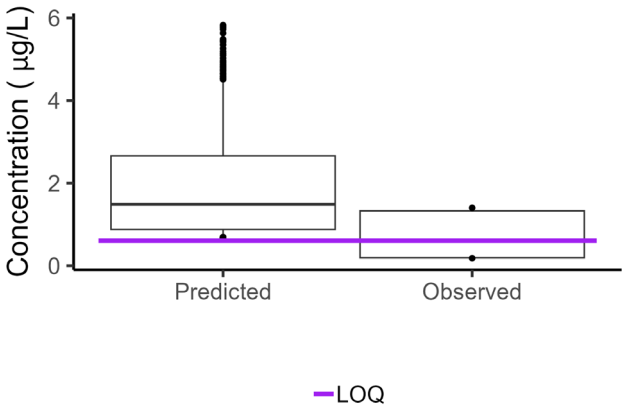
Figure 2. Predicted and observed freshwater column concentrations of triclocarban, sulfamethoxazole, TDCPP, and bifenthrin for the Upper Santa Clara River Watershed from 2005-2014. Boxplot interquartile ranges reflect the 95th percentile of predictions and whiskers the 99th. The median limit of quantification (LOQ) of observations in freshwater is included to illustrate where many monitoring analyses will not detect the contaminant.



a) Sulfamethoxazole, observations n=9



b) Triclocarban, observations n=5



c) TDCPP, observations n=8

For the river water column, the predictions generated by OrganoFate successfully encompassed the maximum observed concentration of each chemical. This outcome is desired to ensure high-risk events are captured and anticipated since the model simulates all days of the analysis period while monitoring data captures very limited temporal extents. Predicted maxima demonstrated good agreement for maximum observations of CECs, with all predictions within a factor of 1.7-4.2 of observed (**Figure 2**).

In addition to predictions encompassing maximum observations, there was reasonable agreement between the median modeled and observed concentrations. The log-transformed quotient of predicted and observed concentrations, pQPEC, was between 0.16-0.39. This indicated that the predicted median concentrations were conservative estimates, tending to be higher than the observed values. Additionally, values less than 0.5 indicated that the predicted mean was within a half order of magnitude of the observed mean. The USEPA considers predictions of environmental concentrations of chemicals within an order of

magnitude reasonable(48) owing to concentrations varying by orders of magnitudes and the numerous environmental conditions affecting instream concentrations.

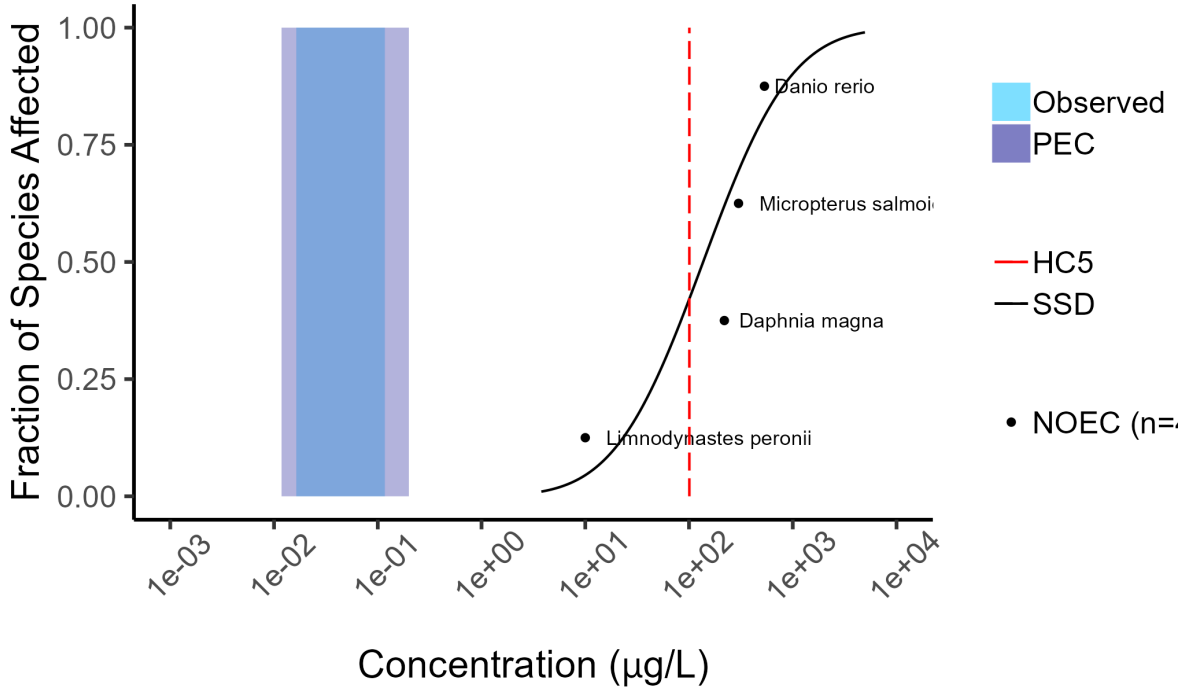
To assess potential hazards to aquatic health, we compared predicted and observed concentrations to the HC5, or most sensitive effect endpoint where fewer than 3 species had available data. For CECs, we discuss risk quotients relative to chronic effect data since they were the only effect thresholds where concentrations of contaminants were near or in exceedance. CEC chronic endpoint data employed NOECs due to only one ecotoxicological endpoint being available for the chronic EC50 of each chemical (see *Methods 2.5*).

The calculated RQ from the HC5 of sulfamethoxazole for both observed and predicted concentrations was three orders of magnitude lower than unity and did not exceed any individual ecotoxicological effect thresholds. This suggests that no adverse effects are predicted for sulfamethoxazole.

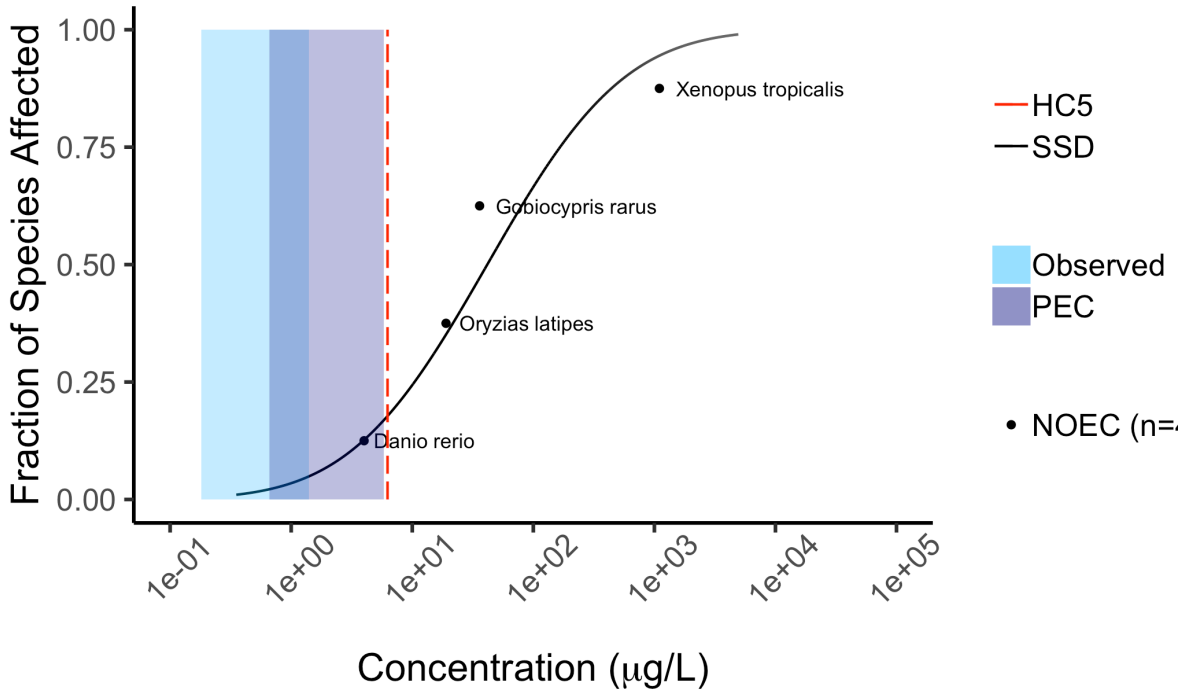
However, for TDCPP, the RQ for the chronic HC5 for predicted concentrations was 0.92 and exceeded the minimum effect threshold for the fish species *Danio rerio*, indicating possible adverse effects. The RQ for observed concentrations was lower, at 0.22. However, it's important to note that the temporal coverage of TDCPP data was limited, with only 8 events over a 5-year simulation period.

The RQs of triclocarban for predicted and observed concentrations were 0.54 and 0.26 respectively and did not surpass the HC5. When comparing the RQ for the most sensitive chronic NOEC endpoint (0.25 µg/L) and the maximum predicted concentration of triclocarban (0.22 µg/L), we found an RQ of 0.88. These findings indicate that triclocarban and TDCPP may pose a hazard in the Santa Clara River, warranting further investigation of aquatic health hazards through additional monitoring, ecotoxicological and risk assessments.

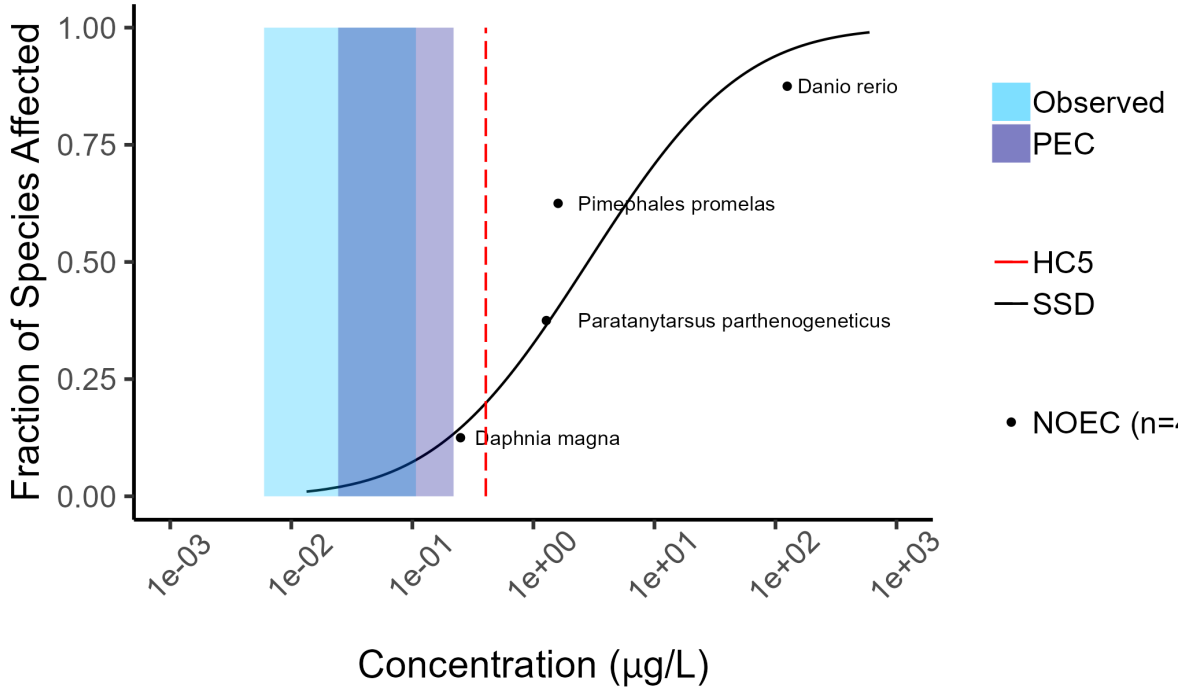
Figure 3. Species sensitivity distributions and hazardous fifth percentiles for chronic effects of CECs in the Upper Santa Clara River Watershed for a) sulfamethoxazole, b) TDCPP, and c) triclocarban.



a)


Fraction of Species Affected
1.00
0.75
0.50
0.25
0.00
Xenopus tropicalis
Gobiocypris rarus
Oryzias latipes
Danio rerio
1e-01
1e+00
1e+01
1e+02
1e+03
1e+04
1e+05
Concentration (µg/L)
HC5
SSD
Observed
PEC
NOEC (n=

b)


Fraction of Species Affected
1.00
0.75
0.50
0.25
0.00
Danio rerio
Pimephales promelas
Paratanytarsus parthenogeneticus
Daphnia magna
1e-03
1e-02
1e-01
1e+00
1e+01
1e+02
1e+03
Concentration (µg/L)
Observed
PEC
HC5
SSD
NOEC (n=

c)

1.3.3 Agricultural PECs

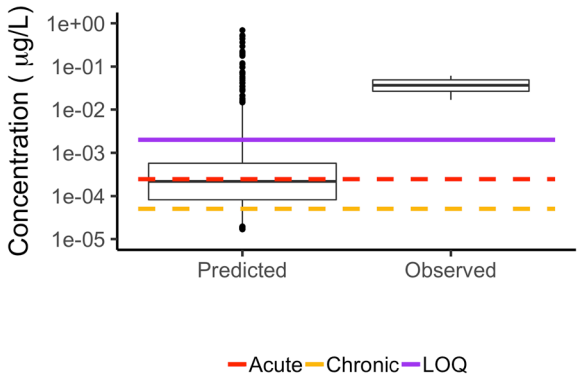
To assess the effectiveness of OrganoFate as a predictive tool for waterbodies affected by agricultural runoff, three commonly used insecticides (bifenthrin, chlorpyrifos, and esfenvalerate) were evaluated. The study focused on two watersheds in the Central Valley: the Visalia Watershed and the San Joaquin Watershed.

In the Visalia Watershed, the maximum predicted concentrations for bifenthrin and esfenvalerate were both conservative and realistic estimates. These predicted maximum concentrations encompassed all observed data, and the 99th percentile of the predicted values closely matched the observed values, falling within a factor of 1.5-4.3 of each other (**Figure 4**). Given the fact that OrganoFate predicts concentrations for each day of the simulation, this level of accuracy is considered good.

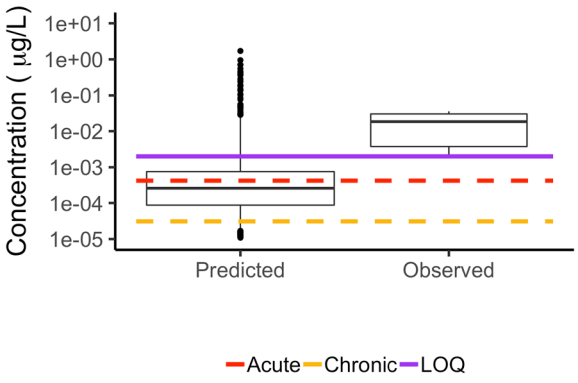
In the Visalia Watershed, it is worth highlighting that a substantial portion of the predicted concentrations for bifenthrin and esfenvalerate were below the Limit of Quantification (LOQ) for these pesticides. The lack of data in the lower range of concentrations makes it challenging to fully assess the model's performance in that particular region. As observations cannot capture concentrations below the LOQ, the predicted median concentrations appeared to be significantly lower, around 2-3 orders of magnitude, than the observed concentrations. Considering the ability of OrganoFate to predict concentrations each day of the simulation and below the LOQ limited availability of observation data, where most predictions are lower than the LOQ, median accuracy is not quantifiable.

Figure 4. Predicted and observed concentrations of **a)** bifenthrin, **b)** esfenvalerate, and **c)** chlorpyrifos in the freshwater column of the Visalia Watershed, as well as for the San Joaquin River Watershed, **d)** concentrations of chlorpyrifos. Boxplot interquartile ranges reflect the 95th percentile of predictions and whiskers the 99th. Also displayed are the median

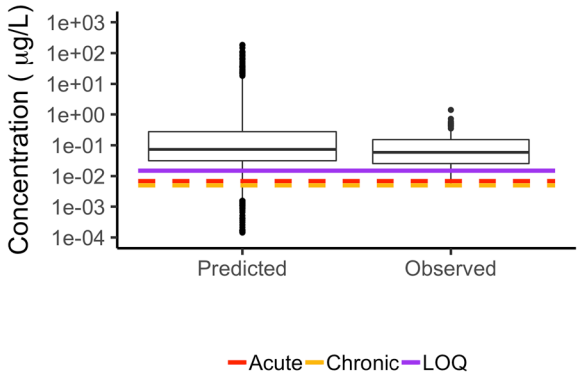
limit of quantification (LOQ) of observed concentrations and USEPA acute and chronic Aquatic Life Benchmarks.



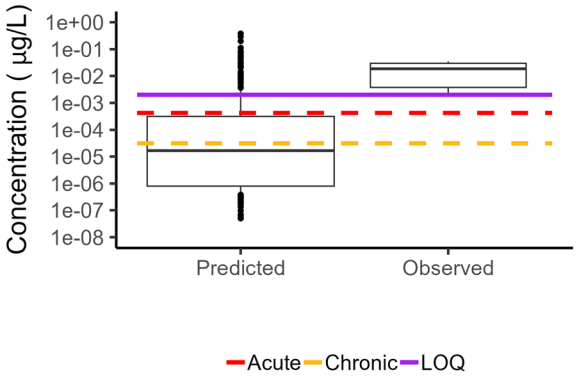
a) Bifenthrin, observations n=3



b) Esfenvalerate, observations n=8



c) Chlorpyrifos, observations n=91



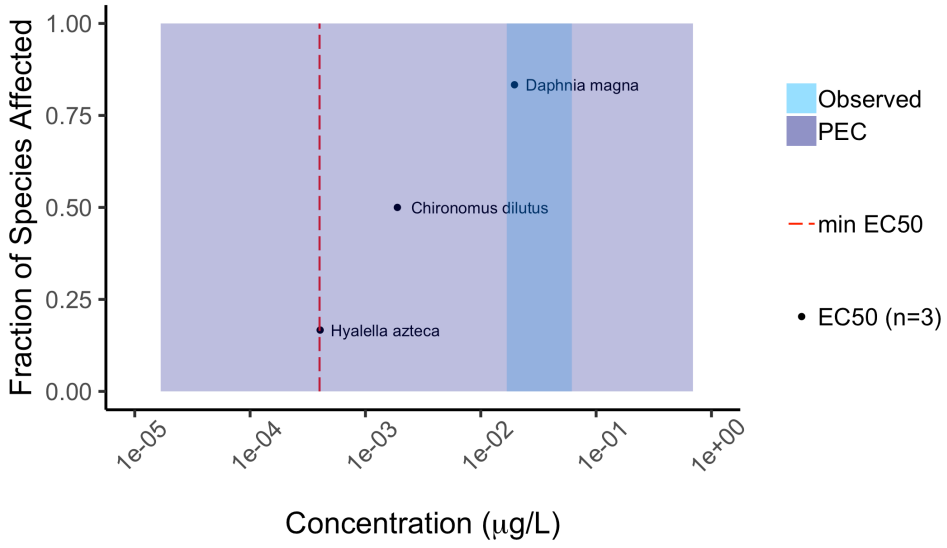
d) Chlorpyrifos, observations n=56

PECs for chlorpyrifos in the Visalia and San Joaquin River Watersheds, similar to bifenthrin and esfenvalerate, encompassed all observed concentrations. The median predictions demonstrated close agreement to observed with a pQPEC of 0.1 and 0.16 for the Visalia and San Joaquin River Watersheds respectively.

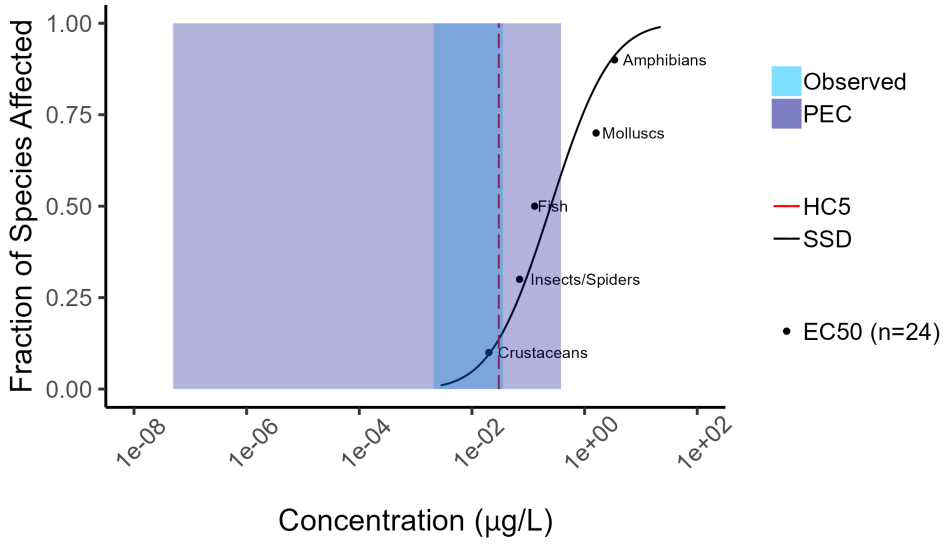
However, for predicted maxima, concentrations were 1-2 orders of magnitude higher. Closer agreement was observed for 99th percentile predictions, which were within an order of magnitude of observed concentrations, which is considered reasonable by the USEPA(48). A greater difference in peak predicted chlorpyrifos concentrations and observed relative bifenthrin and esfenvalerate is likely attributable to an organic partitioning coefficient that is two orders of magnitude lower. Since predictions capture all events and observed concentrations relatively few, maximum predictions may provide reasonable predictions for events not captured in monitoring campaigns.

Concerning the USEPA benchmarks, both the observed and predicted concentrations for bifenthrin, esfenvalerate, and chlorpyrifos were found to be in exceedance of acute and chronic risks, as was observed for the other pesticides, signaling potential risks to the environment. The assessment of acute and chronic aquatic community risks also revealed concentrations to exceed the HC5 and the EC50 for several taxonomic groups, as shown in **Figure 4** For instance, chlorpyrifos concentrations in the Visalia watershed were observed to exceed the EC50 for water fleas, aquatic flies (such as caddis flies, mayflies, and damselflies), mosquitoes, pigmy backswimmers, and crustaceans. Predicted chlorpyrifos concentrations also exceeded the EC50 for fish, mussels, and frogs. Collectively, observed and predicted concentrations provide strong supporting evidence that protection goals for aquatic fauna are not achieved with current pesticide use regimes in the watershed.

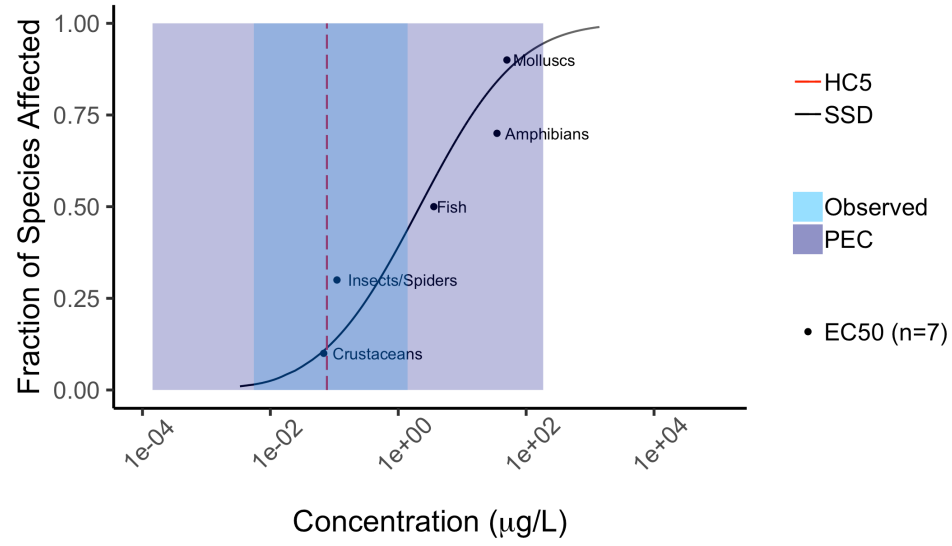
Figure 4(a-d). Observed and predicted concentrations relative to the most sensitive species sensitivity distributions (SSDs) of available acute and chronic toxicity where available. Depicted in **(a-c)** are results for the Visalia Watershed where **a)** are chronic thresholds for bifenthrin (insufficient data for acute or chronic SSD), **b)** the acute SSD for esfenvalerate (insufficient data for chronic SSD), and **c)** the chronic SSD for chlorpyrifos; **d)** depicts the SSD for chlorpyrifos in the San Joaquin River Watershed. Note for chlorpyrifos and esfenvalerate, where many species thresholds were available, the distribution was calculated for broader taxonomic groups.


Fraction of Species Affected
1.00
0.75
0.50
0.25
0.00
Daphnia magna
Chironomus dilutus
Hyalella azteca
1e-05
1e-04
1e-03
1e-02
1e-01
1e+00
Concentration (µg/L)
Observed
PEC
min EC50
EC50 (n=3)

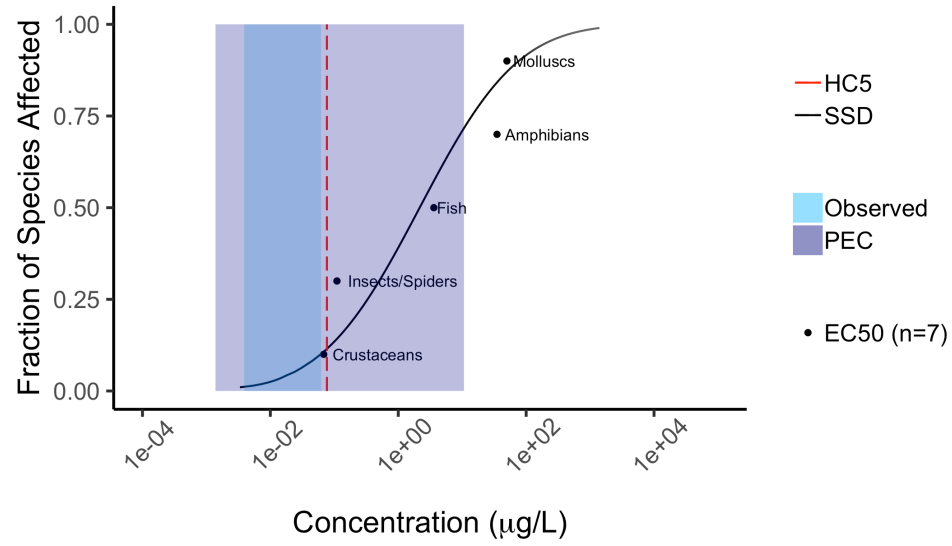
a)


Fraction of Species Affected
1.00
0.75
0.50
0.25
0.00
Amphibians
Molluscs
Fish
Insects/Spiders
Crustaceans
1e-08
1e-06
1e-04
1e-02
1e+00
1e+02
Concentration (µg/L)
Observed
PEC
HC5
SSD
EC50 (n=24)

b)



c)



d)

1.3.4 Limitations and Significance

Environmental models, including multimedia and watershed scale models, commonly use homogenous compartments to represent various environmental media at different scales. However, this approach overlooks the significant variability in properties, such as organic carbon in soils and sediments, as well as locations of higher concentration within a given compartment due to incomplete mixing. Notably, smaller water bodies within a watershed,

like small streams and creeks, may also exhibit considerably higher concentrations compared to larger rivers, as they experience less dilution(57). Despite this simplification, the model effectively mitigates over-parameterization in data-limited regions, thereby reducing complexity and enhancing efficiency. Although predictive tools like OrganoFate do not replace the need for monitoring or more discretized risk assessment models, they offer valuable insights into environmental concentrations and ecological risks at a higher spatiotemporal resolution than is typically attainable with monitoring data.

The significance of employing OrganoFate for this analysis lies in its integration with ChemFate, a comprehensive tool capable of predicting concentrations for diverse chemical classes, including pesticides based on ionizable organics, metal ions, or nanomaterials, covering a wide range of commercial products. This unified approach streamlines analyses, sparing users the considerable effort of parameterizing multiple models and familiarizing themselves with various tools needed for studying current-use chemicals. Notably, this investigation demonstrates that parameterization of OrganoFate using publicly available data can reliably predict environmental concentrations of diverse organic contaminants, generally falling within the observed range.

Furthermore, this investigation sheds light on potential threats to aquatic ecosystems posed by CECs and pesticides. For CECs, the reliability of risk evaluations is hindered by the absence of limited monitoring and toxicological data. On the other hand, contaminants such as pesticides may have more comprehensive monitoring and effect datasets. However, monitoring data often fails to capture concentrations at which severe adverse effects may occur due to the highly targeted mode of action and low limit of quantification. Consequently, predictive screening-level tools like OrganoFate play a crucial role in

complementing field assessments of the impact of these contaminants on biodiversity in surface waters.

Overall, our study demonstrates that OrganoFate is a valuable tool for understanding the fate and concentrations of diverse organic contaminants in environmental systems. Its integration into risk evaluations of data-limited watersheds allows researchers to gain valuable insights into chemical hazards, aiding in the formulation of effective environmental management strategies. Nonetheless, it is essential to interpret results carefully and consider additional monitoring data to make informed decisions regarding ecological risk assessment and management.

1.4 Conclusion

Our study addresses the pressing need for accessible and easy-to-implement tools to perform screening-level ecological risk assessments in the face of increasing chemical use in society. Due to the limited availability of field data for calibration and validation, we evaluated the effectiveness of the uncalibrated fate and transport model, OrganoFate, in predicting environmental concentrations of non-ionizable organic contaminants in watersheds heavily impacted by urban or agricultural development. The results showed that OrganoFate performed well in predicting the range of observed environmental concentrations in surface water.

Furthermore, we utilized OrganoFate to assess the potential impacts on aquatic health, revealing risks associated with certain Contaminants of Emerging Concern (CECs) like TDCPP and triclocarban. Monitoring data and predictions indicated that USEPA Aquatic Life Benchmarks were exceeded for each investigated insecticide, as well as for ecotoxicological thresholds associated with severe effects documented in peer-reviewed

literature. This suggested possible adverse effects on invertebrates, fish, mollusks, and amphibians.

Our findings highlight the value of OrganoFate as an informative tool for conducting screening-level ecological risk assessments, particularly in data-limited conditions. It provides valuable insights to support informed decision-making and environmental management efforts, enabling better risk evaluation and mitigation strategies.

1.5 References

1. USEPA. How EPA Evaluates the Safety of Existing Chemicals – Assessing and Managing Chemicals under TSCA (Internet). 2017 (cited 2020 Jan 23). Available from: https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/how-epa-evaluates-safety-existing-chemicals

2. Krimsky S. The unsteady state and inertia of chemical regulation under the US Toxic Substances Control Act. PLoS Biol. 2017 Dec 18;15(12):e2002404.

3. Wilson M, Schwarzman M. Toward a New U.S. Chemicals Policy: Rebuilding the Foundation to Advance New Science, Green Chemistry, and Environmental Health. Environ Health Perspect. 2009 Aug;117(8):1202–9.

4. Malaj E, von der Ohe PC, Grote M, Kühne R, Mondy CP, Usseglio-Polatera P, et al. Organic chemicals jeopardize the health of freshwater ecosystems on the continental scale. Proc Natl Acad Sci USA. 2014 Jul 1;111(26):9549–54.

5. Snyder SA, Westerhoff P, Yoon Y, Sedlak DL. Pharmaceuticals, personal care products, and endocrine disruptors in water: implications for the water industry. Environ Eng Sci. 2003 Sep;20(5):449–69.

6. USEPA. Contaminants of Emerging Concern including Pharmaceuticals and Personal Care Products (Internet). (cited 2020 Jul 26). Available from: https://www.epa.gov/wqc/contaminants-emerging-concern-including-pharmaceuticals-and-personal-care-products

7. Gogoi A, Mazumder P, Tyagi VK, Tushara Chaminda GG, An AK, Kumar M. Occurrence and fate of emerging contaminants in water environment: A review. Groundwater for Sustainable Development. 2018 Mar;6:169–80.

8. Jones RL, Mangels G. Review of the validation of models used in Federal Insecticide, Fungicide, and Rodenticide Act environmental exposure assessments. Environ Toxicol Chem. 2002 Aug;21(8):1535–44.

9. USEPA. Models for Pesticide Risk Assessment - Pesticide Science and Assessing Pesticide Risks (Internet). (cited 2020 Jul 8). Available from: https://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/models-pesticide-risk-assessment

10. Tao M, Keller AA. ChemFate: A fate and transport modeling framework for evaluating radically different chemicals under comparable conditions. Chemosphere. 2020 Sep;255:126897.

11. Garner KL, Suh S, Keller AA. Assessing the Risk of Engineered Nanomaterials in the Environment: Development and Application of the nanoFate Model. Environ Sci Technol. 2017 May 16;51(10):5541–51.

12. Parker N, Keller AA. Variation in regional risk of engineered nanoparticles: nanoTiO_2 as a case study. Environ Sci: Nano. 2019;

13. Hollander A, Schoorl M, van de Meent D. SimpleBox 4.0: Improving the model while keeping it simple. Chemosphere. 2016 Apr;148:99–107.

14. USEPA. Stochastic Human Exposure and Dose Simulation (SHEDS) to estimate human exposure to chemicals (Internet). (cited 2020 Feb 21). Available from: https://www.epa.gov/chemical-research/stochastic-human-exposure-and-dose-simulation-sheds-estimate-human-exposure

15. Mckone TE, Enoch KG. CalTOX, A Multimedia Total Exposure Model Spreadsheet User's Guide Version 4.0 (Beta). 2002;

16. MacLeod M, Woodfine DG, Mackay D, McKone T, Bennett D, Maddalena R. BETR North America: a regionally segmented multimedia contaminant fate model for North America. Environ Sci Pollut Res Int. 2001;8(3):156–63.

17. Xie Y, Luo Y, Singhasemanon N, Goh KS. Regulatory modeling of pesticide aquatic exposures in california's agricultural receiving waters. J Environ Qual. 2018;47(6):1453–61.

18. CDPR. California Pesticide Information Portal (CalPIP) (Internet). (cited 2018 Oct 20). Available from: https://calpip.cdpr.ca.gov/main.cfm

19. Boithias L, Sauvage S, Srinivasan R, Leccia O, Sánchez-Pérez J-M. Application date as a controlling factor of pesticide transfers to surface water during runoff events. CATENA. 2014 Aug;119:97–103.

20. Young DF, Fry MM. PRZM5 A Model for Predicting Pesticides in Runoff, Erosion, and Leachate–Revision B . USEPA; 2020 Aug.

21. Mackay D. Multimedia Environmental Models–The Fugacity Approach. 2nd ed. Lewis Publishers; 2001.

22. Zhang X, Luo Y, Goh KS. Modeling spray drift and runoff-related inputs of pesticides to receiving water. Environ Pollut. 2018 Mar;234:48–58.

23. Yao Y, Harner T, Blanchard P, Tuduri L, Waite D, Poissant L, et al. Pesticides in the atmosphere across Canadian agricultural regions. Environ Sci Technol. 2008 Aug 15;42(16):5931–7.

24. Srinivasan R, Ramanarayanan TS, Arnold JG, Bednarz ST. Large area hydrologic modeling and assessment part ii: model application. J Am Water Resources Assoc. 1998 Feb;34(1):91–101.

25. Arnold JG, Srinivasan R, Muttiah RS, Williams JR. Large area hydrologic modeling and assessment part i: model development. J Am Water Resources Assoc. 1998 Feb;34(1):73–89.

26. Wang R, Yuan Y, Yen H, Grieneisen M, Arnold J, Wang D, et al. A review of pesticide fate and transport simulation at watershed level using SWAT: Current status and research concerns. Sci Total Environ. 2019 Jun 15;669:512–26.

27. Zheng Y, Keller AA. Understanding parameter sensitivity and its management implications in watershed-scale water quality modeling. Water Resour Res. 2006 May;42(5).

28. Keller AA, Chen X, Fox J, Fulda M, Dorsey R, Seapy B, et al. Attenuation coefficients for water quality trading. Environ Sci Technol. 2014 Jun 17;48(12):6788–94.

29. USEPA. Hydrological Simulation Program - FORTRAN (HSPF) (Internet). (cited 2020 Feb 10). Available from: https://www.epa.gov/ceam/hydrological-simulation-program-fortran-hspf

30. Xie H, Lian Y. Uncertainty-based evaluation and comparison of SWAT and HSPF applications to the Illinois River Basin. J Hydrol (Amst). 2013 Feb;481:119–31.

31. A. Saleh and B. Du. Evaluation of SWAT and HSPF within BASINS program for the Upper North Bosque River Watershed in central Texas. Transactions of the ASAE. 2004;47(4):1039–49.

32. Jutkina J, Marathe NP, Flach CF, Larsson DGJ. Antibiotics and common antibacterial biocides stimulate horizontal transfer of resistance at low concentrations. Sci Total Environ. 2018 Mar;616–617:172–8.

33. Wang C, Chen H, Li H, Yu J, Wang X, Liu Y. Review of emerging contaminant tris(1,3-dichloro-2-propyl)phosphate: Environmental occurrence, exposure, and risks to organisms and human health. Environ Int. 2020 Jul 12;143:105946.

34. CDPR. Chlorpyrifos Cancellation (Internet). California Department of Pesticide Regulation. 2019 (cited 2019 Oct 10). Available from: https://www.cdpr.ca.gov/docs/chlorpyrifos/index.htm

35. Mohan G. California banned chlorpyrifos. Now the pesticide won't be made . Los Angeles Times. 2020 Feb 6;

36. USGS, USDA. Federal Standards and Procedures for the National Watershed Boundary Dataset (WBD). US Geological Survey Techniques and Methods 11-A3. 2nd ed. 2011.

37. Multi-Resolution Land Characteristics (MRLC) Consortium. National Land Cover Database (NLCD) (Internet). (cited 2019 Jun 6). Available from: https://www.mrlc.gov/data?f%5B0%5D=category%3Aland%20cover&f%5B1%5D=category%3Aurban%20imperviousness&f%5B2%5D=region%3Aconus&f%5B3%5D=category%3Aland%20cover&f%5B4%5D=category%3Aurban%20imperviousness&f%5B5%5D=region%3Aconus

38. Tao M, Keller A. ChemFate User Guide.

39. Su C, Zhang H, Cridge C, Liang R. A review of multimedia transport and fate models for chemicals: Principles, features and applicability. Sci Total Environ. 2019 Jun 10;668:881–92.

40. MacLeod M, Fraser AJ, Mackay D. Evaluating and expressing the propagation of uncertainty in chemical fate and bioaccumulation models. Environ Toxicol Chem. 2002 Apr;21(4):700–9.

41. Mackay D. Multimedia Environmental Models - The Fugacity Approach. 2nd ed. Lewis Publishers; 2001.

42. Voice TC, Rice CP, Weber WJ. Effect of solids concentration on the sorptive partitioning of hydrophobic pollutants in aquatic systems. Environ Sci Technol. 1983 Sep;17(9):513–8.

43. Le TDH, Scharmüller A, Kattwinkel M, Kühne R, Schüürmann G, Schäfer RB. Contribution of waste water treatment plants to pesticide toxicity in agriculture catchments. Ecotoxicol Environ Saf. 2017 Nov;145:135–41.

44. Köck-Schulmeyer M, Villagrasa M, López de Alda M, Céspedes-Sánchez R, Ventura F, Barceló D. Occurrence and behavior of pesticides in wastewater treatment plants and their environmental impact. Sci Total Environ. 2013 Aug 1;458–460:466–76.

45. Southern Coastal Califonrnia Water Research Project. Screening Study for Constituents of Emerging Concern (CECs) in Selected Freshwater Rivers in the Los Angeles Region–Phase 2. Southern California Coastal Water Research Project; 2015 Mar.

46. CDPR. Surface Water Database (Internet). (cited 2018 Oct 20). Available from: https://www.cdpr.ca.gov/docs/emon/surfwtr/surfcont.htm

47. Moriasi DN, Arnold JG, M. W. Van Liew, Bingner RL, Harmel RD, T. L. Veith. Model Evaluation Guidelines for Systematic Quantification of Accuracy in Watershed Simulations. TransASABE. 2007;50(3):885–900.

48. USEPA. Risk Assessment Guidance for Superfund (RAGS): Part B (Internet). United States Environmental Protection Agency. (cited 2023 Jun 1). Available from: https://www.epa.gov/risk/risk-assessment-guidance-superfund-rags-part-b

49. USEPA. Aquatic Life Benchmarks and Ecological Risk Assessments for Registered Pesticides (Internet). (cited 2022 Jun 8). Available from: https://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/aquatic-life-benchmarks-and-ecological-risk

50. Marshack J. A Compilation of Water Quality Goals 17th Edition. State Water Resources Control Board; 2016 Jan.

51. Regional Water Quality Control Board Central Valley Region. Proposed Ammendment to the Water Quality Control Plan for the Sacramento River and San Joaquin River Basins for the Control of Pyrethroid Pesticides Discharges. Regional Water Quality Control Board Central Valley Region; 2017 Jun.

52. USEPA. ECOTOX (Internet). (cited 2018 Mar 4). Available from: https://cfpub.epa.gov/ecotox/

53. Wheeler JR, Grist EPM, Leung KMY, Morritt D, Crane M. Species sensitivity distributions: data and model choice. Mar Pollut Bull. 2002;45(1–12):192–202.

54. Kooijman SALM. A safety factor for LC50 values allowing for differences in sensitivity among species. Water Res. 1987 Mar;21(3):269–76.

55. Fox DR, van Dam RA, Fisher R, Batley GE, Tillmanns AR, Thorley J, et al. Recent developments in species sensitivity distribution modeling. Environ Toxicol Chem. 2021 Feb;40(2):293–308.

56. Williams ES, Berninger JP, Brooks BW. Application of chemical toxicity distributions to ecotoxicology data requirements under REACH. Environ Toxicol Chem. 2011 Aug;30(8):1943–

57. Schulz R. Field studies on exposure, effects, and risk mitigation of aquatic nonpoint-source insecticide pollution: a review. J Environ Qual. 2004 Apr;33(2):419–48.

Chapter 2. Leveraging high spatiotemporal resolution data of pesticides applied to agricultural fields in California to identify toxicity reduction opportunities

Pesticides remain a leading environmental hazard, imperiling aquatic and terrestrial ecosystems. Reducing pesticide toxicity is hampered by the ability to evaluate toxicity over large extents, the spatiotemporal resolution of pesticide use data, the ability to assess cumulative toxicity, and the identification of health/economic contributions of different pesticide application sites. We introduce the Environmental Release Tool, a sub-tool of the Pesticide Mitigation Prioritization Model, to advance these four areas. Using daily pesticide use reports required for agricultural applicators in California, we quantify the applied toxicity of pesticides to fish as well as aquatic invertebrates, nonvascular plants, and vascular plants. With the tool's ability to quantify applied toxicity for hundreds of pesticides and watersheds simultaneously, we explore the significance of accounting for cumulative applied pesticide toxicity for application sites and watersheds statewide. Our results show that 14 pesticides account for 99.9% of applied toxicity, and 16 of 432 application site types introduce 90% of toxicity for taxa investigated. We also find cumulative applied toxicity within watersheds was significantly greater ($p < 1.0$ E-16) than the maximum impact pesticide for all taxonomic groups, with a mean-annual difference of 460-630%. While cumulative applied toxicity was significant, and sources varied in individual watersheds, the net applied toxicity can be approximated with a short list of active ingredients and site types.

2.1 Introduction

Per year ~ 2 billion kilograms of pesticides are applied directly to the environment worldwide.(1) Due to their widespread use, pesticides are a leading cause of chemical hazards in aquatic environments(2–4) and have contributed to global declines in

pollinators(5) and other species. Recent European legislative initiatives have sought to reduce toxic contributions via use fees tiered according to risk(6,7) and toxicity reduction targets(8). These legislative initiatives are important but do not identify taxon-specific toxicity nor quantify chemical and application site-specific information that would enable more targeted mitigation aims. Other mitigation tools are available to derive toxicity reduction strategies which include fate models(9,10), toxicity/risk maps(11,12), risk indices(13–15), and summaries of pesticide use(16,17). However, the individual tools are limited by their ability to evaluate large extents, toxicity sources, cumulative applied toxicity, and/or ability to consider the economic benefits of application sites. To address the limitations of existing tools, we have developed a tool to integrate these features into a single framework, the Environmental Release Tool. The tool aims to improve the information available for targeting pesticide reduction strategies for experts, stakeholders, and the public. The tool is the first stage of development for the Pesticide Mitigation Prioritization Model (the second stage is a companion fate model) and quantifies the spatiotemporal distribution of applied toxicity, defined here as the mass of pesticide released into the environment, weighted by toxicity to user-defined priority species.

2.1.1 Scale

The first objective of the Environmental Release Tool (ERT) is to identify the applied toxicity of pesticides over large extents to promote targeted pesticide toxicity reduction strategies. While governments largely regulate pesticides at the national/multinational level(18,19), few tools are available to model pesticide impacts across the large and heterogeneous scales managed by regulators (e.g., SYNOPS-WEB(13)). Existing watershed fate and transport models adaptable to specific regions, such as SWAT(20–22) or HSPF(23–

25) often require global calibration methods due to limited data for model parameters, and global calibrations can mask toxicity sources. Global calibrations also require monitoring data(26), and for many watersheds, no or limited observations are available for pesticides. Moreover, a fate and transport model's parameterization and calibration for a single pesticide and watershed can take hundreds of hours, and its uncertainty is compounded over large extents (26–28). Collectively, these factors can obscure important variations and hinder the identification of toxicity reduction opportunities at scale.

2.1.2 Sources

Another key obstacle to mitigating applied toxicity is identifying pesticide sources and application timing(29–31). Pesticide use data are often not recorded and reported, making it difficult to predict watershed-level, applied toxicity. While the Pesticide National Synthesis Project(32) provides the best dataset for pesticide use across the United States, the data are too coarse for this purpose. However, the state of California is unique; its Department of Pesticide (CDPR) has the most comprehensive pesticide use database in the world, with daily reports of agricultural applications since 1990.(33) Currently, no tool is available with which to efficiently use the database to summarize or map the spatiotemporal distribution of pesticide toxicity. The second objective of the ERT is to automatically load and process data to prioritize toxicity reduction while providing the flexibility to quantify the applied toxicity distribution of pesticides in the United States and beyond.

2.1.3 Cumulative applied toxicity

Pesticide-contaminated soils and surface waters typically contain mixtures of active ingredients(3,34–36). The cumulative applied toxicity is the sum of the toxicity of all

pesticides applied at a given site within a particular time period (e.g., daily, monthly, annually). Often, the pesticide with the highest toxicity is considered the most relevant one, and it is common to assume that the most toxic pesticide can approximate the cumulative applied toxicity in a given sample (37,38); however, to reduce pesticide toxicity in a water body throughout the year, it is imperative to understand the cumulative applied toxicity, which can exhibit significant temporal variation in the pesticides responsible for most toxicity(31).

Most watershed models, even where high-resolution pesticide use data is available, cannot accommodate the evaluation of a pesticide mixture within a single simulation; nor are pesticide mixtures regulated in the United States(18,39), with few state-level exceptions for specific pesticide classes(40). The variability of mixtures(41) and knowledge gaps related to the synergism or antagonism of a pesticide mixture to non-target organism toxicity(42) often make quantifying their combined effect challenging. Although tools are available that simulate and summarize pesticide mixture toxicity, such as regression models(43) and cumulative risk maps(12), they have limited spatiotemporal extent. To address the cumulative risk knowledge gaps, our third aim is to quantify the spatiotemporal applied toxicity of various pesticides at specific application site types to facilitate toxicity reduction initiatives.

2.1.4 Economic and health scores

Reducing pesticide-applied toxicity can affect the economic prosperity of agricultural stakeholders.(44,45) Many options exist for considering the economic benefits and health concerns of pesticides, and consideration of economic impacts is mandated by current US

legislation(39). However, no tools are known to the authors to dynamically quantify health and economic indices for pesticide application sites. Therefore, the fourth objective of the ERT is to generate scores for the various application site types that prioritize toxicity reduction opportunities while also considering the economic benefits relative to health impacts. Though external factors affecting treatment areas, such as water and stress to crop yields, make it difficult to quantify pesticide use benefits, simple health, and economic scores can be leveraged to explore effective strategies.

2.1.5 Toxicity Reduction Targets

The ERT is a novel tool for targeting toxicity reduction designed to be user-friendly for experts (researchers) and non-experts (e.g., the public), with results presented in an interactive heatmap with graphical summaries. The development of the ERT sought to overcome the limitations of existing tools for prioritizing pesticide mitigation opportunities by integrating features to 1) assess variation in applied toxicity at the regulation extent (1,000+ watersheds), 2) identify primary sources of environmental toxicity, 3) calculate cumulative toxicity, and 4) generate impact scores that consider economic and health aspects of toxicity reduction.

To identify toxicity reduction strategies in diverse landscapes, California is an ideal study site due to available information on over 400 agricultural application site types and the substantial pesticide use, accounting for 20% of the mass of pesticide sales in the United States and 3% worldwide(46,47). Our study leveraged the ERT to identify toxicity reduction targets for aquatic taxa in California's watersheds. It aimed to answer four questions: 1) How is toxicity distributed among pesticides for diverse taxa? 2) What are the opportunities for

toxicity reduction in specific application site types? 3) Does quantifying the cumulative toxicity enhance our understanding of environmental toxicity? 4) Which application sites have the greatest applied toxicity, and what economic benefits do they have?

2.2.0 Methods

The Environmental Release Tool has two platforms: a web application for California and a desktop version for all study areas in the United States, which offer different advantages. The web-based tool, available on any internet-accessible device, summarizes applied toxicity in seconds and provides a simpler user interface. The offline tool offers a high degree of customization, more detailed information, and custom simulations. To assist experts and non-experts, the desktop and web tools were built in RStudio(48) version 1.4. The development environment accommodates full customization of the tool's code for experts and the ability to run unique simulations for non-experts via editing spreadsheet files in Google Sheets and clicking a start button.

This tool does not quantify fate or exposure but rather illustrates the location and amount of applied toxicity(49) for designing toxicity reduction strategies and planning monitoring campaigns by identifying areas where higher toxicity is released in the environment, and its sources. Although the ERT is a spatial tool designed for large extents, the tool works best to understand sources of pesticide exposures for species with a small habitat range. However, for organisms whose activities are more widespread and who have less direct contact with environmental compartments where pesticides are most likely to persist, the location of applied toxicity may be less useful for understanding sources of potential exposure.

2.2.1 Scale

To enable evaluations of the variability of pesticide toxicity over large extents, the tool summarizes pesticide applications and toxicity by watershed. The data is summarized by watershed, and applications sites as well as pesticides within since pesticide losses via runoff and eroded sediments share a common outlet. Summarizing applied toxicity by watersheds is important to conceptualize areas that share common hydrologic routes for pesticide transport. Though the Environmental Release Tool does not simulate loss processes, it is the first stage of development of the Pesticide Mitigation Prioritization Model, and the product of the second stage of development is a companion, mechanistic fate and transport tool where loss processes are simulated.

Watersheds in the ERT are delineated using the Watershed Boundary Dataset(50), a data product of the United States Geological Survey. Each watershed is assigned a hydrologic unit code (HUC), which is based on the hydrologic connectivity and scale of the watershed. Watersheds with shorter HUCs, such as HUC 2-digit codes, are large watersheds encompassing hundreds of thousands of square kilometers, while longer HUCs such as HUC 8-digit codes (HUC8) represent subwatersheds of the shorter digit codes (e.g., HUC2). The assignment of pesticide use data to watersheds of various spatial extents is facilitated by the tool (see *SI Section 3.0*).

2.2.2 Sources

To evaluate the spatiotemporal distribution of pesticides, the ERT benefits from the ability to autoload daily pesticide use report data in California from statewide agricultural applicators(33). The tool internally hosts the data, and using an autoload script, aggregates

data for the area of interest to the user, which watersheds or counties may define. Where counties are used, the tool automatically aggregates data to watersheds in the county. For other pesticide input options (e.g., manual inputs or for analyses of other land uses or regions), see *Appendix X Section 3.0.*

The amount of pesticide applied on application sites (e.g., a specific crop) in California is substantial, millions of pounds for widely cultivated crops, and as high as ~40 million for almonds(51). To assist efficient analyses, the ERT extracts pesticide usage data for California from CDPR Pesticide Use Reports(33) by active ingredient (AI) and for the 432 agricultural site types for the study area of interest to the user. These reports record daily applications at the County Meridian Township Range Section (referred to as Section) spatial scale (2.6 km^2). For Sections where pesticide use data is reported that overlaps multiple watersheds, the area fraction of overlap is used to weight the mass of AI applied. Notably, urban applications were not included in the autoload feature. The reports do not include household applications, and professional urban applications are recorded at the county level and at a monthly time step, which cannot be allocated to a specific watershed or date.

For evaluating pesticide sources of toxicity, ERT facilitates the summarization of similar AIs. This feature is useful because many AIs have a similar chemical make-up (e.g., isomers or are produced in several forms, including acids, salts, amines, and esters), but have no or limited toxicity data for the various AI forms. Provided that AI forms can have very different effect concentrations, where possible, the user should provide AI form-specific toxicity. To accommodate specific endpoints where available, but to enable simplification of tool outputs, unique toxicity endpoints are accepted and calculated for pesticides within a user-defined pesticide group, and the group ID reports the group's total applied toxicity in

tool output. In this investigation, we considered AIs detected (2014-2018) within California's surface waters with available toxicity data (n = 151). From the CDPR's Pesticide Use Reports, 290 forms of the AIs were observed (e.g., 12 unique esters and 15 salts of 2,4-D).

In addition to pesticide sources of applied toxicity, a key feature of ERT is the ability to preserve information relating to application site types. However, too many application sites make the interpretation of results difficult. The tool thus enables users to group similar application sites (e.g., alfalfa and alfalfa-grass mixture) by assigning the same ID to multiple site types. By default, 432 agricultural application site types from Pesticide Use Reports are simplified to 116 based on the similarity of the crops. Groupings can be viewed and modified in the tool input file for application sites.

To identify pesticide toxicity reduction targets, the ERT quantifies applied pesticide toxicity. Applied toxicity refers to the mass of pesticide applied to an area with the potential to do harm(49). The applied toxicity for the i^{th} pesticide in the j^{th} watershed is calculable from applications to the k^{th} site type and toxic endpoint of the m^{th} taxon of interest as:

$$TI_{j,i} = \sum \frac{M_{i,j,k,m}}{T_{i,j,k,m}} \quad \textit{Equation (1)}$$

Where TI is the Toxicity Index (kg-m^3/kg), M (kg) is the mass of applied AI, and T (kg/m^3) is the adverse health-effect concentration of concern (e.g., the lethal concentration of fifty percent of the test organism population) for the species or taxonomic groups of interest. Within a simulation, the tool is suitable for quantifying the applied toxicity to taxa within the same compartment, not across environmental compartments, because variation in the transport of pesticides based on physicochemical properties is not simulated. The tool illustrates applied toxicity within the soil compartment or available for transport to the

compartment of interest. While the transport of pesticides from the application site is sensitive to their physicochemical properties(52), property correlation to surface water detection frequencies has been demonstrated to the more robust for pesticide sales data than physicochemical properties in a monitoring campaign of 72 pesticides of diverse properties in over 100 streams(53). Though this approach is not suitable for risk assessments, it facilitates an understanding of where mitigation opportunities exist(54) without data requirements and uncertainty of fate and transport models over large extents(26,27,55).

Our investigation considers the applied toxicity of pesticides for fish, as well as aquatic invertebrates, nonvascular plants, and vascular plants. Toxicity endpoints employed were acute values from the United States Environmental Protection Agency (USEPA) Aquatic Life Benchmarks Database[60,61]. The USEPA derives Benchmarks from the concentration at which fifty percent of a species sample in single-dose laboratory investigations experience severe effects derived from mortality endpoints or, for plants, significant changes in growth/biomass (LC50 or EC50). A genera endpoint is then calculated based upon a 0.05 cumulative probability of toxicity for represented species, which typically reflects the most sensitive species within the taxonomic group. For fish and invertebrates, the USEPA calculates the final acute value as the product of the taxonomic group endpoint multiplied by a safety factor of 0.5 and does not adjust plants. Where no toxicity endpoints were reported for the pesticide in the Aquatic Life Benchmark database (n = 10), the Pesticide Properties DataBase(56) acute toxicity endpoints were employed, and unverified data were excluded.

The first applied toxicity index reported by ERT for pesticides, sites, and watersheds is the Relative Toxicity Index (RTI) (kg-m^3/kg-m^2). The index weights the toxicity of the i^{th} applied pesticide by the size of the application area within the j^{th} watershed as:

$$RTI_{j,i} = \frac{TI_{i,j}}{A_j} \quad Equation\ (2)$$

where A (m^2) is the area affected by pesticide applications.

To estimate the areas affected by pesticide applications, agricultural land use datasets are used. In California, the Pesticide Use Reports can be used to retrieve the impacted area. However, there are known inaccuracies. The planted area is often recorded for all the grower's land; although reported for a specific crop, and fields are subject to multiple crop rotations within a year. For the applied area, multiple applications are typical for a crop that renders the net-application area unknown. Due to these concerns, alternative land use datasets were evaluated for use(57–59).

After reviewing several datasets, the California Department of Water Resources land use surveys(55) were found to be the most accurate with a median accuracy of 97.5% and positional quality of 8m. However, a limitation of the dataset, as well as the others, is that it provides fewer site types (43) compared to Pesticide Use Reports (432). Using this dataset to determine the affected area of specific application site types would require highly reducing the resolution of pesticide source data. Attempts to recategorize crops to fit available land use data did not obtain reliable results. As a result, we chose to consider the affected area to be all agricultural land in the California Department of Water Resources dataset. The representation of the affected compartment to all agricultural land was deemed appropriate

because only 5% of agricultural fields in California employ organic cultivation practices(60) and use non-synthetic pesticides recorded in use reports.

As the quantification of the affected compartment area is frequently limited, and the fraction of a watershed subject to pesticide application is highly variable, we provide a second applied toxicity index independent of area, the Net Toxicity Index (NTI). The NTI is a relative rank toxicity index to determine if the applied toxicity is greater than what is typical for the i^{th} pesticide in the j^{th} watershed. As our reference of what is typical, we calculate for the study area the 50th percentile ($perc_{50}$) of the applied toxicity for any applied pesticide (pst) in watershed (w). The NTI is calculable from the TI of the i^{th} pesticide in the j^{th} watershed as:

$$NTI_{i,j} = \frac{TI_{i,j}}{perc_{50}\ (TI_{pst_1,w_1}, TI_{pst_1,w_1}, TI_{pst_1,w_2}, TI_{pst_2,w_2}, \ldots TI_{pst_n,w_n})} \quad \textit{Equation (3)}$$

The NTI approach can quickly identify applied toxicity above typical levels in the study extent. For example, if the 50th percentile of the applied toxicity of pesticides to a watershed in the study area is applications of imidacloprid in the San Joaquin Watershed, (e.g., 1000 TI), to calculate the NTI, the TI of the i^{th} pesticide and the j^{th} watershed of interest is divided by 1000 TI. Using this approach, pesticide applications within a watershed over the simulation period with an NTI greater than unity have applied toxicity above the 50th percentile. This normalization provides a unitless applied toxicity index that does not affect the relative rank of the applied toxicity for pesticides, sites, or watersheds, and can identify effective toxicity reduction targets specific to the study area.

2.2.3 Cumulative applied toxicity

For single taxonomic group investigations with the ERT (e.g., only fish), the cumulative applied toxicity, the potential of all pesticides released to the environment and under investigation to do harm to the taxon, is calculated via the concentration addition method (61,62). We calculate the cumulative toxicity indices of pesticides for each index for *n* pesticides for a watershed (here w_1) as:

$$RTI_j = \sum RTI_{pst_1,w_1} + RTI_{pst_2,,w_1} + RTI_{pst_3,j,w_1} \dots RTI_{pst_n,j,w_1} \quad \textit{Equation (4)}$$

$$NTI_j = \sum NTI_{pst_1,w_1,k} + NTI_{pst_2,w_1,k} + NTI_{pst_3,w_1,k} \dots NTI_{pst_n,w_1,k} \quad \textit{Equation (5)}$$

The method used in this study relies on the assumption of additive toxicity and non-interacting chemical species. While this assumption is theoretically unsound for chemicals of diverse modes of action, and this limitation is not addressed by the ERT, pesticides rarely express synergism at environmentally relevant concentrations, and cumulative addition has been empirically demonstrated to be a reliable method for quantifying pesticide mixture toxicity(63). For example, in studies with hundreds of pesticide mixtures, the method has predicted mortality within a factor of 2 for 90% of samples(64–66). Additionally, the method is robust to independent modes of action(65). However, the approach is not suited to simultaneously understand the cumulative toxicity to diverse taxa due to the presence of unique organism receptors and responses(67). To address this issue, we conducted independent simulations for fish, invertebrates, nonvascular aquatic plants, and vascular

aquatic plants in addition to the simulation that quantified the net applied toxicity for all organisms simultaneously.

Available literature considers that most acute toxicity in a pesticide mixture can be represented by a single pesticide(38,68). However, the frequency of use of pesticides varies throughout the year, as do pesticides detected in surface waters(31). To evaluate whether the tool's ability to rapidly quantify cumulative applied toxicity improves understanding of environmental toxicity relative to evaluations targeting the highest impact pesticide, the cumulative toxicity index (NTI) of sites and watersheds was compared to the index of the pesticide with the highest applied toxicity using a one-way, paired t-test. Paired t-tests are commonly employed for samples measured at two-time points and to compare predictions relative to observed data (the cumulative toxicity)(69).

2.2.4 Economic and health scores

The health and economic impacts of application sites are quantified over the study extent with a Health Score (ha/NTI), an Economic Score (USD/ha), as well as an Economic and Health Score (USD/NTI per ha). These scores are calculated over the study extent (California) rather than in specific watersheds due to the low resolution of reliable land use data (see *2.2 Sources)*. The health and economic scores with higher values represent more favorable outcomes. Health and economic scores are calculated for the application site areas of the study extent as:

$$Economic\ Score = \frac{Gross\ Value\ (USD)}{Harvested\ Hectares} \quad Equation\ (6)$$

$$Health\ Score = \frac{Harvested\ Hectares}{Toxicity\ Index\ (NTI\ or\ RTI)} \quad Equation\ (7)$$

The Economic and Health Score penalizes crops with high applied toxicity and is calculated as:

$$Economic\ and\ Health\ Score = \frac{Gross\ Value\ (USD\ per\ Harvested\ Hectare)}{Toxicity\ Index\ (NTI\ or\ RTI\ per\ Harvested\ Hectare)} \quad Equation\ (8)$$

For health and economic scores, the harvested hectares and gross value of application site types were compiled from the United States Department of Agriculture National Agricultural Statistics Service (https://www.nass.usda.gov/). We considered the median economic value and harvested hectares for a crop in California from 2014-2018 to minimize single-year anomalies.

In addition to numeric scores, users are also provided with categorical scores based upon percentiles for the study area to facilitate interpretation. Scores are divided into 20th percentiles and range from 'Very Low' (0-20th percentile) to 'Very High' (80-100th percentile).

2.2.5 Toxicity Reduction Targets

To demonstrate the effectiveness of the ERT in providing pesticide toxicity reduction targets, we conducted a comprehensive analysis of pesticide use across the 140 HUC8 watersheds in California (mean area ~3,600 km^2); see **Figure 1(a)**. Moreover, we leverage the tools' ability to perform higher resolution analyses to investigate the applied toxicity to the 208 HUC12 subwatersheds (mean area ~100 km^2) of the San Francisco Bay Delta Watershed (BDW) with agricultural pesticide applications; see **Figure 1(b)**. The BDW is an area of ecological significance within California and is home to over 90 threatened or endangered species(70). To evaluate toxicity reduction targets for aquatic taxa in these study

areas, we summarized the applied toxicity to fish, invertebrates, nonvascular aquatic plants, and vascular aquatic plants. To explore temporal trends in the net applied toxicity (10 years) of the study areas, we employed a two-sided Mann-Kendall test.

The evaluations of toxicity reduction targets in the study areas employs pesticide use data recorded at the Section level, which is smaller than a watershed, and a Section may overlap multiple watersheds (see *Section 2.1*). To evaluate the accuracy of the method used to assign pesticide use report data to watersheds with Section level data, predicted applications were compared to field-level pesticide use data in Kern County, one of the few counties with field-level data. The accuracy of pesticide use assignment to application sites within watersheds was evaluated relative to field-level predictions using the median absolute percent error (MdAPE). While the root mean square error or mean absolute percentage error are more sensitive metrics, they are both sensitive to outliers, whereas the MdAPE has been demonstrated to be more robust.(71) Since watersheds can vary in pesticide loads by many orders of magnitude, the MdAPE was employed.

2.3.0 Results

The ERT results presented in this study cover 140 major watersheds of California (HUC8, mean area ~3,600 km^2) and 208 HUC12 watersheds (mean area ~100 km^2) that receive agricultural pesticide applications in an ecologically important region of California, the BDW. *Sections 3.1 and 3.3* present the results of the simulation which summarize the net applied toxicity to fish, aquatic invertebrates, nonvascular plants, and vascular plants. This approach illustrates applied toxicity for any investigated taxa, with 18% of the most sensitive endpoints for investigated pesticides from fish, 38% from aquatic invertebrates, 27% from

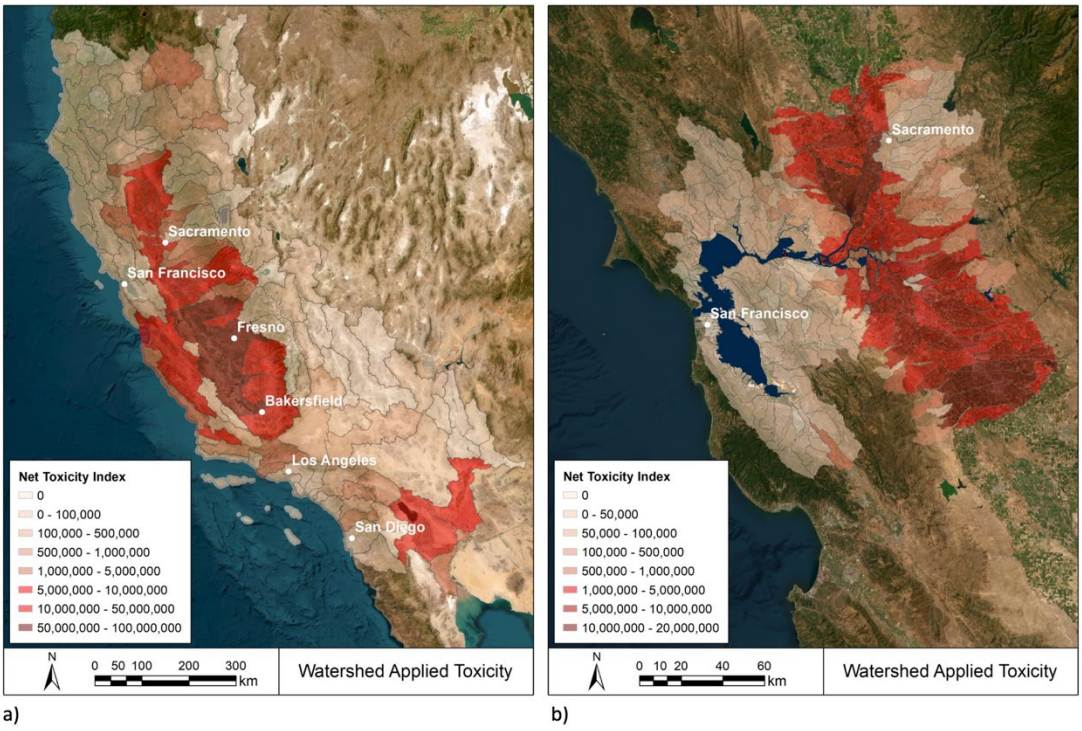
nonvascular aquatic plants, and 17% from vascular aquatic plants. In section *3.3 Cumulative Toxicity*, we explore the cumulative applied toxicity observed for specific taxonomic groups.

2.3.1 Scale

The evaluation of applied toxicity at the statewide management scale in California illustrated that toxicity reduction targets are concentrated in relatively few watersheds. The net applied toxicity (NTI) to all aquatic taxa investigated from all pesticides used over the simulation period showed 80% of toxicity was applied in only 11% of California's HUC8 watersheds; see **Figure 1(a)**. NTI varies by several orders of magnitude across California, from the lower end of the range (1-100,000) to the high end (>50,000,000). This reflects not only the difference in loading but also the wide range of toxicities for different pesticides. Watersheds in the 97th percentile, those with NTI values exceeding 50,000,000, received up to 8 orders of magnitude more applied toxicity compared to other watersheds across the state. These findings enable the identification of areas with high applied toxicity within data-limited watersheds during the analysis period. The information can be utilized to determine specific locations where further investigation of pesticide impacts, such as monitoring or simulating fate and transport, should be focused.

In the case of the BDW (agricultural watersheds exclusively considered), the study revealed that 20% of the watersheds accounted for 80% of the applied toxicity; see **Figure 1(b)**. For the California and BDW scales, results highlight the effectiveness of targeting a relatively small fraction of watersheds that receive the highest levels of applied toxicity as a strategy for reducing overall toxicity.

Figure 1 (a and b). The heat map and legend values represent applied toxicity as the Net Toxicity Index (NTI), the total applied toxicity of pesticide applications to all aquatic taxa investigated over the simulation period, fish, invertebrates, nonvascular aquatic plants, and vascular aquatic plants. Results are displayed for each study extent, a) California's HUC8 watersheds and b) the HUC12 subwatersheds in the Bay-Delta Watershed. The NTI ranges identify the magnitude of toxicity released during pesticide applications, with values in the upper range, greater than 50,000,000, illustrating areas of applied toxicity that are up to 8 orders of magnitude greater than other watersheds. Base map source:http://goto.arcgisonline.com/maps/Reference/World_Imagery.



At scale, the ERT also facilitates the quick identification of changes over time for different resolutions (daily, monthly, and annual). We leveraged this feature to identify if watersheds were increasing in applied toxicity and may benefit from mitigation efforts. For temporal analyses, we extended the evaluation to the most recent 10 years of available pesticide use data. Our analysis covered 2009 to 2018, during which the total NTI of pesticides used in California's watersheds increased by 150% in the last five years (2014-2018) compared to the first five years. To assess the significance of the changes in individual

watersheds, we used a two-sided Mann-Kendall test ($\alpha = 0.05$). Our analysis found that applied toxicity significantly increased in 63% of watersheds (p-value < 0.001, tau = 0.9). In subwatersheds of the BDW, a similar trend was observed, with 58% of subwatersheds showing a significant increase in applied toxicity (p-value < 0.001, tau = 0.9). Although the ERT does not simulate transport of pesticides to aquatic ecosystems, these results suggest that to preserve environmental health, efforts may be required to manage increases in applied toxicity.

2.3.2 Sources

The source of 99.9% of applied toxicity (NTI) was identified in the ERT analysis to be attributed to just 14 chemicals, as outlined in **Table 1**. Among these chemicals, 10 were classified as insecticides/miticides/acaricides, while the remaining 4 were categorized as herbicides. This represents a concise list of toxicity reduction targets, considering 290 AIs were evaluated.

The analysis also revealed that the top two pesticides in terms of applied toxicity, cyhalothrin and bifenthrin, accounted for approximately 90% of the NTI, despite constituting only 1% of the applied mass. This indicates that these two AIs have a disproportionately significant contribution to the overall applied toxicity. Similarly, when focusing on subwatersheds of the BDW, bifenthrin and cyhalothrin were found to contribute approximately 90% of the applied toxicity.

Table 1. Summary of the Net Toxicity Index (NTI) from the release of evaluated pesticides which comprise 99.9% of California's active ingredient (AI) applied toxicity for 2014-2018. The results summarize the applied toxicity across all pesticides and taxonomic groups investigated (fish, invertebrates, nonvascular plants, and vascular plants).

Pesticide	Type	Class	Mass Applied (kg)	NTI	NTI (% total)
cyhalothrin	insecticide/miticide/arcaricide	pyrethroid/pyrethrin	153,540	337,877,241	59.27%
bifenthrin	insecticide/miticide/arcaricide	pyrethroid/pyrethrin	472,461	168,788,061	29.61%
cypermethrin	insecticide/miticide/arcaricide	pyrethroid/pyrethrin	69,669	21,874,831	3.84%
esfenvalerate	insecticide/miticide/arcaricide	pyrethroid/pyrethrin	78,766	16,405,165	2.88%
fenpropathrin	insecticide/miticide/arcaricide	pyrethroid/pyrethrin	116,580	6,719,464	1.18%
permethrin	insecticide/miticide/arcaricide	pyrethroid/pyrethrin	229,446	6,164,708	1.08%
chlorpyrifos	insecticide/miticide/arcaricide	organophosphate	2,129,745	3,948,126	0.69%
diflubenzuron	insecticide/miticide/arcaricide	urea	56,871	3,565,646	0.63%
malathion	insecticide/miticide/arcaricide	organophosphate	794,035	1,456,397	0.26%
oxyfluorfen	herbicide	NA	1,752,547	998,332	0.18%
paraquat dichloride	herbicide	NA	2,665,716	594,586	0.10%
cyhalothrin	insecticide/miticide/arcaricide	pyrethroid/pyrethrin	35,934	350,429	0.06%
indaziflam	herbicide	NA	54,634	252,411	0.04%
diuron	herbicide	urea	326,286	229,973	0.04%

Available surface water and sediment monitoring data during the analysis period indicate that pesticide loads identified as having high applied toxicity have been observed at lethal concentrations to the aquatic taxa investigated. For instance, in monitoring data for agricultural ditches in California for 2014-2018, all pesticides contributing to 99.9% of applied toxicity (**Table 1**), except for indaziflam, were observed at lethal concentrations or at

concentrations where plant growth is inhibited (above Aquatic Life Benchmarks)(CDPR, n.d.). Furthermore, concerning the pesticides with the highest NTIs, namely cyhalothrin and bifenthrin, it was found that all 121 samples in which they were detected exceeded the Aquatic Life Benchmarks. It is important to note that even samples where no pesticides were detected may still contain concentrations of concern. This is due to the fact that in 99% of the sample analyses (n=533), the concentrations could not be detected at levels as low as the Aquatic Life Benchmark (limit of quantification too high).

Notably, cyhalothrin and bifenthrin have a high affinity to sediment and applied toxicity to benthic invertebrates. However, our study did not include an assessment of their effects on benthic invertebrates, as the Environmental Risk Targeting (ERT) analysis was specifically designed to analyze taxa residing in the same environmental compartment (see *Section 2.2)*. Nevertheless, to understand if pesticides with high applied toxicity are reaching sediment compartments, we explored the frequency of their detection of bifenthrin and cyhalothrin and if they were observed at hazardous concentrations. For effect endpoints, we considered acute mortality values published for benthic invertebrates in the PPDB(56) (unavailable through the USEPA benchmark database).

Similar to surface water, all detections (n=161) in sediment samples (n=268) exceeded life benchmarks, indicating potentially hazardous levels of bifenthrin and cyhalothrin. Furthermore,100% of sample analyses could not detect concentrations as low as life benchmarks. For these pesticides, an ecotoxicological study in a waterbody in California,

with little development besides agriculture, has also observed lethal concentrations in sediment(72).

Notably, bifenthrin and cyhalothrin are among the most challenging pesticides to measure at levels of concern to aquatic taxa. Their benchmarks are in the parts per trillion range, and they have the lowest limit of quantification of pesticides studied except for deltamethrin. Earlier work by Parker et al. (2021) also expressed concern that the limits of quantification used in sample analyses are generally too high for a number of pesticides with high toxicity(74), further emphasizing the need to improve our knowledge in this area

Regarding California's diverse pesticide application sites as sources of environmental toxicity for the most recent 5-year data, the ERT identified 90% of toxicity (NTI) was concentrated in only 16 of the 116 site classes investigated. Out of the total released toxicity, 25% was applied to almonds, the most widely cultivated crop analyzed, and 19% was applied to pistachios. The other seven crops with the highest applied toxicity contributed 1%-11%. Furthermore, in most watersheds, a few site types contributed most of the NTI, although the sites with the highest applied toxicity varied from one watershed to another. For example, in the Salton Sea watershed, which is one of the most heavily impacted in the state, 80% of the toxicity was caused by 4 of 72 application site types: alfalfa, sweet corn, lettuce, and broccoli.

When examining the sources of applied toxicity in California's watersheds with increasing NTIs across the state, the analysis revealed that the largest increase in applied toxicity was primarily attributed to two pesticides: cyhalothrin (63%) and bifenthrin (27%). In terms of application site types in these watersheds, the highest NTI was applied to almonds (36%) and pistachios (30%). In the BDW, the rise in applied toxicity was also

primarily contributed by cyhalothrin (75%) and bifenthrin (23%) and nut orchards, with the site types with the greatest applied toxicity being almonds (75%) and walnuts (19%). It is noteworthy that these nut orchards are among the most widely cultivated crops, with almond, pistachio, and walnut orchards spanning ~800,000 ha.

2.3.3 Cumulative applied toxicity

The ERT is unique in its ability to assess the applied toxicity of all pesticides used in specific application sites over time. Typically, when evaluating the acute toxicity of pesticide mixtures, researchers often rely on a single pesticide to approximate within a given time frame, given differences in timing within a given season, application amount per event, and frequency of use of a given pesticide within a mixture (31). It is also inadequate for large areas with diverse pesticide usage patterns, where the most toxic chemical applied can vary. The cumulative applied toxicity provides a more complete representation of the potential impact. To determine whether the tool's ability to rapidly quantify cumulative applied toxicity enhances our understanding of environmental toxicity, we compared the cumulative applied toxicity to that of the single pesticide with the highest applied toxicity using one-way, paired student’s t-test, with a significance level of 0.05. This analysis was conducted for all watersheds and sites within watersheds, considering monthly and annual intervals for each of the four aquatic taxonomic groups under investigation. To provide a more robust evaluation of cumulative toxicity, the analysis of significance was performed at the watershed level rather than the overall study extent. This approach was chosen for two main reasons. Firstly, it allowed for a larger sample size (n=226), enabling a more comprehensive assessment of cumulative applied toxicity. Secondly, within a watershed, the landscape where pesticide applications occur is hydrologically connected with its waterbodies.

Results of the analysis evaluating the significance of accounting for cumulative applied toxicity demonstrated cumulative applied toxicity to be significantly greater ($p < 1.0E-16$) than the maximum applied toxicity of individual pesticides (**Figure 2**). These results are also valid when evaluating each taxonomic group at monthly and annual time steps (**Table 2**), as well as for site types in each watershed. Across taxa, extents, and time steps, the mean cumulative NTI predictions were 118-634% greater than the mean NTI of individual pesticides. The significance observed in accounting for cumulative applied toxicity aligns with previous chronic and sub-lethal mixture studies (75,76). However, our findings differ from previous studies that have focused on acute, single-sample mixture toxicity. These acute studies often suggest that toxicity can be represented by the pesticide that contributes the most toxicity (38,68). This discrepancy is likely observed because acute mixture analyses of individual samples do not account for seasonal and interannual variability (31,77–79), while our results capture greater temporal variability in pesticide use and presence.

Figure 2. Cumulative applied toxicity (red) for the simulation period versus the maximum individual pesticide NTI (blue) for fish in the ten watersheds with the highest applied toxicity in California, 2014-2018. Cumulative applied toxicity to fish was significantly greater than the maximum individual pesticide toxicity for watersheds in the study extent ($a = 0.05$, $p < 1.0E\text{-}16$).

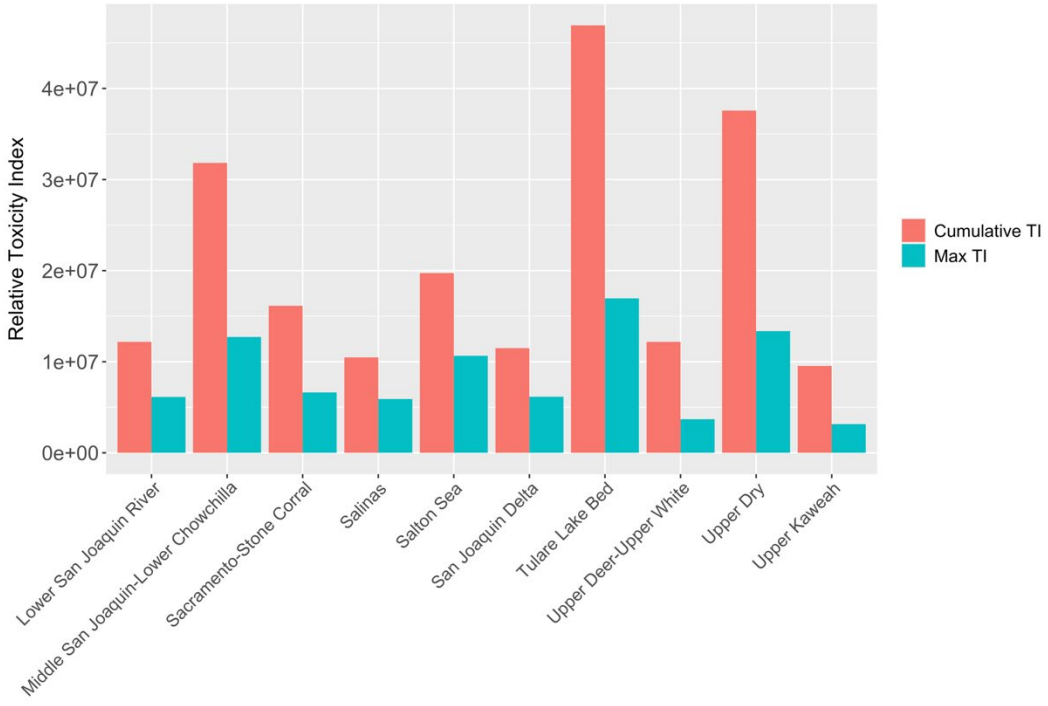


Table 2. Results are presented for the one-way, paired t-test ($\propto = 0.05$), the percent difference of means, and the median absolute percent error (MDAPE) for the maximum applied toxicity (NTI) of individual pesticides relative to the cumulative applied toxicity across California's HUC8 watersheds for the analysis period. Analyses were performed for four aquatic taxonomic groups by watershed and by site, at monthly and annual time steps. Cumulative applied toxicity was significantly greater than maximum for all taxa, sites, watersheds, and time-steps (a = 0.05, p < 1.0E-16).

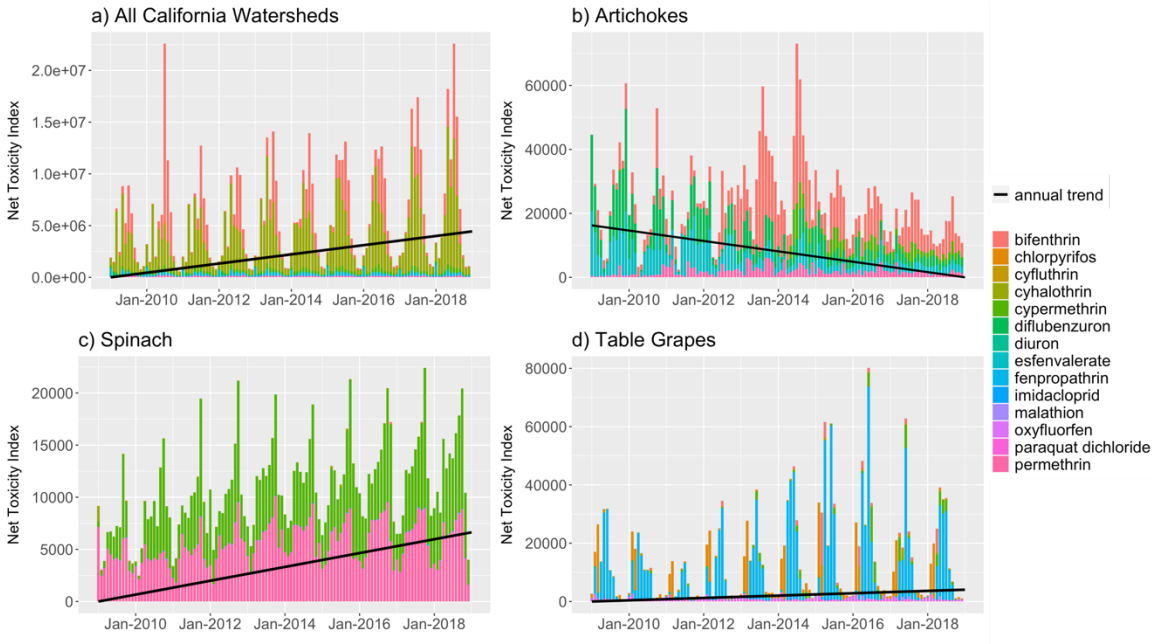
Taxonomic Group	Summary Interval	p-value	Mean of Differences (%)	MDAPE (%)
Invertebrates	Monthly Watershed	< 1.0E-16	180	31
Fish	Monthly Watershed	< 1.0E-16	218	42
Nonvascular Plants	Monthly Watershed	< 1.0E-16	217	44
Vascular Plants	Monthly Watershed	< 1.0E-16	201	40
Invertebrates	Annual Watershed	< 1.0E-16	460	68
Fish	Annual Watershed	< 1.0E-16	605	76
Nonvascular Plants	Annual Watershed	< 1.0E-16	634	76
Vascular Plants	Annual Watershed	< 1.0E-16	496	70
Invertebrates	Monthly Site Type	< 1.0E-16	118	1.4
Fish	Monthly Site Type	< 1.0E-16	126	3.3
Nonvascular Plants	Monthly Site Type	< 1.0E-16	125	5.9
Vascular Plants	Monthly Site Type	< 1.0E-16	125	4.1
Invertebrates	Annual Site Type	< 1.0E-16	208	35
Fish	Annual Site Type	< 1.0E-16	240	42
Nonvascular Plants	Annual Site Type	< 1.0E-16	248	44
Vascular Plants	Annual Site Type	< 1.0E-16	240	43

In addition to improving our understanding of net environmental toxicity, quantifying cumulative toxicity reveals notable spatiotemporal patterns for targeting toxicity reduction. Here we provide examples of the cumulative toxicity to aquatic invertebrates seasonally and interannually.

Examining monthly cumulative applied toxicity trends to invertebrates revealed that relying solely on single chemical analyses would not capture the chemical with the highest toxicity for a month or season. For example, in the first year of the simulation across all

watersheds in California, esfenvalerate had the highest individual monthly applied toxicity at the beginning of the year, followed by bifenthrin in the middle of the year, and cyhalothrin towards the end of the year (**Figure 3**). Different trends were observed for specific application sites and watersheds. In the case of the widely cultivated crop table grapes, the primary contributors to monthly cumulative applied toxicity during fall and winter were chlorpyrifos and oxyfluorfen, while most of the cumulative toxicity in summer resulted from fenpropathrin applications (**Figure 3**).

Figure 3 (a-d). Temporal trends. Temporal trends of monthly cumulative applied toxicity to aquatic invertebrates, the Net Toxicity Index (NTI), for pesticides which introduce 99.9% of released toxicity for California's HUC8 watersheds **(a)**, as well as select, high-impact crops which include artichokes **(b)**, spinach **(c)**, and table grapes **(d)**. Annual trend lines (black) illustrate average year-to-year increases in cumulative toxicity to aquatic invertebrates (NTI).



The cumulative toxicity contributed by all pesticides to a taxon also varied in intensity over the year. Grapes had the greatest monthly cumulative applied toxicity in the spring and other crops, like artichokes, in the late summer/fall (**Figure 3**). Since California's

wet season begins in late fall/winter, later pesticide applications may introduce higher pesticide concentrations in runoff than those performed earlier in the year.

Interannually for invertebrates, cumulative toxicity was observed to increase in California's watersheds. Year-to-year, a significant increase was revealed by a Mann-Kendall test ($\propto = 0.95$, $p<0.001$), with an average increase over the study extent of 7.6%. While some sites, such as spinach, exhibited similar trends with a 6.9% increase, there were significant differences observed, highlighting the need for targeted risk reduction. Artichokes showed a mean year-to-year NTI decrease of -6.9%, making them a less effective target compared to table grapes, which had a higher NTI and an average yearly increase in toxicity of 2.8% (**Figure 3**).

2.3.4 Economic and health scores

To evaluate the trade-offs between the health and economic impacts of reducing the toxicity of application sites, we calculated health and economic scores. A higher score indicates a more favorable outcome. The Health Score (ha/NTI) considers the cultivated hectares and the applied toxicity of site types. Of application sites contributing 90% of the applied toxicity, crops with the lowest Health Score (greatest applied toxicity per hectare) include strawberries, sweet corn, and pistachios (**Table 3**). Among these three crops, the Economic Score, as well as the Economic and Health Score, were least favorable for sweet corn and most advantageous for strawberries. Our findings suggest sweet corn may have the lowest health and economic benefit with contemporary pesticide use practices of the study area and should be targeted in mitigation efforts.

Table 3. Environmental Release Tool outputs for pesticide application site types which introduce 90% of the applied toxicity in California where: NTI the Net Toxicity Index; NTI (%) the percent of the total NTI of the application site type; Economic, Economic Health, and Health Scores reflect the numeric score of different site types; and the Economic, Economic Health, and Health Values the quantiles of scores where 0-20th quantile is 'Very Low' and 80-100th 'Very High'.

Site Type	NTI	NTI (% Total)	Economic Score (USD/ha)	Economic Health Score (USD/NTI)	Health Score (NTI/ha)	Relative Economic Score	Relative Economic Health Score	Relative Health Score
Almond	1.41E+08	24.7	1.32E+04	2.78E+02	2.11E-02	3-Medium	2-Low	2-Low
Pistachio	1.07E+08	18.8	1.32E+04	1.86E+02	1.42E-02	3-Medium	2-Low	1-Very Low
Alfalfa	6.08E+07	10.7	1.58E+03	1.64E+02	1.04E-01	1-Very Low	1-Very Low	4-High
Lettuce	4.59E+07	8.0	1.75E+03	2.67E+02	1.53E-01	2-Low	2-Low	4-High
Walnut	2.96E+07	5.2	9.95E+03	2.54E+02	2.55E-02	3-Medium	2-Low	2-Low
Rice	2.84E+07	5.0	1.21E+03	1.91E+03	1.58E+00	1-Very Low	4-High	5-Very High
Cotton	2.09E+07	3.7	1.24E+02	6.74E+00	5.45E-02	1-Very Low	1-Very Low	3-Medium
Tomato (Processing)	2.03E+07	3.6	8.57E+03	4.00E+02	4.67E-02	2-Low	2-Low	3-Medium
Corn (Sweet)	1.53E+07	2.7	5.74E+03	5.27E+01	9.17E-03	2-Low	1-Very Low	1-Very Low
Broccoli	8.71E+06	1.5	8.98E+03	2.70E+02	3.01E-02	3-Medium	2-Low	2-Low
Cherry	7.66E+06	1.3	5.84E+03	8.68E+02	1.48E-01	2-Low	4-High	4-High
Peach	6.36E+06	1.1	8.61E+03	3.25E+02	3.77E-02	2-Low	2-Low	3-Medium
Strawberry	5.93E+06	1.0	1.25E+05	8.57E+02	6.88E-03	5-Very High	4-High	1-Very Low
Orange	5.67E+06	1.0	4.51E+02	1.29E+01	2.86E-02	1-Very Low	1-Very Low	2-Low
Onion Misc.	4.09E+06	0.7	1.83E+04	3.05E+02	1.67E-02	3-Medium	2-Low	2-Low
Bean (Dry)	3.75E+06	0.7	1.42E+03	1.77E+02	1.25E-01	1-Very Low	1-Very Low	4-High

2.3.5 Toxicity Reduction Targets

To prioritize targets for reducing pesticide toxicity, we used the ERT to identify a shortlist of pesticides, application site types, and watersheds responsible for 80% or more of the applied toxicity. If efforts targeted just one pesticide, or one pesticide and application site type, it would act on 50% or more of the applied toxicity for 89% of watersheds in California. However, the specific pesticide or pesticide and site type with the most applied toxicity varied by watershed.

The accuracy of the ERT for predicting applied toxicity with available information depends on the reliability of pesticide use assignment to watersheds (see *Section 2.2*). To evaluate the accuracy of applied mass of pesticides to watersheds with the CDPR database

(resolution of 2.6 km^2), ERT predictions using these data were compared to predictions that employed pesticide use data available at the field level in Kern County. The evaluation showed the ERT provides a reasonable estimate of the spatiotemporal distribution of pesticides, with an observed MdAPE of 1.7% for AIs applied in watersheds. Furthermore, all predictions of the applied mass of pesticides to watersheds were within 5% of the field-level data. An improved MdAPE of 0.01% was observed for application site predictions per watershed.

2.4.0 Discussion

We introduce the Environmental Release Tool to enable users to target toxicity reduction strategies. It caters to experts and nonexperts and provides insights into reduction strategies at various scales and temporal resolutions, identifies sources of toxicity, quantifies variation in cumulative toxicity, and provides economic and health scores for application site types. The tool provides a statewide, clickable heatmap interface with graphical and tabular summaries highlighting high-impact AIs and including application site health and economic impact scores to achieve these aims.

In our study of toxicity reduction opportunities in California, nut orchards had the highest applied toxicity when considering the net toxicity for all taxonomic groups evaluated which includes fish, aquatic invertebrates, nonvascular plants, and vascular plants. Most applied toxicity resulted from pyrethroids, particularly cyhalothrin and bifenthrin. In most of California's watersheds, over half of applied toxicity within a watershed could be targeted by considering the pesticide with the greatest NTI for the watershed, and for the site type with the highest NTI, the pesticide of greatest applied toxicity for the simulation period. However,

our analysis of the cumulative applied toxicity revealed that for each watershed and taxonomic group, cumulative toxicity was significantly greater than the maximum of any pesticide for monthly or annual time steps (at the annual time-step, typically over 460%). These results indicate that while targeting a short list of pesticides within a watershed can address most applied toxicity, an evaluation of cumulative pesticide impacts is required to understand environmental toxicity, and are congruent with other investigations(31,80). Notably, the pesticides observed to have the highest impact also commonly share the same mode of action. For pesticides responsible for 99.9% of the applied toxicity (net of all investigated taxa), 7 of 13 affect neurotransmission via sodium ion-gated channels of neurons(81). Though conservative assumptions are often employed when individual pesticide indices are used as an index of toxicity, these results and previous work(38,82) demonstrate the need to consider cumulative impacts, despite challenges in modeling and regulating mixture toxicity in the environment(41).

For toxicity reduction efforts, the ERT can prove an important complement to monitoring campaigns. The tool can identify which watersheds and application site types require further investigation for pesticides difficult to detect at hazardous levels, such as pyrethroids and neonicotinoids, for which effects are observed in the parts per trillion range(64). This need was observed for the two pesticides with the highest applied toxicity, cyhalothrin and bifenthrin (pyrethroids). Monitoring data for the pesticides reported in the CDPR Surface Water Database(73), which includes data from the CDPR, United States Geological Survey, the California State Water Resources Control Board, and other municipalities and researchers, could not detect the concentrations of AIs as low as their Aquatic Life Benchmark in 99% of samples. Further investigations of pesticide impacts may

include monitoring with improved limits of quantification or employing fate and transport models to generate predicted environmental concentrations for risk assessment. Agencies such as the CDPR already employ models to prioritize future monitoring efforts(83), and tools such as the ERT can assist others in planning monitoring campaigns. However, it is essential to note that pesticides with high applied toxicity may have a low potential for transport to surface water, and vice versa, owing to their unique physicochemical properties(84). Therefore, users should compare the applied toxicity for the same pesticide across site types and watersheds when prioritizing further investigations to avoid this variation affecting prioritization efforts.

The evaluation of opportunities for best management practices for toxicity mitigation is also supported by the ERT. In California, bifenthrin use on strawberries and oranges, two of the highest impact application site types, introduced the greatest applied toxicity. Based on this information, near-field evaluations of bifenthrin in runoff and eroded sediment from the crop fields could be prioritized to quantify aquatic taxa risk. If risks are identified, mitigation options can be explored based on crop value. For strawberries whose Economic Score is 'Very High', financial resources may exist to implement mitigation infrastructure such as detention ponds or to upgrade irrigation technologies. For crops with a 'Very Low' Economic Score, such as oranges, chemical alternatives, integrated pesticide mitigation practices, or incentives for cultivating lower-impact crops may be preferred for at-risk areas. While the ERT does not consider important factors such as the cost of cultivation, it can still serve to prioritize application sites for further investigation based on available crop value data.

Another mitigation option, which may lead to unintended consequences, is the discouragement or ban of pesticides for the benefit of a single species. For instance, consumers or agencies may consider discontinuing the use of glyphosate (banned in 20 countries(85)) to reduce applied toxicity to humans. However, information about the human health impacts of glyphosate remains uncertain(86), and replacement AIs could increase toxicity for other taxa(87). In this study for four aquatic taxonomic groups, AI forms of glyphosate ranked 69th or greater of the pesticides investigated for applied toxicity, although it had the highest applied mass. Glufosinate-ammonium, a common alternative, has very similar application rates per treatment area but introduced an order of magnitude greater applied ecotoxicity to evaluated taxa, despite its applied mass being 10-fold lower. Moreover, it is more mobile and similarly persistent to glyphosate. Due to glyphosate's lower aquatic toxicity and mobility in the aqueous phase, using glufosinate-ammonium as an alternative could shift greater toxicity to aquatic taxa. The shift from human to aquatic toxicity may already occur due to California's recent ban on chlorpyrifos(74). Hence, when implementing pesticide bans or restrictions, the ERT can help prioritize further investigation to reduce applied toxicity to diverse taxa.

An important limitation of the ERT is that it does not predict pesticide risk, it provides valuable insights for toxicity reduction opportunities. Risk prediction depends on receptor exposure(88) and factors governing the fate of pesticides(89). Though simulating and monitoring the fate of pesticides and organism exposure is imperative to risk assessment, given data paucity for many pesticides and watersheds for model parameterization and calibration(55), we determined an applied toxicity tool to be important to informing mitigation efforts. Key factors that affect exposure, such as the pesticide application method

to drift, the irrigation method and schedule, and the location of tiling or detention ponds, are unknown for most application areas. Other toxicity index tools, such as the PURE[14], also do not simulate the processes of pesticide fate and exposure, rather, they weight toxicity indices by pesticide susceptibility to transformation and transport(14). This feature is not integrated into the ERT given the uncertainty of these approaches is unknowable for the heterogeneous conditions that exist(14) and the physicochemical properties of pesticides which render different effects on their fate under typical environmental conditions. Aerobic degradation alone is highly variable; an investigation of 10 pesticides in 8 soil types under identical conditions demonstrated a mean difference of 540% in the minimum and maximum half-lives of the investigated pesticides.(90) Furthermore, while the transport of pesticides to surface water bodies is sensitive to their physicochemical properties(52), property correlation to surface water detection frequencies has been demonstrated to more robust for pesticide sales. Halbach et al. (2021) performed a 2-year monitoring campaign of 76 pesticides in over 100 streams, and evaluated the explanatory power of pesticide sales data, the half-life of pesticides in water and soil, and solubility. The most robust relationship was for pesticide sales, and significance for the other factors was only observed for the half-life in water(53).

2.5.0 Conclusion

Our study developed the Environmental Release Tool (ERT) to provide an integrated framework for targeting pesticide toxicity reductions. We applied the tool to high-resolution pesticide use data to quantify toxicity released to aquatic taxa in California, representing ~20% of the pesticide mass in the United States and covering hundreds of commodities(46,47). The ERT demonstrated that mitigation actions on just two pesticides

and sixteen site types would affect ~90% of applied toxicity to fish, aquatic invertebrates, nonvascular plants, and vascular plants in California's agricultural landscapes. In addition, for each watershed, if the mitigation focus was solely on the pesticide of highest impact, and the primary source of toxicity to the greatest impact application site type, it would affect over 50% of agricultural applied toxicity in most of California's watersheds. These findings were consistent across large and small watersheds, though the high-impact sources varied. Our results indicate that the ERT can be a valuable tool for identifying pesticide environmental toxicity and should be considered in future agricultural management strategies.

2.6 References

1. Sharma A, Shukla A, Attri K, Kumar M, Kumar P, Suttee A, Singh G, Barnwal RP, Singla N. Global trends in pesticides: A looming threat and viable alternatives. Ecotoxicol Environ Saf. 2020 Sep 15;201:110812.
2. Malaj E, von der Ohe PC, Grote M, Kühne R, Mondy CP, Usseglio-Polatera P, Brack W, Schäfer RB. Organic chemicals jeopardize the health of freshwater ecosystems on the continental scale. Proc Natl Acad Sci USA. 2014 Jul 1;111(26):9549–54.
3. Bradley PM, Journey CA, Romanok KM, Barber LB, Buxton HT, Foreman WT, Furlong ET, Glassmeyer ST, Hladik ML, Iwanowicz LR, Jones DK, Kolpin DW, Kuivila KM, Loftin KA, Mills MA, Meyer MT, Orlando JL, Reilly TJ, Smalling KL, Villeneuve DL. Expanded Target-Chemical Analysis Reveals Extensive Mixed-Organic-Contaminant Exposure in U.S. Streams. Environ Sci Technol. 2017 May 2;51(9):4792–802.
4. Stehle S, Schulz R. Agricultural insecticides threaten surface waters at the global scale. Proc Natl Acad Sci USA. 2015 May 5;112(18):5750–5.
5. Goulson D, Nicholls E, Botías C, Rotheray EL. Bee declines driven by combined stress from parasites, pesticides, and lack of flowers. Science. 2015 Mar 27;347(6229):1255957.
6. Kudsk P, Jørgensen LN, Ørum JE. Pesticide Load–A new Danish pesticide risk indicator with multiple applications. Land use policy. 2018 Jan;70:384–93.
7. State of California. California State Budget 2021-2022. State of California; 2021.
8. European Commission. Farm to Fork Strategy. COM/2019/640 2020.
9. Young DF, Fry MM. PRZM5 A Model for Predicting Pesticides in Runoff, Erosion, and Leachate–Revision B . USEPA; 2020 Aug.
10. Alterra - Environmental risk assessment, WOT Natuur & Milieu, ter Horst MMS, Beltman WHJ, van den Berg F. The TOXSWA model version 3.3 for pesticide behaviour in small surface waters : description of processes. Wageningen: Statutory Research Tasks Unit for Nature & the Environment; 2016.

11. Pistocchi A, Groenwold J, Lahr J, Loos M, Mujica M, Ragas AMJ, Rallo R, Sala S, Schlink U, Strebel K, Vighi M, Vizcaino P. Mapping Cumulative Environmental Risks: Examples from the EU NoMiracle Project. Environ Model Assess. 2011 Apr;16(2):119–33.
12. Schriever CA, Liess M. Mapping ecological risk of agricultural pesticide runoff. Sci Total Environ. 2007 Oct 1;384(1–3):264–79.
13. Strassemeyer J, Daehmlow D, Dominic AR, Lorenz S, Golla B. SYNOPS-WEB, an online tool for environmental risk assessment to evaluate pesticide strategies on field level. Crop Prot. 2017 Jul;97:28–44.
14. Zhan Y, Zhang M. PURE: a web-based decision support system to evaluate pesticide environmental risk for sustainable pest management practices in California. Ecotoxicol Environ Saf. 2012 Aug;82:104–13.
15. Ropke B, Bach M, Frede H. DRIPS—a DSS for estimating the input quantity of pesticides for German river basins. Environmental Modelling & Software. 2004 Nov;19(11):1021–8.
16. AGIS Lab, University of California, Davis. PUR Web GIS (Internet). (cited 2021 May 3). Available from: http://purwebgis.ucdavis.edu/PURwebGIS.html
17. Maggi F, Tang FHM, la Cecilia D, McBratney A. PEST-CHEMGRIDS, global gridded maps of the top 20 crop-specific pesticide application rates from 2015 to 2025. Sci Data. 2019 Sep 12;6(1):170.
18. U.S. Congress. The Code of Laws of the United States of America. Title 7 2012.
19. European Commission. DIRECTIVE 2009/128/EC. 2009.
20. Srinivasan R, Ramanarayanan TS, Arnold JG, Bednarz ST. Large area hydrologic modeling and assessment part ii: model application. J Am Water Resources Assoc. 1998 Feb;34(1):91–101.
21. Arnold JG, Srinivasan R, Muttiah RS, Williams JR. Large area hydrologic modeling and assessment part i: model development. J Am Water Resources Assoc. 1998 Feb;34(1):73–89.
22. Wang R, Yuan Y, Yen H, Grieneisen M, Arnold J, Wang D, Wang C, Zhang M. A review of pesticide fate and transport simulation at watershed level using SWAT: Current status and research concerns. Sci Total Environ. 2019 Jun 15;669:512–26.
23. USEPA. Hydrological Simulation Program - FORTRAN (HSPF) (Internet). (cited 2020 Feb 10). Available from: https://www.epa.gov/ceam/hydrological-simulation-program-fortran-hspf
24. Xie H, Lian Y. Uncertainty-based evaluation and comparison of SWAT and HSPF applications to the Illinois River Basin. J Hydrol (Amst). 2013 Feb;481:119–31.
25. A. Saleh and B. Du. Evaluation of SWAT and HSPF within BASINS program for the Upper North Bosque River Watershed in central Texas. Transactions of the ASAE. 2004;47(4):1039–49.
26. Zheng Y, Keller AA. Understanding parameter sensitivity and its management implications in watershed-scale water quality modeling. Water Resour Res. 2006 May;42(5).
27. Srivastava P, Migliaccio K, Simunek J. LANDSCAPE MODELS FOR SIMULATING WATER QUALITY AT POINT, FIELD, AND WATERSHED SCALES. ASABE. 2007;50(5):1683–93.

28. Leu C, Singer H, Stamm C, Müller SR, Schwarzenbach RP. Variability of herbicide losses from 13 fields to surface water within a small catchment after a controlled herbicide application. Environ Sci Technol. 2004 Jul 15;38(14):3835–41.
29. Luo Y, Zhang M. Spatially distributed pesticide exposure assessment in the Central Valley, California, USA. Environ Pollut. 2010 May;158(5):1629–37.
30. Boithias L, Sauvage S, Srinivasan R, Leccia O, Sánchez-Pérez J-M. Application date as a controlling factor of pesticide transfers to surface water during runoff events. CATENA. 2014 Aug;119:97–103.
31. Curchod L, Oltramare C, Junghans M, Stamm C, Dalvie MA, Röösli M, Fuhrimann S. Temporal variation of pesticide mixtures in rivers of three agricultural watersheds during a major drought in the Western Cape, South Africa. Water Research X. 2020 Jan 1;6:100039.
32. Baker N, Stone W. Estimated Annual Agricultural Pesticide Use for Counties of the Contimerous United States, 2008-12. USGS; 2015.
33. California Department of Pesticide Regulation. A Guide to Pesticide Regulation in California. CDPR; 2017.
34. Stone WW, Gilliom RJ, Ryberg KR. Pesticides in U.S. streams and rivers: occurrence and trends during 1992-2011. Environ Sci Technol. 2014 Oct 7;48(19):11025–30.
35. Sanders C, Orlando J, Hladik M. Detections of Current-Use Pesticides at 12 Surface Water Sites in California During a 2-Year Period Beginning in 2015. USGS; 2018.
36. De Parsia M, Woodward EE, Orlando JL, Hladik ML. Pesticide Mixtures in the Sacramento–San Joaquin Delta, 2016–17: Results from Year 2 of the Delta Regional Monitoring Program. USGS; 2019 p. 33. Report No.: 1120.
37. Covert SA, Shoda ME, Stackpoole SM, Stone WW. Pesticide mixtures show potential toxicity to aquatic life in U.S. streams, water years 2013-2017. Sci Total Environ. 2020 Nov 25;745:141285.
38. Nowell LH, Moran PW, Schmidt TS, Norman JE, Nakagaki N, Shoda ME, Mahler BJ, Van Metre PC, Stone WW, Sandstrom MW, Hladik ML. Complex mixtures of dissolved pesticides show potential aquatic toxicity in a synoptic study of Midwestern U.S. streams. Sci Total Environ. 2018 Feb 1;613–614:1469–88.
39. USEPA. Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) and Federal Facilities (Internet). (cited 2019 Mar 5). Available from: https://www.epa.gov/enforcement/federal-insecticide-fungicide-and-rodenticide-act-fifra-and-federal-facilities
40. California Regional Water Quality Control Board. Amendment to the Water Quality Control Plan for the Sacramento River and San Joaquin River Basins for the Control of Pyrethroid Pesticide Discharges. R5-2017–0057 2017.
41. Lydy M, Belden J, Wheelock C, Hammock B, Denton D. Challenges in regulating pesticide mixtures. E&S. 2004;9(6).
42. Rodney SI, Teed RS, Moore DRJ. Estimating the toxicity of pesticide mixtures to aquatic organisms: A review. Human and Ecological Risk Assessment: An International Journal. 2013 Nov 2;19(6):1557–75.
43. Shoda ME, Stone WW, Nowell LH. Prediction of pesticide toxicity in midwest streams. J Environ Qual. 2016 Nov;45(6):1856–64.
44. Zilberman D, Schmitz A, Casterline G, Lichtenberg E, Siebert J. The Economics of Pesticide Use and Regulation. Science. 1991 Aug 2;253:518–22.

45. Goodhue RE, Bolda M, Farnsworth D, Williams JC, Zalom FG. Spotted wing drosophila infestation of California strawberries and raspberries: economic analysis of potential revenue losses and control costs. Pest Manag Sci. 2011 Nov;67(11):1396–402.
46. Atwood D, Paisley-Jones C. Pesticide Industry Sales and Usage – 2008-2012 Market Estimates. U.S. Environmental Protection Agency; 2017.
47. CDPR. Summary of Pesticide Use Report Data 2017 (Internet). 2019 (cited 2019 Oct 17). Available from: https://www.cdpr.ca.gov/docs/pur/pur17rep/17sum.htm
48. RStudio Team. RStudio: Integrated Development for R. RStudio; 2020.
49. DiBartolomeis M, Kegley S, Mineau P, Radford R, Klein K. An assessment of acute insecticide toxicity loading (AITL) of chemical pesticides used on agricultural land in the United States. PLoS ONE. 2019 Aug 6;14(8):e0220029.
50. USGS, USDA. Federal Standards and Procedures for the National Watershed Boundary Dataset (WBD). US Geological Survey Techniques and Methods 11-A3. 2nd ed. 2011.
51. California Department of Pesticide Regulation. Summary of Pesticide Use Report Data 2018. California Department of Pesticide Regulation; 2020.
52. Xie Y, Luo Y, Singhasemanon N, Goh KS. Regulatory modeling of pesticide aquatic exposures in california's agricultural receiving waters. J Environ Qual. 2018;47(6):1453–61.
53. Halbach K, Möder M, Schrader S, Liebmann L, Schäfer RB, Schneeweiss A, Schreiner VC, Vormeier P, Weisner O, Liess M, Reemtsma T. Small streams-large concentrations? Pesticide monitoring in small agricultural streams in Germany during dry weather and rainfall. Water Res. 2021 Sep 15;203:117535.
54. United States Environmental Protection Agency Office of Pollution Prevention and Toxics. EPA's Risk-Screening Environmental Indicators (RSEI) Methodology. Washington D.C.: United States Environmental Protection Agency; 2020 Dec.
55. Dubus IG, Brown CD, Beulke S. Sources of uncertainty in pesticide fate modelling. Sci Total Environ. 2003 Dec 30;317(1–3):53–72.
56. Agriculture and Environment Research Unit, University of Hertfordshire. PPDB - Pesticides Properties DataBase (Internet). (cited 2018 Oct 20). Available from: https://sitem.herts.ac.uk/aeru/ppdb/en/
57. USDA. CropScape - NASS CDL Program (Internet). (cited 2018 Mar 19). Available from: https://nassgeodata.gmu.edu/CropScape/
58. Multi-Resolution Land Characteristics (MRLC) Consortium. National Land Cover Database (NLCD) (Internet). (cited 2019 Jun 6). Available from: https://www.mrlc.gov/data?f%5B0%5D=category%3Aland%20cover&f%5B1%5D=category%3Aurban%20imperviousness&f%5B2%5D=region%3Aconus&f%5B3%5D=category%3Aland%20cover&f%5B4%5D=category%3Aurban%20imperviousness&f%5B5%5D=region%3Aconus
59. CADWR Land Use Viewer (Internet). (cited 2019 Jul 10). Available from: https://gis.water.ca.gov/app/CADWRLandUseViewer/
60. USDA. 2017 Census of Agriculture . USDA; 2019 Apr. Report No.: AC-17-A-51.
61. Sprague JB, Ramsay BA. Lethal levels of mixed copper–zinc solutions for juvenile salmon. J Fish Res Bd Can. 1965 Feb;22(2):425–32.

62. Bliss CI. The toxicity of poisons applied jointly. Ann Applied Biology. 1939 Aug;26(3):585–615.
63. Belden JB, Brain RA. Incorporating the joint toxicity of co-applied pesticides into the ecological risk assessment process. Integr Environ Assess Manag. 2018 Jan;14(1):79–91.
64. Nowell LH, Norman JE, Moran PW, Martin JD, Stone WW. Pesticide Toxicity Index--a tool for assessing potential toxicity of pesticide mixtures to freshwater aquatic organisms. Sci Total Environ. 2014 Apr 1;476–477:144–57.
65. Belden JB, Gilliom RJ, Lydy MJ. How well can we predict the toxicity of pesticide mixtures to aquatic life? Integr Environ Assess Manag. 2007 Jul;3(3):364–72.
66. Deneer JW. Toxicity of mixtures of pesticides in aquatic systems. Pest Manag Sci. 2000 Jun;56(6):516–20.
67. Anderson BS, Phillips BM, Voorhees JP, Deng X, Geraci J, Worcester K, Tjeerdema RS. Changing patterns in water toxicity associated with current use pesticides in three California agriculture regions. Integr Environ Assess Manag. 2018 Mar;14(2):270–81.
68. von der Ohe PC, De Deckere E, Prüss A, Muñoz I, Wolfram G, Villagrasa M, Ginebreda A, Hein M, Brack W. Toward an integrated assessment of the ecological and chemical status of European river basins. Integr Environ Assess Manag. 2009 Jan;5(1):50–61.
69. Dietterich TG. Approximate statistical tests for comparing supervised classification learning algorithms. Neural Comput. 1998 Sep 15;10(7):1895–923.
70. Center for Biological Diversity. San Francisco Bay Area and Delta Protection (Internet). (cited 2019 Oct 18). Available from: https://www.biologicaldiversity.org/campaigns/san_francisco_bay_area_and_delta_protection/index.html#
71. Armstrong JS, Collopy F. Error measures for generalizing about forecasting methods: Empirical comparisons. Int J Forecast. 1992 Jun;8(1):69–80.
72. Weston DP, Zhang M, Lydy MJ. Identifying the cause and source of sediment toxicity in an agriculture-influenced creek. Environ Toxicol Chem. 2008 Apr;27(4):953–62.
73. CDPR. Surface Water Database (Internet). (cited 2018 Oct 20). Available from: https://www.cdpr.ca.gov/docs/emon/surfwtr/surfcont.htm
74. Parker N, Keller AA. Screening ecological risk of pesticides and emerging contaminants under data limited conditions - Case study modeling urban and agricultural watersheds with OrganoFate. Environ Pollut. 2021 Jul 4;288:117662.
75. Hernández AF, Gil F, Lacasaña M. Toxicological interactions of pesticide mixtures: an update. Arch Toxicol. 2017 Oct;91(10):3211–23.
76. Bundschuh M, Goedkoop W, Kreuger J. Evaluation of pesticide monitoring strategies in agricultural streams based on the toxic-unit concept--experiences from long-term measurements. Sci Total Environ. 2014 Jun 15;484:84–91.
77. Yu S. The Toxicology and Biochemistry of Insecticides. 2nd ed. Boca Raton: CRC Press; 2008.
78. Stehle S, Knäbel A, Schulz R. Probabilistic risk assessment of insecticide concentrations in agricultural surface waters: a critical appraisal. Environ Monit Assess. 2013 Aug;185(8):6295–310.

79. Beketov MA, Kefford BJ, Schäfer RB, Liess M. Pesticides reduce regional biodiversity of stream invertebrates. Proc Natl Acad Sci USA. 2013 Jul 2;110(27):11039–43.
80. Weisner O, Frische T, Liebmann L, Reemtsma T, Roß-Nickoll M, Schäfer RB, Schäffer A, Scholz-Starke B, Vormeier P, Knillmann S, Liess M. Risk from pesticide mixtures - The gap between risk assessment and reality. Sci Total Environ. 2021 Nov 20;796:149017.
81. Casida JE. Pest toxicology: the primary mechanisms of pesticide action. Chem Res Toxicol. 2009 Apr;22(4):609–19.
82. Mullin CA, Frazier M, Frazier JL, Ashcraft S, Simonds R, Vanengelsdorp D, Pettis JS. High levels of miticides and agrochemicals in North American apiaries: implications for honey bee health. PLoS ONE. 2010 Mar 19;5(3):e9754.
83. Luo Y. Methodology for Prioritizing Pesticides for Surface Water Monitoring in Agricultural and Urban Areas III: Watershed-Based Prioritization. CDPR; 2015.
84. Luo Y, Zhang M. Management-oriented sensitivity analysis for pesticide transport in watershed-scale water quality modeling using SWAT. Environ Pollut. 2009 Dec;157(12):3370–8.
85. Meftaul IM, Venkateswarlu K, Dharmarajan R, Annamalai P, Asaduzzaman M, Parven A, Megharaj M. Controversies over human health and ecological impacts of glyphosate: Is it to be banned in modern agriculture? Environ Pollut. 2020 Aug;263(Pt A):114372.
86. Tarazona JV, Court-Marques D, Tiramani M, Reich H, Pfeil R, Istace F, Crivellente F. Glyphosate toxicity and carcinogenicity: a review of the scientific basis of the European Union assessment and its differences with IARC. Arch Toxicol. 2017 Aug;91(8):2723–43.
87. Morrissey CA, Mineau P, Devries JH, Sanchez-Bayo F, Liess M, Cavallaro MC, Liber K. Neonicotinoid contamination of global surface waters and associated risk to aquatic invertebrates: a review. Environ Int. 2015 Jan;74:291–303.
88. USEPA. Guidelines for Ecological Risk Assessment. USEPA; 1998. Report No.: FRL-6011-2.
89. Mackay D. Multimedia Environmental Models–The Fugacity Approach. 2nd ed. Lewis Publishers; 2001.
90. Kah M, Beulke S, Brown CD. Factors influencing degradation of pesticides in soil. J Agric Food Chem. 2007 May 30;55(11):4487–92.

2.7 Environmental Release Tool User Guide

Throughout the United States, a high degree of pesticide toxicity is introduced into the environment and has been observed to have severe effects on pollinators and aquatic taxa.(1–7) In California, 13% of river and stream reaches assessed for non-point sources by California Environmental Protection Agency under section 303(d) of the Clean Water Act are impaired by pesticides(8). Other mitigation tools are available to derive toxicity reduction strategies which include fate models(9,10), toxicity/risk maps(11,12), risk indices(13–15), and summaries of pesticide use(16,17). However, the individual tools are limited by their ability to evaluate large extents, toxicity sources, cumulative toxicity, and ability to consider the economic benefits of application sites. To improve the information available for pesticide mitigation via integrating features that address these limitations, we have developed the Environmental Release Tool (ERT) for experts, stakeholders, and the public. The tool is the first stage of development for the Pesticide Mitigation Prioritization Model (the second stage is a companion fate model) and quantifies the spatiotemporal distribution of applied toxicity, defined here as the mass of pesticide released into the environment, weighted by toxicity to user-defined priority species.

The ERT accommodates analyses anywhere users can provide pesticide use data but is particularly useful in California. The California Department of Pesticide Regulation (CDPR) hosts the world's most comprehensive pesticide use data(18). Their Pesticide Use Reports (PUR) database(19) comprises agricultural pesticide applications recorded at the daily time step and 1 square mile (2.6 km^2) area by application site. We have leveraged the database directly into the ERT to quantify the applied toxicity by active ingredient, source, and watershed across California in seconds to minutes. While many regions have minimal

pesticide use data relative to California, new resources are being developed to provide use estimates for common crops and pesticides such as PEST-CHEMGRIDS(17). These datasets, or future pesticide use collection efforts, can be leveraged with tools such as the ERT to explore mitigation opportunities for reducing environmental toxicity. For study areas where data is unavailable, users may consider employing pesticide use rates for crops observed in California due to pesticide use being recorded for over 400 unique agricultural application sites over more than 400,000 km^2, the mass of pesticides applied is ~20% of that used in the US.(20,21)

2.7.1 Environmental Release Tool Methods

The ERT quantifies toxicity reduction targets by chemical, application site, and watershed for the study area of interest. Reduction targets are quantified by the applied toxicity, defined herein as the mass of pesticide released into the environment as weighted by toxicity to species targeted by tool users. Each pesticide may have very different applied toxicity relative to applied mass, with some being hundreds to thousands of times more toxic for the same amount applied. It is suitable for designing toxicity reduction strategies and planning monitoring campaigns by identifying areas where higher toxicity is released in the environment, which could introduce health hazards to aquatic taxa, terrestrial taxa, or humans. The tool ranks application sites and watersheds by their applied toxicity.

This tool does not quantify fate or exposure but rather illustrates the location and amount of applied toxicity(22) for designing toxicity reduction strategies and planning monitoring campaigns by identifying areas where higher toxicity is released in the environment, and its sources. Although the ERT is a spatial tool designed for large extents, the tool works best to understand sources of pesticide exposures for species with a small

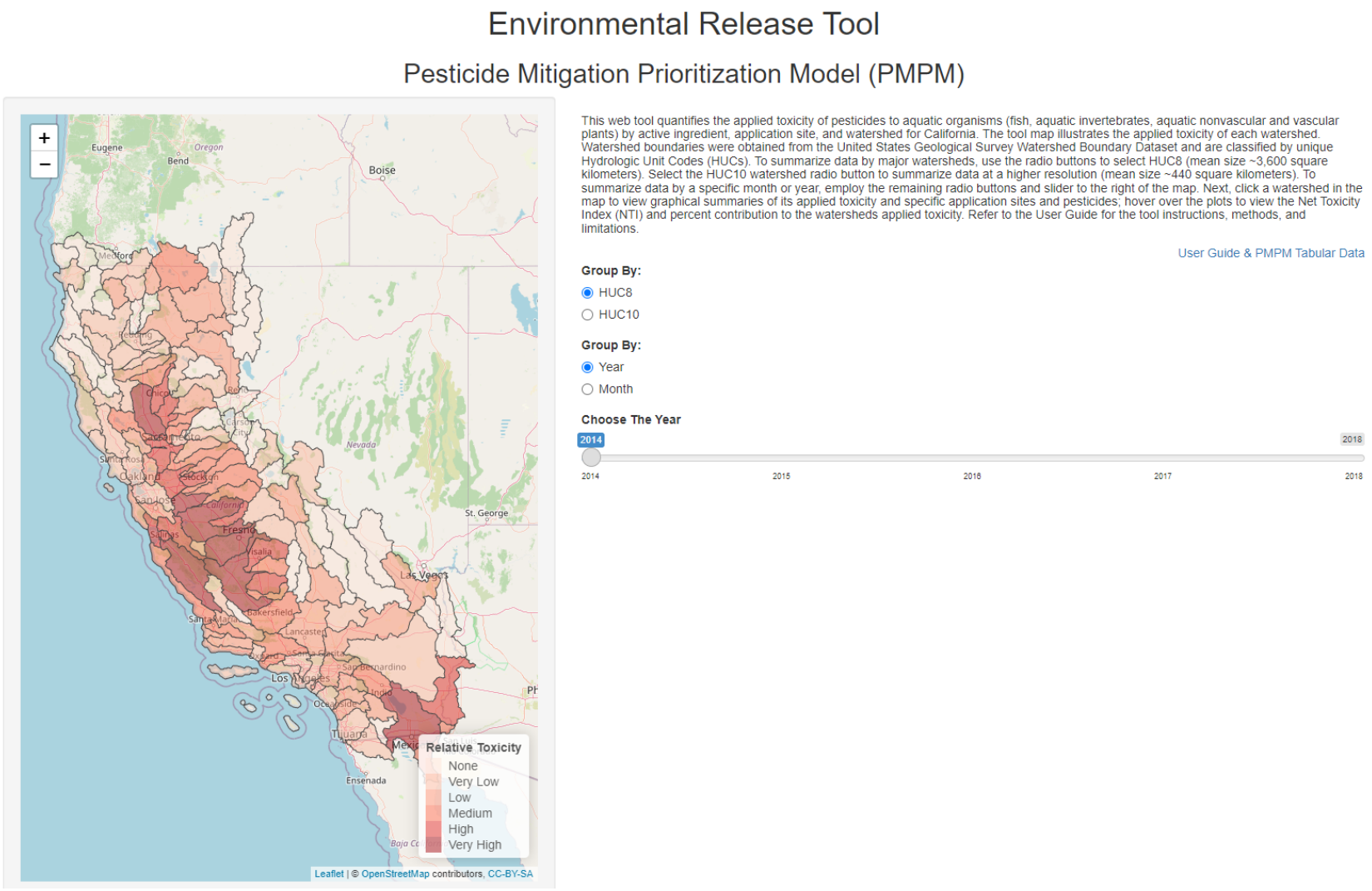
habitat range. For organisms whose activities are more widespread, such as feeding behaviors, and who have less direct contact with environmental compartments where pesticides are most likely to persist, the location of applied toxicity may be less useful for understanding sources of potential exposure. For aquatic organisms, though the transport of pesticides to surface water bodies is sensitive to their physicochemical properties(23), physicochemical property correlation to surface water detection frequencies has been demonstrated to be weaker than for pesticide sales data. Halbach et al. (2021) performed a 2-year monitoring campaign of over 100 streams. They investigated the explanatory power of pesticide frequency of detection with pesticide sales data, the half-life of pesticides in water and soil, and solubility for 76 active ingredients. The most robust relationship was for pesticide sales, and significance for the other factors was only observed for the half-life in water.(24) Though simulating and monitoring the fate of pesticides and organism exposure is imperative to risk assessment, given data paucity for many pesticides and environments for model parameterization and calibration(25), we determined an applied toxicity tool to be important to informing mitigation efforts.

The ERT has two platforms: a web application for California and a desktop version for all study areas in the United States, which offer different advantages. The web-based tool is accessible on any internet-accessible device, summarizes applied toxicity in seconds, and provides a more straightforward user interface. The offline tool offers a high degree of customization, more detailed information, and custom simulations. To assist experts and non-experts, the ERT web tool and desktop version were built in RStudio(26) version 1.4. The development environment accommodates full customization of model code for experts and

the ability to run unique simulations for non-experts via editing spreadsheet files in Google Sheets and clicking a start button.

The user interface of the ERT provides a heatmap of applied toxicity. Within the map, users can zoom in, pan to find a watershed of interest, and click to see applied toxicity summaries by source and chemical for the watershed (**Figure 1**). In addition to graphical summaries, tabular outputs are provided with summaries of applied toxicity for the analysis period and the daily time step. Currently, the online tool only accommodates analyses of applied toxicity to aquatic organisms (fish, aquatic invertebrates, and nonvascular and vascular plants) within California for the most recent 5-year pesticide use data and is not customizable. There is also a couple of years lag in pesticide use data availability, and at the time of this guide's publication (2022), the most recent 5-year period of available data is 2014-2018. The chief advantage of the online platform is that it is accessible from any device and provides applied toxicity summaries for watersheds across California in seconds. The offline tool is advantageous because it works for any species, state, or analysis period and offers a high degree of customization. The online application is available at this web address (https://nicol-parker.shinyapps.io/Environmental-Release-Tool/), and the desktop tool is downloadable from the scientific digital repository Dryad and can be found under the DOI: 10.25349/D9VP6G, or title 'Pesticide Mitigation Prioritization Model (PMPM) - Environmental Release Tool and Results'.

Figure 1. The clickable and graphical user interface of the Environmental Release Tool. Note that other graphical summaries are not shown in this image, which summarizes crop values, applied toxicity by chemical, and illustrates economic and health indices. Base map imagery is a product of OpenStreetMap https://www.openstreetmap.org/copyright.



2.7.1.1 Pesticide Sources

To evaluate targets for pesticide toxicity reduction, the Environmental Release Tool requires manually inputting pesticide use data, or for California, the tool can autoload pesticide use report data from statewide agricultural applicators(18). The Environmental Release Tool internally hosts the pesticide use data. Using an autoload script, the tool aggregates data for the area of interest to the user, which watersheds or counties may define. The data retrieved by the autoload feature is discussed in the remainder of this section.

Pesticide use data are retrieved by active ingredient (AI) and for the 432 site types from CDPR Pesticide Use Reports(18) that are agricultural. Agricultural applications are estimated to account for ~90% of the applied pesticide mass in the United States(21). In Pesticide Use Reports, applications are recorded at the daily time step and by site type at the County Meridian Township Range Section (referred to as Section) spatial scale (2.6 km^2). Urban applications are not included within the CDPR pesticide use database records for household applications, and most professional urban applications are recorded at the county level as well as monthly time-step, which cannot be allocated to a specific watershed or date.

To enable evaluations of the variability of toxicity reduction opportunities over large extents, the tool summarizes pesticide applications and toxicity by watershed. The data is summarized by watershed and applications sites as well as pesticides since pesticide losses via runoff and eroded sediments share a common outlet. Summarizing applied toxicity by watersheds is important to conceptualize areas that share common hydrologic routes for pesticide transport. Though the Environmental Release Tool does not simulate loss processes, it is the first stage of development of the Pesticide Mitigation Prioritization Model.

The product of the second stage of development is a companion, mechanistic fate and transport tool where loss processes are simulated.

To derive watershed-specific applied toxicity, pesticide use data, which is recorded by Section, is assigned to watersheds via geospatial intersection analyses. Section geospatial data is provided by the California Pesticide Information Portal(18), while watershed geospatial data for the United States is available in the Watershed Boundary Dataset(27). The Watershed Boundary Dataset delineates watersheds as hydrologic unit codes (HUCs) by hydrologic connectivity and at multiple scales. Watersheds with shorter HUCs, such as HUC 2-digit codes, are large watersheds that encompass hundreds of thousands of square kilometers, while longer HUCs, such as HUC 8-digit codes (HUC8) represent subwatersheds of the shorter digit codes (e.g., HUC2) that are tens to hundreds of square kilometers. The assignment of pesticide use data to watersheds can be conducted at three watershed spatial scales in the Environmental Release Tool to enable users to adjust the resolution of analysis, which are HUC8, HUC10, and HUC12, whose watershed mean square areas are ~3,600, ~440, and ~100 km^2 respectively. For Sections where pesticide use data is reported that overlaps multiple watersheds, the area fraction of overlap is used to weight the mass of AI applied.

In addition to assigning pesticide use data to a specific watershed, a key feature of the Environmental Release Tool is the ability to preserve information relating to the applied toxicity of application site types. However, too many application sites make the interpretation of results difficult. The tool thus enables users to group similar AIs and application sites (e.g., alfalfa and alfalfa-grass mixture) by assigning the same ID to multiple site types. By default, 432 agricultural application site types from Pesticide Use Reports are simplified to

116 based on the similarity of the crops. Groupings can be viewed and modified in the tool input file for application sites.

2.7.1.2 Affected Compartment

Areas impacted by pesticide applications for terrestrial and aquatic investigations can be estimated with agricultural land use datasets such as the National Land Cover Dataset(28) or the Cropland Data Layer(29). In California, the impacted area can be retrieved from Pesticide Use Reports, which provide the application and planted area of crops(19). However, there are known inaccuracies. The planted area is often recorded for all the grower's land; although reported for a specific crop, fields are subject to multiple crop rotations within a year, and multiple applications are typical for a crop which renders the net-application area unknown. Due to these concerns, alternative land use datasets were evaluated for use(28–30).

The most accurate, high-resolution dataset reviewed was the California Department of Water Resources land use surveys (https://data.cnra.ca.gov/dataset/statewide-crop-mapping) with a median accuracy of 97.5% and positional quality of 8m. However, a limitation of the dataset, as well as the others, is that it provides fewer site types (43) compared to Pesticide Use Reports (432). Using this dataset to determine the affected area of specific application site types would require highly reducing the resolution of pesticide source data. Attempts to recategorize crops to fit available land use data did not obtain reliable results. As a result, we chose to consider the affected area to be all agricultural land in the California Department of Water Resources dataset. The representation of the affected compartment to all agricultural land was deemed appropriate because only 5% of agricultural

fields in California employ organic cultivation practices(31) and use non-synthetic pesticides recorded in use reports.)

2.7.1.3 Applied toxicity

Applied toxicity refers to the mass of pesticide applied to an area with the potential to do harm(22). The applied toxicity for the i^{th} pesticide in the j^{th} watershed is calculable from applications to the of the k^{th} site type and toxic endpoint of the m^{th} taxon of interest as:

$$TI_{j,i} = \sum \frac{M_{i,j,k,m}}{T_{i,j,k,m}} \quad \textit{Equation (1)}$$

Where TI is the Toxicity Index (kg-m^3/kg), M (kg) is the mass of applied AI, and T (kg/m^3) is the adverse health-effect concentration of concern (e.g., the lethal concentration of fifty percent of the test organism population) for the species or taxonomic groups of interest. Within a simulation, the tool is suitable for quantifying the applied toxicity to taxa within the same compartment, not across environmental compartments, because variation in the transport of pesticides based on physicochemical properties is not simulated. The tool illustrates applied toxicity within the soil compartment or available for transport to the compartment of interest. While the transport of pesticides from the application site is sensitive to their physicochemical properties(23), property correlation to surface water detection frequencies has been demonstrated to the more robust for pesticide sales data than physicochemical properties in a monitoring campaign of 72 pesticides of diverse properties in over 100 streams(24). Though this approach is not suitable for risk assessments, it facilitates an understanding of where mitigation opportunities exist(57) without data requirements and uncertainty of fate and transport models over large extents(26,27,58).

For pesticides, the tool facilitates the summarization of similar AIs. This feature is useful because many AIs have a similar chemical make-up (e.g., isomers or are produced in several forms, including acids, salts, amines, and esters) but have no or limited toxicity data for the various AI forms. Provided that AI forms can have very different affect concentrations, where possible, the user should provide AI form-specific toxicity. To accommodate AI form-specific endpoints where available but to simplify tool outputs, unique toxicity endpoints are accepted and calculated for pesticides within a user-defined pesticide group, and the group's total applied toxicity is reported by the group ID in tool output. In this investigation, we considered AIs detected (2014-2018) within California's surface waters with available toxicity data (n = 151). From the CDPR's Pesticide Use Reports, 290 forms of the AIs were observed (e.g., 12 unique esters and 15 salts of 2,4-D).

Our investigation considers the applied toxicity of pesticides for fish, as well as aquatic invertebrates, nonvascular plants, and vascular plants. Toxicity endpoints employed were acute values from the United States Environmental Protection Agency (USEPA) Aquatic Life Benchmarks Database[60,61]. The USEPA derives Benchmarks from the concentration at which fifty percent of a species sample in single-dose laboratory investigations experience severe effects, derived from mortality endpoints, or for plants, significant changes in growth/biomass (LC50 or EC50). A genera endpoint is then calculated based upon a 0.05 cumulative probability of toxicity for represented species, which typically reflects the most sensitive species within the taxonomic group. For fish and invertebrates, the USEPA calculates the final acute value as the product of the taxonomic group endpoint multiplied by a safety factor of 0.5 and does not adjust plants. Where no toxicity endpoints were reported for the pesticide in the Aquatic Life Benchmark database (n = 10), the

Pesticide Properties DataBase(32) acute toxicity endpoints were employed, and unverified data were excluded.

The first applied toxicity index reported by ERT for pesticides, sites, and watersheds is the Relative Toxicity Index (RTI). The index weights the toxicity of the i^{th} applied pesticide by the size of the application area within the j^{th} watershed as:

$$RTI_{j,i} = \frac{TI_{i,j}}{A_j} \quad \textit{Equation (2)}$$

where A (m^2) is the area of the affected compartment.

As the quantification of the affected compartment area is frequently limited, and the fraction of a watershed subject to pesticide application is highly variable, we provide a second applied toxicity index independent of area, the Net Toxicity Index (NTI). The NTI is a relative rank toxicity index to determine if the applied toxicity is greater than what is typical for the i^{th} pesticide in the j^{th} watershed. As our reference of what is typical, we calculate for the study area the 50th percentile ($perc_{50}$) of the applied toxicity for any applied pesticide (pst) in watershed (w). The NTI is calculable from the TI of the i^{th} pesticide in the j^{th} watershed as:

$$NTI_{i,j} = \frac{TI_{i,j}}{perc_{50}\,(TI_{pst_1,w_1}, TI_{pst_1,w_1}, TI_{pst_1,w_2}, TI_{pst_2,w_2}, \ldots TI_{pst_n,w_n})} \quad \textit{Equation (3)}$$

The NTI approach can quickly identify applied toxicity above typical levels in the study extent. For example, if the 50th percentile of the applied toxicity of pesticides to a watershed in the study area is applications of imidacloprid in the San Joaquin Watershed, 1000 TI, to calculate the NTI, the TI of the pesticide and watershed of interest is divided by 1000 TI. Using this approach, pesticide applications within a watershed over the simulation period

with an NTI greater than unity have applied toxicity above typical levels. This normalization provides a unitless applied toxicity index that does not affect the relative rank of the applied toxicity for pesticides, sites, or watersheds and can identify effective toxicity reduction targets specific to the study area.

For single taxonomic group investigations with the ERT (e.g., only fish), the cumulative applied toxicity, the potential of all pesticides released to the environment and under investigation to do harm to the taxon, is calculable via an adaption of the concentration addition method(60,61). We calculate the cumulative toxicity indices of pesticides for each index for *n* pesticides for a watershed (here w_1) as:

$$RTI_j = \sum RTI_{pst_1,w_1} + RTI_{pst_2,,w_1} + RTI_{pst_3,j,w_1} \dots RTI_{pst_n,j,w_1} \quad \textit{Equation (4)}$$

$$NTI_j = \sum NTI_{pst_1,w_1,k} + NTI_{pst_2,w_1,k} + NTI_{pst_3,w_1,k} \dots NTI_{pst_n,w_1,k} \quad \textit{Equation (5)}$$

The method used in this study relies on the assumption of additive toxicity and non-interacting chemical species. While this assumption is theoretically unsound for chemicals of diverse modes of action, and this limitation is not addressed by the ERT, pesticides rarely express synergism at environmentally relevant concentrations, and cumulative addition has been empirically demonstrated to be a reliable method for quantifying pesticide mixture toxicity(62). For example, in studies with hundreds of pesticide mixtures, the method has predicted mortality within a factor of 2 for 90% of samples(63–65). Additionally, the method is robust to independent modes of action(64). However, the approach is not suited to simultaneously understand the effects of pesticide mixtures on diverse taxa due to the

presence of unique organism receptors and responses(66). Where multiple organisms are included for analysis, the net applied toxicity is interpretable as where toxicity reduction opportunities are greatest for all taxa considered.

2.7.1.4 Health and Economic Indices

The health and economic impacts of application sites are quantified over the study extent with a Health Score (ha/NTI), an Economic Score (USD/ha), as well as an Economic and Health Score (USD/NTI per ha). These indices are calculated over the study extent (California) rather than in specific watersheds due to the low resolution of reliable land use data (see *Section 2.2 Affected Compartment)*. For health and economic scores, higher values represent more favorable outcomes. Health and economic scores are calculated for the application site areas of the study extent as:

$$Economic\ Score = \frac{Gross\ Value\ (USD)}{Harvested\ Hectares} \quad Equation\ (6)$$

$$Health\ Score = \frac{Harvested\ Hectares}{Toxicity\ Index\ (NTI\ or\ RTI))} \quad Equation\ (7)$$

The Economic and Health Score penalizes crops with high applied toxicity and is calculated as:

$$Economic\ and\ Health\ Score = \frac{Gross\ Value\ (USD\ per\ Harvested\ Hectare)}{Toxicity\ Index\ (NTI\ or\ RTI\ per\ Harvested\ Hectare)} \quad Equation\ (8)$$

For health and economic scores, the harvested hectares and gross value of application site types were compiled from the United States Department of Agriculture National Agricultural Statistics Service (https://www.nass.usda.gov/). We considered the median economic value

and harvested hectares for a crop in California from 2014-2018 to minimize single-year anomalies.

In addition to numeric scores, users are also provided with categorical scores based upon percentiles for the study area to facilitate interpretation. Scores are divided into 20th percentiles and range from 'Very Low' (0-20th percentile) to 'Very High' (80-100th percentile). See example output in **Table 1**.

Table 1. Environmental Release Tool outputs for pesticide application sites which introduce 90% of the applied toxicity in California to fish, invertebrates, nonvascular aquatic plants, and vascular aquatic plants from 2014-2018, where: NTI the Net Toxicity Index; NTI (%) the percent of the total NTI of the application site type; Economic, Economic Health, and Health Scores the numeric score of sites; and the Economic, Economic Health, and Health Values the quantiles of scores where 0-20th quantile is 'Very Low' and 80-100th 'Very High'.

Site Type	NTI	NTI (% Total)	Economic Score (USD/ha)	Economic Health Score (USD/NTI)	Health Score (NTI/ha)	Relative Economic Score	Relative Economic Health Score	Relative Health Score
Almond	1.41E+08	24.7	1.32E+04	2.78E+02	2.11E-02	3-Medium	2-Low	2-Low
Pistachio	1.07E+08	18.8	1.32E+04	1.86E+02	1.42E-02	3-Medium	2-Low	1-Very Low
Alfalfa	6.08E+07	10.7	1.58E+03	1.64E+02	1.04E-01	1-Very Low	1-Very Low	4-High
Lettuce	4.59E+07	8.0	1.75E+03	2.67E+02	1.53E-01	2-Low	2-Low	4-High
Walnut	2.96E+07	5.2	9.95E+03	2.54E+02	2.55E-02	3-Medium	2-Low	2-Low
Rice	2.84E+07	5.0	1.21E+03	1.91E+03	1.58E+00	1-Very Low	4-High	5-Very High
Cotton	2.09E+07	3.7	1.24E+02	6.74E+00	5.45E-02	1-Very Low	1-Very Low	3-Medium
Tomato (Processing)	2.03E+07	3.6	8.57E+03	4.00E+02	4.67E-02	2-Low	2-Low	3-Medium
Corn (Sweet)	1.53E+07	2.7	5.74E+03	5.27E+01	9.17E-03	2-Low	1-Very Low	1-Very Low
Broccoli	8.71E+06	1.5	8.98E+03	2.70E+02	3.01E-02	3-Medium	2-Low	2-Low
Cherry	7.66E+06	1.3	5.84E+03	8.68E+02	1.48E-01	2-Low	4-High	4-High
Peach	6.36E+06	1.1	8.61E+03	3.25E+02	3.77E-02	2-Low	2-Low	3-Medium
Strawberry	5.93E+06	1.0	1.25E+05	8.57E+02	6.88E-03	5-Very High	4-High	1-Very Low
Orange	5.67E+06	1.0	4.51E+02	1.29E+01	2.86E-02	1-Very Low	1-Very Low	2-Low
Onion Misc.	4.09E+06	0.7	1.83E+04	3.05E+02	1.67E-02	3-Medium	2-Low	2-Low
Bean (Dry)	3.75E+06	0.7	1.42E+03	1.77E+02	1.25E-01	1-Very Low	1-Very Low	4-High

2.7.2 Environmental Release Tool Installation and Operation

To prepare to use the web-based platform, users can navigate to the tool via this link: https://nicol-parker.shinyapps.io/Environmental-Release-Tool/ and skip to *Section 4.0* of this guide. Desktop users will need to follow the stepwise instructions provided for tool installation and use in this section and read *Section 3.0*, model parameterization.

The desktop ERT is run through the RStudio user interface. All model parameterization is done using spreadsheets which can be modified in google sheets or Microsoft Excel. When executing tool simulations in RStudio, a pop-up window with a clickable user interface (see **Figure 2**) is produced with graphical summaries of the data and tabular exports (in spreadsheet format).

2.7.2.1 Installing RStudio

I. Establish an internet connection with your device.

II. Download R version 4.1, the software environment of RStudio. The software is freely available for Mac, Windows, and Linux users here https://cran.rstudio.com/.

III. Download RStudio version 1.4; the software is freely available for Mac, Windows, and Linux users here: https://www.rstudio.com/products/rstudio/download/#download.

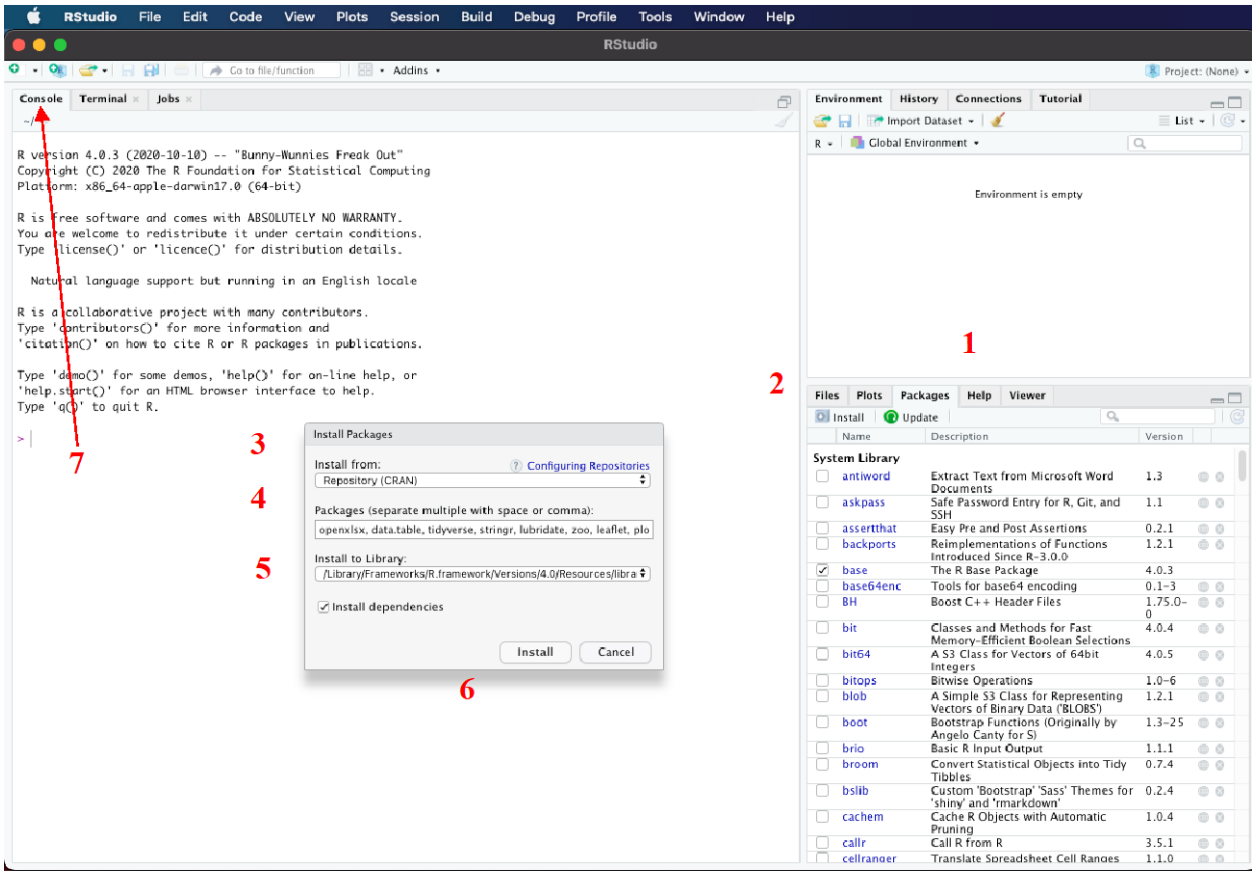
IV. Follow the RStudio download and install instructions.

V. Open RStudio; for new users, some quick tutorials may be helpful to familiarize yourself with the software, but they are unnecessary. The first time you open the software, you'll need to install packages which will take just a few minutes. Packages are functions employed by the ERT and are installed within the RStudio user interface. The packages which need to be installed include ProjectTemplate, data.table, dplyr,

stringr, lubridate, zoo, rgdal, shiny, leaflet, and plotly. To install packages, follow these steps for instructions (see **Figure 2** to view the RStudio interface):

1) Within the RStudio Window, navigate to the 'Packages' tab in the lower right window.
2) Click the 'Install' button.
3) In the pop-up window, data field 'Install From', set the option to 'Repository (CRAN)
4) Type the list of packages separated by a comma above or copy this list of packages and pate into the 'Packages' field:
   data.table, tidyverse, stringr, lubridate, zoo, leaflet, plotly, shiny, rgdal
5) Ensure 'Install dependencies' is checked.
6) Select the 'Install' button at the bottom of the pop-up window.
7) Packages should install without error; if errors are encountered, they will be displayed in the Console as 'Error:' followed by an issue-specific note. If issues are discovered, try installing packages one at a time. To troubleshoot the package-specific problems, typically, another package must be installed for which the name is displayed in the RStudio console. If difficulties persist, RStudio is a widely used platform for which internet searches for error codes will provide troubleshooting assistance for your operating system (macOS, Windows, or Linux).

Figure 2. RStudio package installation. RStudio interface with required user steps/features for package installation.



2.2 Installing the Environmental Release Tool

1) Navigate to the ERT model download via this link (https://datadryad.org/stash/share/BJwLp5INjd3ybsATDQF2fJLvRdH3uDobvBMnFVEmC7M, the temporary link for reviewers and publishers, needs to be updated for the public)
2) Download the tool zip file and save it to your computer.
3) Unzip the ERT download. The ERT model requires a small fraction of the downloaded file memory, 0.6 GB. Still, the entire download package requires 6 GB of memory due to the millions of pesticide use data points for the most recent 10-year period of data

availability for California (as of this guide's publication 2009-2018). To substantially reduce the space the ERT requires on your personal computer; you may delete all pesticide use data not of interest to your analyses (see the sub-directory 'EnvironmentalReleaseTool/data/inputs_simulation/cdpr_pur' to delete from years not of interest to your analyses. For users seeking to conduct analyses beyond this period for California, the required files can be downloaded in minutes, see *Section 3.4* for download instructions.

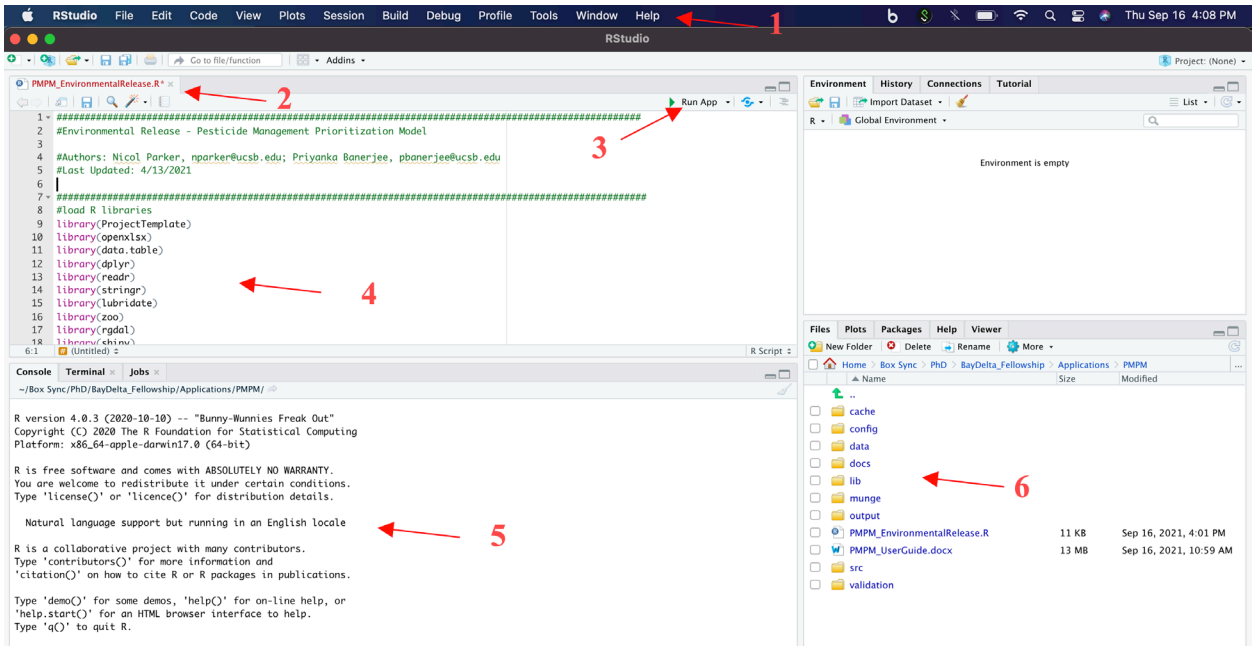
2.7.2.3 Running a Simulation Environmental Release Tool

1) **Open RStudio.**
2) Prior to running the ERT in RStudio, the user needs to provide the path to where they have saved the 'EnvironmentalReleaseTool' directory (folder) on their computer. Setting the path tells RStudio and the ERT where to retrieve and save model files. To set the path:
    a. Navigate to the top of the RStudio window to the tab 'Session', click once, and hover over 'Set Working Directory' (do not click yet).
    b. Scroll down on the sub-menu that pops up and click once on 'Choose Directory'.
    c. Browse to where the 'EnvironmentalReleaseTool' directory is saved and click once; then, at the bottom of the pop-up window, select open. The path has now been set.
3) To open the clickable user interface, a user must open the 'PMPM_EnvironmentalRelease.R' file in the ERT directory (where you saved the downloaded model). To open the file, in the RStudio window, navigate to the 'File'

tab at the top left. In the drop-down menu, select 'Open File'. Navigate to the 'EnvironmentalReleaseTool' directory and open the 'PMPM_EnvironmentalRelease.R' file.

4) The model can now be run with default inputs. Select the 'Run App' button in the RStudio window (**Figure 3**). By default, the model will display ERT outputs for pesticide-applied toxicity at the HUC8 watershed scale (mean watershed size ~3,600 square kilometers) for 2014-2018 in California. For new simulations with the ERT, refer to '*Section 3.0 Parameterization'* of the user guide for instructions to customize the simulation.
5) The clickable user interface will now display (**Figure 1**). Click around to view graphical summaries of data. To view tabular data, open the 'output' sub-directory. See *Section 5. Outputs* for more information on available outputs. Note that model values are displayed in scientific notation for graphical summaries because they are often large values that are otherwise messy to display and difficult to read. Scientific notation expresses the number of zeros that follow or precede a number. 1,000,000 is written in scientific notation as 1×10^{6}, 0.1 is written as 1×10^{-1}. A quick web search of 'scientific notation' will provide useful details on the number format, which is common scientific practice.
6) New simulations will require a few minutes to an hour to summarize results and display them in the clickable user interface (**Figure 1**), depending on your operating system and the number of watersheds and pesticides analyzed. Once a simulation has been run, a user can display an existing simulation result in the user interface in less than a minute. To do so, see *Section 3.1* instructions.

Figure 3. RStudio interface. RStudio interface with key user features for the Environmental Release Tool. 1) Top of the window where tabs for navigating RStudio menus are located. 2) The name of the tool execution file ('PMPM_EnvironmentalRelease.R'. 3) The button the user clicks to run the script; alternatively, the user can highlight all text in the file and press enter. 4) The code in the 'PMPM_EnvironmentalRelease.R' file initiates the module's running and opening of the user interface. 5) The RStudio console window updates the user on what the model is processing. It displays errors if the model does not run correctly. 6) Window within which directories on your computer can be navigated (similar to File Explorer in Windows or Finder in Mac).



2.7.3 Parameterization

This section describes each input file for the ERT, the parameters (input file fields), and provides specific notes on formatting. For inputs, formatting must match the input files; see the Template' input folder with input files and formatting required in the ERT (located in the 'EnvironmentalReleaseTool /data/inputs_simulation/simulations' directory). To modify module inputs discussed below, navigate to the input file of interest, open, edit, and save the

files which are editable in Google Sheets, Microsoft Excel, or text editors (format comma-separated files).

The ERT summarizes pesticide applied toxicity by watershed. Watersheds are delineated using the United States Geological Survey Watershed Boundary Dataset(27). Watersheds in this dataset are delineated as hydrologic unit codes (HUCs), with longer-digit watersheds of higher resolution. Users can choose between three default watershed resolutions to use for the ERT; from lowest to highest resolution, they are eight-digit HUCs digits (HUC8), ten-digit HUCs (HUC10), and twelve-digit HUCs (HUC12). The mean area of the watersheds varies by state, and in California are ~3,600 square kilometers for HUC8 watersheds, ~440 square kilometers for HUC10 watersheds, and ~100 square kilometers for HUC12 watersheds. Other watershed delineation options are available, which the user may choose from, but require manual parameterization of the input files for watersheds and application site types, as well as for the user to download the spatial dataset for the resolution of interest (see *Section 3.3*).

Within the ERT, all default parameters (including pesticide use data) are available at each of the three watershed resolutions in California (see *Section 1.1*). Users seeking to analyze pesticides in areas outside of California will need to modify most input files. By default, the inputs for pesticide use and toxicity consider pesticides detected in statewide surface monitoring campaigns in California that are recorded in the CDPR Surface Water Monitoring Database(18) for 2014-2018 (n=151). Pesticide use data is derived from the CDPR PUR database(19) (see *Section 1.1*). Toxicological data was derived from the United States Environmental Protection Agency Aquatic Life Benchmarks Database[60,61] (see *Section 1.3*).

2.7.3.1 Default Simulations

Default simulations are available at three spatial scales for aquatic species in California's watersheds for 2014-2018 (defaults will be updated when pesticide use reports for later years are publicly available). Two types of simulations can be conducted with toxicity endpoints. One considers the most sensitive taxonomic group per pesticide. For the toxicity endpoints used, the Aquatic Life Benchmarks(33), 18% of the most sensitive endpoints for investigated pesticides were from fish, 38% for aquatic invertebrates, 27% for nonvascular aquatic plants, and 17% for vascular aquatic plants. The second approach employed toxicity endpoints for the individual taxonomic groups. By default, the active pesticide ingredients analyzed are those detected (2014-2018) within California's surface waters (n = 151). From the CDPR's Pesticide Use Reports, 308 forms of the 151 AIs were observed (e.g., 30 unique salts and esters of 2,4-D). If multiple toxicological endpoints exist for the active ingredient, the more sensitive endpoint was employed as a conservative toxicity estimate; pesticides were evaluated, and default groupings can be viewed in the default module input file for pesticides. The custom simulations are under the 'EnvironmentalReleaseTool/data/inputs_simulations/simulations' directory. See the next section to customize input parameters to evaluate other species (terrestrial or aquatic), pesticides, and study areas.

2.7.3.2 Custom Simulations

Within the 'EnvironmentalReleaseTool/data/inputs_simulation' directory, there exists a file, the 'Simulation_Information.csv'. This input file informs the tool which simulation file to run, the analysis period, and how output data will be summarized.

- 'Simulation_Information.csv' fields:

- simulation_name: Name of the simulation input file to run. The simulation input file contains information on the pesticides, application sites, and watersheds to be analyzed (see *Section 3.2*). This field's format can employ characters, underscores, and periods (.). The name used in this field must match exactly match (capitalization sensitive) the name of the simulation file (see *Section 3.2*) BUT not include the file extension (.csv). This name also creates a directory for the simulation to store model outputs.
- watershed_resolution: Input what resolution to analyze pesticides at for watersheds. Users can choose between three default watershed resolutions to use for the ERT; from lowest to highest resolution, they are eight-digit HUCs digits (HUC8), ten-digit HUCs (HUC10), and twelve-digit HUCs (HUC12). To analyze at the HUC8 scale, enter 'huc8' in the field for a HUC10 analysis 'huc10', and a HUC12 analysis 'huc12'. The mean area of the watersheds varies by state, and in California are ~3,600 square kilometers for HUC8 watersheds, ~440 square kilometers for HUC10 watersheds, and ~100 square kilometers for HUC12 watersheds.
- tox_summary: For the graphical summaries provided by the module, this field indicates whether to display the NTI or RTI in the heat map summary of pesticide applied toxicity; see *Equations (2)* and *(3)* in *Section 1.0*.
- new_simulation: Enter 'yes' to run a new simulation or 'no' for the ERT to display existing data. The simulation must have data in the 'output' and 'cache' sub-directories under the simulation name (automatically generated

when a simulation is run) to display graphical summaries for existing simulations.

- print_daily_summary: Provides the option to print daily output of pesticide toxicity by watershed, site, and chemical. To provide daily output, insert 'yes'; to increase the model speed and reduce the memory consumed by ERT outputs, choose not to print daily summary data by entering a 'no'. Tabular summaries will always be provided for the analysis period, and graphical summaries by month and year.
- manual_pest_application: Indicates whether to use manually input pesticide use data or the auto-load pesticide use feature (available only for California, see details in *Section 3.4*). To employ manual data, enter ‘yes’; to use CDPR data, enter ‘no’.
- filter_by_county: This parameter is only used by the module for evaluations in California, where the autoload feature is used for pesticide use data. The field indicates whether the model filters the study area by counties specified by the user or watersheds. If data are filtered by counties, this information will be employed to select watersheds within counties specified by the user in the simulation input file (see *Section 3.2*), and all model outputs will still be summarized by watershed. To function, the user must ensure all watersheds in California are present in the simulation input file ‘Watersheds.csv’ input file (see Section 3.2.2) for the desired scale of analysis (e.g., HUC8). Watershed data is available for HUC8, HUC10, and HUC12 watersheds in California in the default simulation files provided in the

‘EnvironmentalReleaseTool/data/input_simulations/simulations’ directory. To filter by county, insert 'yes', and to filter by watershed, 'no'.

- start_day: First day of simulation with format 'dd'.
- start_month: First month of simulation with format 'mm'.
- start_year: First year of simulation with format 'yyyy'.
- end_day: Last day of simulation with format 'dd'.
- end_month: Last month of simulation with format 'mm'.
- end_year: Last year of simulation with format 'yyyy'.
- affected_depth: This value represents the depth of soil impacted by pesticide application and is with the affected area per watershed provided in the simulation input file (see *Section 3.2*) to calculate the NTI (*Equation (3)*). The default value is 0.01m.
- percentile_NTI: Percentile of the applied toxicity of pesticides in watersheds used to calculate the NTI, see *Equation (3)*. The default is the 50^{th} percentile.
- econ_val: For study areas with uncertain harvested hectares or gross value for pesticide application site types, the user can select to use a gross economic value for the study area provided by default in the ‘ApplicationSite.csv’ input file. To use the economic value for the entire study area to calculate the economic score, insert ‘yes’. To use user-defined harvested hectares and gross crop value to calculate the economic score for the study region, insert ‘no’.
- health_val: For study areas with uncertain harvested hectares for pesticide application site types within the study region, the user can select to use the health score calculated from the application site area across the study area

provided by default in the 'ApplicationSite.csv' input file. To use the health score for the entire study area, insert 'yes'. To use user-defined harvested hectares to calculate the economic score for the study region, insert 'no'.

2.7.3.2 Simulations

The simulation files describe the pesticides to be evaluated, toxic endpoints to employ, the extent of analysis, and the output summarization method. Each simulation will have a folder with the simulation name and all input files. The user customizes the folder name to represent their unique scenario. *Section 3.2.1* lists the steps to prepare the ERT to run a new simulation. *Section 3.2.2* discusses simulation parameters and data resources.

2.7.3.2.1 Simulation Overview

1) To run a new simulation, a user can employ one of the simulations provided in the 'EnvironmentalReleaseTool/data/inputs_simulation/simulations' or customize a simulation using input files in the 'Template' folder.
    a. By default, the ERT is parameterized to analyze pesticide-applied toxicity in California for 2014-2018 at the HUC8 watershed resolution (~3,600 km^2, 140 watersheds). Default simulation files are also available for users seeking to summarize applied toxicity in California at the resolution of HUC10 watersheds (~440 km^2, 1,038 watersheds) or HUC12 (~100 km^2, 4,463 watersheds) for 2014-2018. These simulation inputs are in the directory 'EnvironmentalReleaseTool/data/inputs_simulation/simulations.
    b. Custom simulations must follow the field names and formats of the files in the 'EnvironmentalReleaseTool/data/inputs_simulation/simulations/Template'

folder. For custom scenarios, save a copy of the 'Template' input folder and rename it to reflect the new simulation (e.g., 'SacramentoWatershed_2021).

2) To employ the correct simulation files in an ERT model run, the user must enter the unique simulation file name into the 'Simulation_Information.csv' input file (located in the 'EnvironmentalReleaseTool/data/inputs_simulation' directory) field 'simulation_name'. The simulation name must NOT include the input file extension (*.csv) and is capitalization sensitive. The simulation name must also match the folder containing all simulation input files in the 'EnvironmentalReleaseTool/data/inputs_simulation/simulations/' directory (e.g., folder name 'SacramentoWatershed_2021').
3) For simulations in California, no further parameterization is necessary. For simulations outside of California, watershed spatial data acquisition is required. This effort requires only a few minutes; see *Section 3.3*. The simulation file specifies the number of watersheds and chemicals to analyze. Typically, the ERT can handle simulations at the state level. However, analyses over five years for more than 200 chemicals and 5,000 watersheds may cause the ERT to run out of RAM and for the model not to run. If an error is encountered for large simulation spaces, reduce the number of watersheds, chemicals, or years considered.

2.7.3.2.2 Simulation Parameters

The simulation input files required are in the 'EnvironmentalReleaseTool/data/inputs_simuation/simulations/Template' directory. The simulation run is based on the simulation name provided in the 'Simulation_Information.csv'

input file (see *Section 3.1*). Default simulation files are available, or users can create a custom scenario with the template files. A simulation employs six input files: 'Pesticides.csv', 'Toxicity.csv', 'Watersheds.csv', 'Counties.csv', 'Application_Sites.csv', and 'Pesticide_Application.csv'.

- 'Pesticides.csv' fields:
    - pesticide_id: Unique identifier which will be used to summarize highly similar pesticides. This may be unique from the 'pesticide' field to merge similar applied chemicals such as isomers. IMPORTANT NOTE, for pesticide use reports in the CDPR PUR database, many active ingredients with slight variation in form (e.g., 2,4-D and 2,4-D LITHIUM SALT) exist. If using the autoload feature or database, a user will want to ensure they explore all chemical names similar to their active ingredient of interest, or the applied toxicity may be underestimated. To ensure all pesticide loads associated with an active ingredient are included, list all relevant CDPR PUR chemical names in the 'pesticide' field. For each chemical for which the same toxicity value will be used, provide the same 'pesticide_id' field value; see **Table 2**.
    - pesticide: Name of the active ingredient of the pesticides under investigation. If the user seeks to use the autoload feature for pesticide use data, the module requires this field to match pesticide names within the CDPR PUR(19) database (including capitalization). The chemical name formatting can be found in the ERT directory under 'EnvironmentalReleaseTool/docs/ChemicalFormatting.csv'.

- tox_ 1: Toxicity endpoint (kg/m^3) used to calculate applied toxicity. Numeric formatting with no commas must be employed (e.g., no thousands placeholder nor comma used as the decimal); to represent decimals, employ a period (.) For sediment or soil toxicity endpoints, typically (mg/kg), convert to (kg/m^3) using a typical value for the compartment density (e.g., 1,400 kg/m^3). For example, if the soil toxicity endpoint is 0.001 mg/kg, then:

$$0.001 \frac{mg\ pst}{kg\ soil} = 1000 \frac{kg\ pst}{kg\ sol}$$

$$tox\_1 = 1000 \frac{kg\ pst}{kg\ soil} * 1{,}400 \frac{kg\ soil}{m^3\ soil} = \ 1{,}400{,}000 \frac{kg\ pst}{m^3\ soil}$$

- tox_2 to tox_10: The user has the option to add toxicity endpoints for a total of 10 species; **however, species evaluated in the same simulation must all have toxicity endpoints in the same environmental compartment (see *Section 1.3*)**. The Environmental Release Tool is a relative ranking tool that quantifies the net applied toxicity to species, showing where the relative applied toxicity is highest. When multiple species are considered, in tool outputs, the net applied toxicity to all species of interest (sum of all applied toxicity to individual species). Note that to evaluate the cumulative applied toxicity of pesticides to a specific species, a user must run individual simulations (provide only a value for tox_1). By default, tox_1 to tox_4 are provided and are the toxicity endpoints, obtained from the USEPA Aquatic Life Benchmarks(33) (or Pesticide Properties DataBase(32) where USEPA benchmarks were unavailable) for fish, invertebrates, nonvascular aquatic plants, and vascular aquatic plants respectively.

Table 2. Pesticide groups. Example inputs that group chemical names in the pesticide use data to chemical names used in model outputs.

pesticide_id	pesticide	tox_1
2,4-d ester	2,4-D, BUTOXYETHANOL ESTER	152
2,4-d ester	2,4-D, ISOOCTYL ESTER	152
2,4-d salt	2,4-D, DIMETHYLAMINE SALT	299
2,4-d ester	2,4-D, BUTYL ESTER	152
2,4-d salt	2,4-D, TRIISOPROPANOLAMINE SALT	299

- 'Watersheds.csv' fields:
    - huc: Unique hydrologic unit code watershed identifier. Formatting is character, with the string 'HUC' followed by the digits of the HUC watersheds of interest (e.g., HUC18070301 for HUC8 or HUC1807030111 for HUC10).
    - huc_name: Name of hydrologic unit code watershed. Users can use WBD default names or create custom names that employ characters, numbers, or underscores (no special characters).
    - affected_area_ha: Area (ha) of the watershed impacted by pesticide application in hectares (whole watershed area may be used if the affected area is unknown). The tool converts the value from ha to m^2 internally for toxicity index calculations. Numeric formatting with no commas must be employed (e.g., no thousands placeholder nor comma used as the decimal); to represent decimals, employ a period (.).

- ‘Counties.csv’ fields only need to be populated if the user opts for the autoload feature for pesticide use data (available only for California study areas) and to filter pesticide use data by county (see *Section 3.1*).
    - county_cd: County code employed by the CDPR. Formatting must match codes in the ‘county_cd.txt’ file in the ERT directory under the ‘data/model_configuration/cdpr_pur’ sub-directory.
    - county_name: Name of the county. Formatting is up to the user.
- ‘ApplicationSites.csv’ fields provide information about which application sites to consider in watersheds (e.g., agricultural sites). The input file also enables users to group similar site types considered into one toxicity index (e.g., table grapes and wine grapes to a toxicity index for ‘GRAPES’). The fields also describe the value of the application sites per hectare. For crop values, default data was aggregated from the United States Department of Agriculture National Agricultural Statistics Service (USDA NASS)(34) for California for the most recent 5-year pesticide application data (2014-2018). For users seeking to customize crop values, the same database provides crop values at the state and county levels for the United States.
    - ‘app_site_id’: Unique pesticide application site identifier. For users employing the CDPR PUR database, the ‘app_site_id’ must match the ‘site_code’ field identifier in the CDPR PUR database (see ‘EnvironmentalReleaseTool/docs/ApplicationSiteForamtting.csv’). If the user manually inputs pesticide use data (via the ‘Pesticide_Applications.csv’ input file), the ‘app_site_id’ used here must match the pesticide use data.

- ‘pmpm_id’: Unique application site identifier in outputs of the Environmental Release Tool (ERT) of the Pesticide Mitigation Prioritization Model (PMPM). This field can summarize outputs from unique application sites in pesticide use data into application site type groups, see **Table 3**.

Table 3. Application site groups. Example Environmental Release Tool inputs that group application site names (app_site_id) into a ‘pmpm_id’ to enable summarization of applied toxicity across similar sites.

app_site_id	pmpm_id	harvested_ha	gross_usd
AIRPORT	Urban	NA	NA
ALFALFA	Alfalfa	308,864	1,027,626,000
ALFALFA-GRASS MIXTURE	Alfalfa	308,864	1,027,626,000

- ‘harvested_ha’: The statewide harvested hectares for each crop type. Numeric formatting with no commas must be employed (e.g., no thousands placeholder nor comma used as the decimal); to represent decimals, employ a period (.). This data is available in the USDA NASS(34) database.
- ‘gross_usd’: Gross value of crop per year. Numeric formatting with no commas must be employed (e.g., no thousands placeholder nor comma used as the decimal); to represent decimals, employ a period (.). This data is available in the USDA NASS(34) database.
- ‘health_val’: Health score calculated for the entire study area for application site types.
- ‘econ_val’: Economic score calculated for the entire study area for application site types.

- ‘PesticideApplications.csv’ fields to input pesticide use data; populating this file is ONLY required for users manually inputting pesticide use data (not employing the ERT autoload feature). We recommend that users who evaluate California agricultural study sites employ the module's automatic pesticide use population feature; see *Section 3.4* for more information about the autoload feature. Users with analyses external to California may benefit from exploring the pesticide use databases provided by the United States Geological Survey(35,36) or PEST-CHEMGRIDS(17).
    - date: Date of pesticide application, format dd/mm/yy.
    - huc: Unique hydrologic unit code watershed identifier. Formatting is the number of digits of the HUC with no characters (e.g., eight, ten, or twelve) and must match values in the ‘huc’ field of the ‘Watersheds.csv’ input file.
    - huc_name: Name of hydrologic unit code watershed. Formatting is up to the user. Users can use WBD default names or create custom names that employ characters, numbers, or underscores (no special characters).
    - app_site_id: The name of the application site should match the name of the source data frame, but this is not a requirement. This field must match the ‘app_site_id’ present in the ‘Application_Sites.csv’ input file.
    - pesticide: Name of pesticide applied; the field must match the names employed in the ‘pesticide’ field in the ‘Pesticides.csv’ input file (can be unique from the ‘pesticide_id’ field).
    - pesticide_kg: Mass of active ingredient applied. Formatting is numeric with no commas (employ ‘.’ to indicate decimal places).

2.7.3.3 Watershed Spatial Data

The watershed spatial data is employed to visualize the distribution of pesticide applied toxicity across watersheds in the graphical user interface. The watershed spatial data file formats are shapefiles (*.shp) stored in the directory 'EnvironmentalReleaseTool/data/inputs_watershed_spatial_data'. Users conducting simulations in California are provided with watershed spatial data files by default in the ERT; for other states/counties in the United States, the files can be downloaded from the Natural Resources Conservation Service Geospatial Gateway in a few minutes(37). The watershed file for the area of interest (e.g., the entire state) will likely be large (>5 MB). For the ERT to run efficiently, the polygons should be simplified if the user has the technical expertise. An efficient method for simplifying the polygons is to employ the 'ms_simplify' function in the 'rmapshaper' package for RStudio (other software users may be more familiar with can be used to simplify polygons such as QGIS). Polygons should be simplified to less than 2 MB; the smaller the file, the more efficiently the tool will run. Simplifying polygons does NOT affect the analysis resolution, only the graphical summary heatmap in the user interface.

Follow these steps to download the watershed shapefile:

1) Navigate to the Geospatial Data Gateway via this link: https://datagateway.nrcs.usda.gov/
2) In the lower right-hand corner, select the link to 'Order by County or Counties' or 'Order by State'.
3) Choose the study area of interest (State or Counties) from the drop-down list.
4) Scroll down to the heading 'Hydrologic Units' (headings are in alphabetical order).

5) Select the resolution to download by 8 Digit Watershed Boundary Dataset (HUC8), 10 Digit Watershed Boundary Dataset (HUC10), 12 Digit Watershed Boundary Dataset (HUC12), or other.
6) Select the 'Continue' button at the bottom of the page.
7) Under the 'Format' heading, select the 'ESRI Shape' files from the list. Do not select 'Separate ESRI Shapefiles'.
8) Under the 'Projection' heading, select 'Geographic NAD83'.
9) Press 'Continue' at the bottom of the page.
10) Enter your email address to receive a link to the requested data, and press 'Continue' at the bottom of the page.
11) Review your order and click 'Place Order' on the window's lower left.
12) Open the data download link on your device. Save the downloaded data files (shapefiles have multiple files associated with them to display spatial data) into the 'inputs_watershed_spatial_data' directory under the sub-directory of the watershed delineation downloaded. For example, save HUC8 watershed data under the 'EnvironmentalReleaseTool/data/inputs_watershed_spatial_data/huc8' directory and HUC10 watershed data under the 'EnvironmentalReleaseTool/data/inputs_watershed_spatial_data/huc10' directory. If saved under the incorrect directory (e.g., HUC10 data under 'huc8'), the module will not run. Also, ensure the file extensions *.shp, *.prj, *.dbf, and *.shx are present. Other files will be present from the data download, which can be copied into the folder but are unnecessary for the ERT.

2.7.3.3 Pesticide Autoload Feature

Pesticide use for agricultural applications can be autoloaded in the ERT for California study areas if opted for by the user (see *Section 3.1*). The data employed are derived from the CDPR pesticide use reports(19) and are stored in the 'EnvironmentalReleaseTool/data/cdpr_pur' directory. The pesticide use is reported at the daily time step by application site type at a resolution of 2.6 km^2 (1 mi^2), the county/range/township/section (COMTRS). This data is assigned to a given watershed in the ERT via geospatial intersect analyses. For pesticide use reporting units (COMTRS) overlapping multiple watersheds, the fraction of the total area of the pesticide reporting unit within a given watershed is used to weigh the amount of pesticide applied.

By default, pesticide use reports are available for the most recent 10-year period for available pesticide use data (2008-2018 at the time of this guide's publication). They are not to be modified by the user without the potential for model disruption. For users seeking to conduct analyses before this period, follow these instructions to download data for additional years (1990 onward). This is a quick process that will take a few minutes. This data is not included by default because they are large files that require a lot of memory on your device (~60 MB per year of data).

1) Visit the California Pesticide Information Portal website operated by the CDPR and navigate to the 'Data Archives'. At the time of this guide's publication, the link to the homepage with the 'Data Archives' link is https://calpip.cdpr.ca.gov/main.cfm. Windows users may need to use Firefox or Internet Explorer as their web browser to avoid known issues with Chrome.
2) Download data for years of interest to your analyses.

3) Drag or copy data from all years of interest to the ERT sub-directory 'EnvironmentalReleaseTool/data/cdpr_pur'. Unzip each file in this location (may be done by opening the zip file for many users or using a secondary software on your device for exporting zip files).
4) The ERT can now use data for additional years.

2.7.4 Outputs

The ERT offers users graphical and tabular summaries to prioritize toxicity reduction strategies detailed in this section.

2.7.4.1 Graphical Outputs

When the ERT is opened in the web application, the user can summarize applied toxicity by HUC8 watersheds (~3,600 km^2) or HUC10 watersheds (~440 km^2); for more information on the watershed delineations, see the Watershed Boundary Dataset.(27) They can then choose to summarize data by month or year. Default data summarizations are by HUC8 watershed, time-step year, with the first year 2014 and last 2018 (**Figure 1**). In the desktop application, the watershed resolution displayed will depend on the watershed identifier employed in the simulation inputs file ('Simulation_Information.csv'). If an 8-digit value is entered in the 'Watersheds' sheet of the input file in the 'huc' field, the tool will automatically display HUC8 watersheds; if a 10-digit value is entered, HUC10 watersheds, etc. To change the watershed scale at which applied toxicity is summarized graphically, a user can display simulations that have been run previously (see *Section 3.1*) or run a new simulation for watersheds at a different spatial resolution. The desktop tool can summarize applied toxicity by at any scale of interest to the user (**Figure 1**). The HUC12 is not offered in the web tool due to the high memory storage required for the high-resolution data.

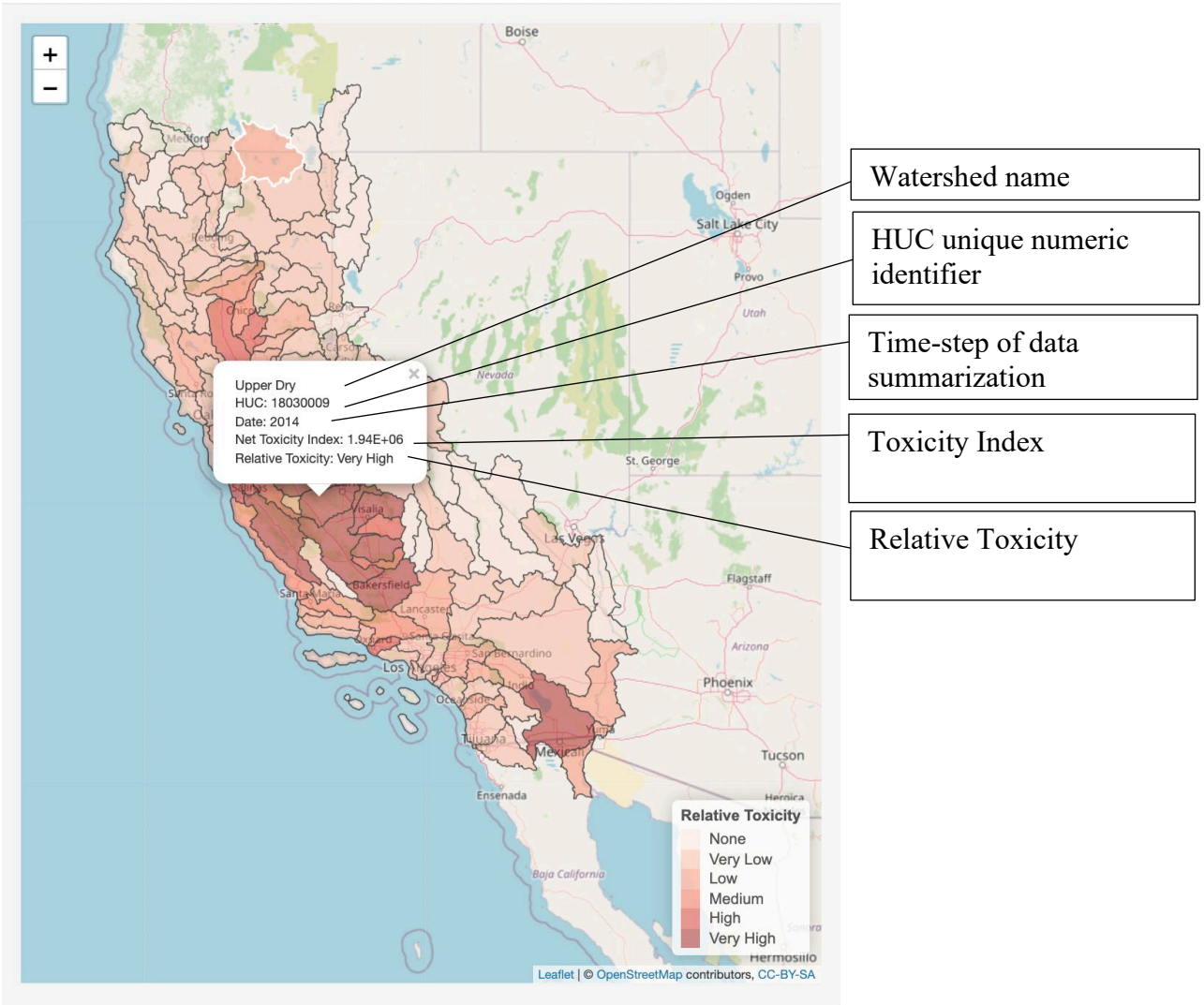
To view watershed-specific data, click the watershed of interest on the map; see **Figure 4**. The watersheds are partially transparent, so users can see the names of cities and water bodies on the map to help orientate their search. When hovering over the map, the following information is provided: the name and number of the HUC, the date by which the data is currently summarized, the applied toxicity during the time step, and the applied toxicity relative to other watersheds. The applied toxicity relative ranking of low to very high is determined via the percentiles of watersheds analyzed; very low represents watersheds in the lower 20th percentile of toxicity, low 20-40th percentile, medium 40-60th percentile, high 60-80th percentile, and very high 80-100th percentile. Watersheds with no pesticides applied are not considered in the percentile analysis and are depicted as having no pesticides applied.

Relative toxicity index in the heat map and other graphical summaries are displayed in the side panel. The toxicity index presented on the map in the graphs are in scientific notation, a standard format for writing large or small numbers in science. The format indicates where the decimal place is relative to the reported digits. For instance:

Scientific Notation	**Value**
1.00E+06	1000000
1.00E+05	100000
1.00E+04	10000
1.00E+03	1000
1.00E+02	100
1.00E+01	10
1.00E+00	1

1.00E-01	0.1
1.00E-02	0

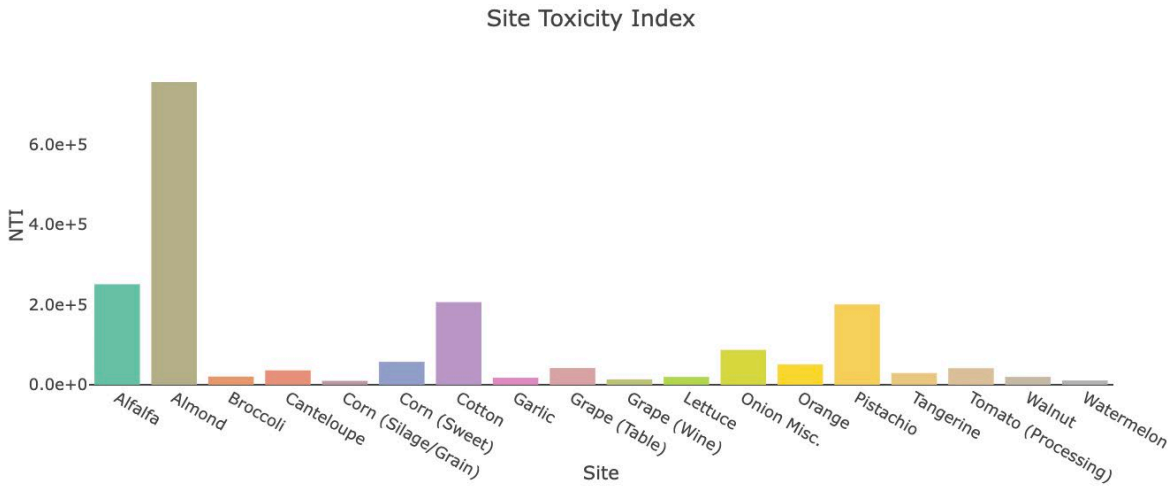
Figure 4. Clickable heatmap. Information provided by the Environmental Release Tool within the heatmap when a watershed is selected. Base map imagery is a product of OpenStreetMap https://www.openstreetmap.org/copyright.



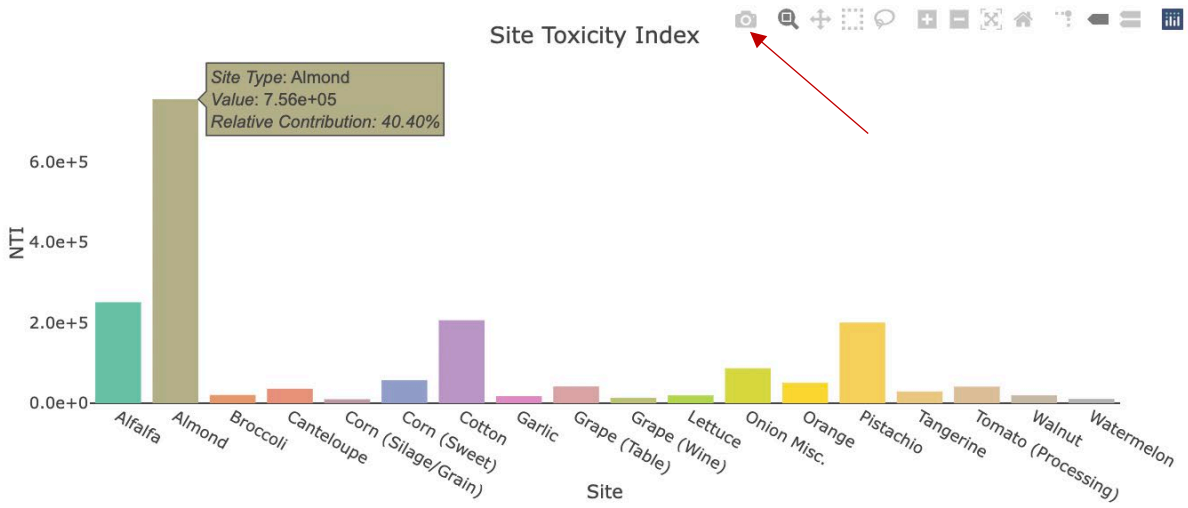
When a watershed is selected in the heatmap, the additional graphical summaries will appear in the side panel. A user can view additional value-specific information for each

graph by hovering over the plot. For instance, in the 'Site Applied Toxicity' graph for watershed HUC 18030009, it's observable that almonds contribute 39% of watershed applied toxicity (**Figure 5(a)**). To save graphical summaries from the user interface, a user can hover over the summary graphic of interest, and in the top right, icons will appear. If the user selects the camera icon (**Figure 5(b)**), they are given the option to download the image.

Figure 5 (a and b). Pesticide and site applied toxicity. a) Example of the Environmental Release Tool graphical summary of applied toxicity from pesticide application site types and **b)** how hovering provides additional details. To download a graphic of interest, hover over the image. In the upper right-hand corner, select the camera icon (see red arrow) to prompt the tool to download the image.



a)



b)

2.7.4.2 Tabular Outputs

For the web tool, users can obtain tabular data by following the data download link in the upper right of the tool window. For desktop users, the data will automatically be saved into a sub-directory named after the simulation in the 'EnvironmentalReleaseTool/output/' directory. For each simulation, a new sub-directory with the simulation is created in the output directory and is provided to the user in the format of '*.csv'. Each file name begins with the simulation name and ends with file name descriptors (e.g., SimulationName_Watershed.csv').

Tabular outputs the user is provided within the 'output/SimulationName' include:

- 'SimulationName_Pesticides.csv': Applied toxicity per pesticide for the simulation period.
- 'SimulationName _ApplicationSites.csv': Applied toxicity per application site for the simulation period.

- ‘SimulationName _Watershed.csv’: Applied toxicity per watershed for the simulation period.
- ‘SimulationName_PesticidesPerApplicationSite’: Applied toxicity for each pesticide per application site for the simulation period.
- ‘SimulationName _PesticidesPerWatershed.csv’: Applied toxicity for each pesticide per watershed for the simulation period.
- ‘SimulationName _ApplicationSitesPerWatershed’: Applied toxicity for each application site per watershed for the simulation period.
- ‘SimulationName_PesticidesPerApplicationSitePerWatershed’: Applied toxicity for each pesticide per application site within each watershed for the analysis period.
- ‘SimulationName _PMPM_Output_Daily_Summary.csv’: Optional output (user selects to view this output in the input file ‘Simulation_Information.csv’), which provides a daily level summary of applied toxicity by site, chemical, and watershed for the simulation period.

Fields of the output data frames include:

- huc: Unique hydrologic unit code watershed identifier.
- huc_name: Name of hydrologic unit code watershed.
- pesticide: Name of pesticide evaluated.
- pmpm_id: Unique pesticide application site type for the Environmental Release Tool (ERT) in the Pesticide Mitigation Prioritization Model (PMPM). By default, the tool simplifies 268 unique application site types in pesticide use reports to 96).
- pesticide_kg: The mass of pesticide applied (kg).

- RTI: The applied toxicity (TI/ha) weighted by the affected compartment area in a watershed, *Equation (2)*.
- NTI: The applied toxicity (unitless) of pesticide applied weighted by the applied toxicity of a pesticide and watershed in the n^{th} percentile of applied toxicity, see *Equation (3)*.
- NTI_perc: Percentile of pesticide applied toxicity in watersheds used to calculate the NTI, see *Equation (3)*.
- econ_score: Score of the economic value of application sites (USD/ha).
- econ_val: Relative magnitude of the economic value of application sites. Calculated in 20^{th} percentile bins as 'Very Low', 'Low', 'Medium', 'High', and 'Very High'.
- econ_health_score: Index of the economic value of an application site and its protectiveness of environmental health (USD/NTI).
- econ_health_val: Relative magnitude of an application site's economic value and environmental protectiveness. Calculated in 20^{th} percentile bins as 'Very Low', 'Low', 'Medium', 'High', and 'Very High'.
- health_score: Index of an application site's protectiveness of environmental health (NTI/ha).
- health_val: Relative magnitude of an application site's protectiveness of environmental health. Calculated in 20^{th} percentile bins as 'Very Low', 'Low', 'Medium', 'High', and 'Very High'.

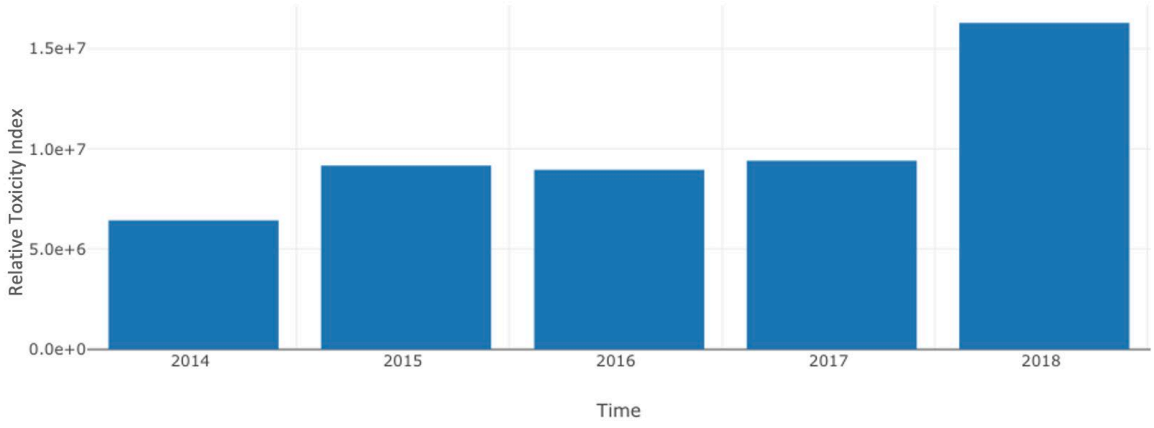
2.7.5 Example Applications – Environmental Release Tool

This section provides examples of how users might employ the ERT to attain pesticide mitigation insights. Recall that the module does not predict exposure, enabling an evaluation of health risks (see *Section 1.0*). Instead, the ERT allows users to explore sources of applied toxicity, regional variability, and mitigation options for reducing toxicity. Similarly, economic and health indices flag high applied toxicity application sites relative to their gross economic value. Still, they do not account for other important considerations, such as how much pesticides migrate to air and water or the costs of cultivating a crop.

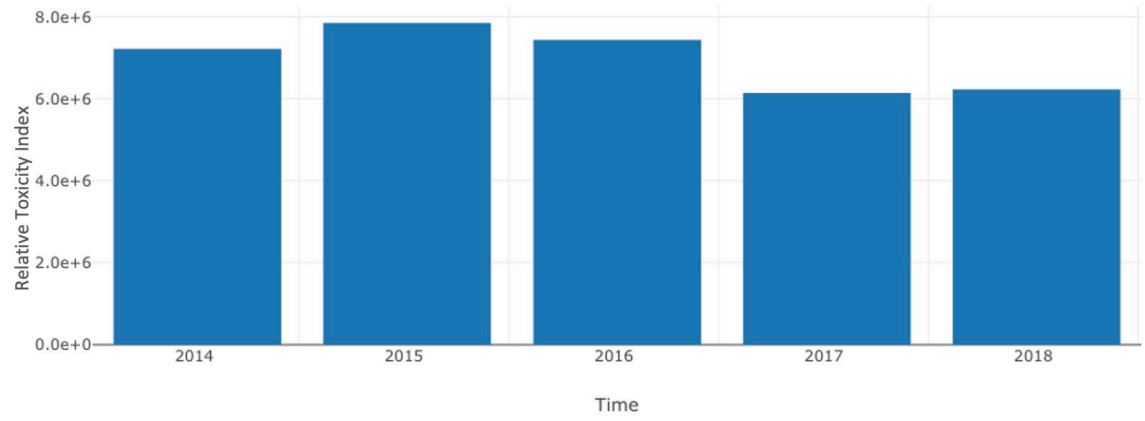
2.7.5.1 Temporal Trends

The Bay Delta Watershed in California is home to a rich community of organisms, including over 90 threatened or endangered species(38–40). Significant concerns for pesticide toxicity in waterways have been observed within the watershed.(41) In reviewing results from the ERT for sub-watersheds of the Bay Delta for 2014-2018, two sub-watersheds that contribute to high applied toxicity are the Dry Creek and the Lower Feather River. Graphical summaries provided by the ERT of temporal trends in the Dry Creek subwatershed demonstrate the applied toxicity increased from 2014-2018 (**Figure 6**). In the Lower Feather River Watershed, applied toxicity has remained relatively steady and decreased marginally. These insights suggest mitigation efforts should prioritize better understanding and mitigating the increased pesticide-applied toxicity in the Dry Creek Watershed, which is also higher than that of the Lower Feather River Watershed.

Figure 6 (a and b). Example of temporal trends of pesticide-applied toxicity provided by the Environmental Release Tool for **a)** the Dry Creek subwatershed and **b)** the Lower Feather River subwatershed.



a)



b)

2.7.5.2 Chemical Alternatives

From the ERT heatmap of statewide watersheds, an almond farmer observes that her Upper Poso watershed receives high applied toxicity. In the review of the crops contributing to toxicity in the watershed, almonds introduce over 60% of applied toxicity. Moreover, of the hundreds of different pesticide and crop treatment types in the watershed, bifenthrin on almonds accounts for 30% of all pesticide-applied toxicity. The almond farmer considers her

routine use of bifenthrin to combat mites, one of the watershed's most damaging pests to almonds. Given this knowledge of the high environmental impact of bifenthrin on bees and aquatic fauna, she reviews a chemical alternatives database (42). In the review of alternatives, she observes that bifenazate is a pesticide that targets mites and has a substantially lower toxicity profile and environmental persistence. If bifenazate were employed as an alternative to bifenthrin to treat almond mites, the applied toxicity per hectare would be reduced by 400-fold for fish and over 100,000-fold for aquatic invertebrates. For the subsequent treatment of mite pests, the farmer employs bifenazate.

2.7.5.3 Prioritizing Monitoring

For pesticide use practices in California, it was observable from outputs of the ERT for 2014-2018 that of the hundreds of pesticides in use, 15 introduced 99% of environmental applied toxicity. Moreover, 80% of applied toxicity was applied to 14 different site types and 14 watersheds. Exemplary actions that may be taken from these insights include exerting more effort in the registration/re-registration process for the chemicals and sites identified as contributing the majority of applied toxicity or designing monitoring campaigns to more closely monitor high-impact chemicals and application sites.

2.7.5.4 Health and Economic Tradeoffs

The ERT provides health and economic indices of the sites to which pesticides are applied. By considering health protectiveness *and* the economic value of sites targeted during pesticide application, users can evaluate approaches for working with pesticide users to reduce applied toxicity in at-risk watersheds. For example, from 2014-2018 in California, cotton was observed to have a low economic value per hectare of site types with the highest

applied toxicity. In high-risk watersheds, farmers may be incentivized to cultivate crops with lower applied toxicity and higher economic value (see **Table 1**).

2.7.6 Errors and Updates

The ERT was developed as a part of an ongoing PhD dissertation and has limited capacity for user assistance at the time of this guide's publication. Accordingly, the tool was developed in one of the most widely used data science tools for which a plethora of online assistance exists for errors encountered during simulation runs. Users can explore solutions to errors encountered via googling the error codes or exploring question and answer websites such as Stack Exchange. Users troubleshooting errors should prioritize ensuring all inputs match the EXACT formatting of template files and input field formats described in *Section 3.0 Parameterization*. Second, a user should explore device-specific errors for running the RStudio software and packages via an internet search of the error code. Third, the user should revisit the ERT download link and look for model updates.

2.7.7 Acknowledgements

This project was funded by the California Sea Grant Delta Science Fellowship SEADSR4/183BCA/416701/440000.

2.7.8 References

1. Stone WW, Gilliom RJ, Ryberg KR. Pesticides in U.S. streams and rivers: occurrence and trends during 1992-2011. Environ Sci Technol. 2014 Oct 7;48(19):11025–11030. PMID: 25209419
2. Nowell LH, Moran PW, Schmidt TS, Norman JE, Nakagaki N, Shoda ME, Mahler BJ, Van Metre PC, Stone WW, Sandstrom MW, Hladik ML. Complex mixtures of dissolved pesticides show potential aquatic toxicity in a synoptic study of Midwestern U.S. streams. Sci Total Environ. 2018 Feb 1;613–614:1469–1488. PMID: 28802893
3. Bradley PM, Journey CA, Romanok KM, Barber LB, Buxton HT, Foreman WT, Furlong ET, Glassmeyer ST, Hladik ML, Iwanowicz LR, Jones DK, Kolpin DW,

Kuivila KM, Loftin KA, Mills MA, Meyer MT, Orlando JL, Reilly TJ, Smalling KL, Villeneuve DL. Expanded Target-Chemical Analysis Reveals Extensive Mixed-Organic-Contaminant Exposure in U.S. Streams. Environ Sci Technol. 2017 May 2;51(9):4792–4802. PMCID: PMC5695041
4. Mullin CA, Frazier M, Frazier JL, Ashcraft S, Simonds R, Vanengelsdorp D, Pettis JS. High levels of miticides and agrochemicals in North American apiaries: implications for honey bee health. PLoS One. 2010 Mar 19;5(3):e9754. PMCID: PMC2841636
5. Main AR, Hladik ML, Webb EB, Goyne KW, Mengel D. Beyond neonicotinoids - Wild pollinators are exposed to a range of pesticides while foraging in agroecosystems. Sci Total Environ. 2020 Nov 10;742:140436. PMID: 32623160
6. Hladik ML, Vandever M, Smalling KL. Exposure of native bees foraging in an agricultural landscape to current-use pesticides. Sci Total Environ. 2016 Jan 15;542(Pt A):469–477. PMID: 26520270
7. Forister ML, Cousens B, Harrison JG, Anderson K, Thorne JH, Waetjen D, Nice CC, De Parsia M, Hladik ML, Meese R, van Vliet H, Shapiro AM. Increasing neonicotinoid use and the declining butterfly fauna of lowland California. Biol Lett. 2016;12(8). PMCID: PMC5014040
8. State Water Resources Control Board. 2014 and 2016 Clean Water Act Section 303(d) and 305(b) Integrated Report — Statewide (Internet). State Water Resources Control Board. 2018 (cited 2019 Mar 11). Available from: https://https://www.waterboards.ca.gov/water_issues/programs/tmdl/integrated2014_2016.shtml
9. Young DF, Fry MM. PRZM5 A Model for Predicting Pesticides in Runoff, Erosion, and Leachate–Revision B . USEPA; 2020 Aug.
10. Alterra - Environmental risk assessment, WOT Natuur & Milieu, ter Horst MMS, Beltman WHJ, van den Berg F. The TOXSWA model version 3.3 for pesticide behaviour in small surface waters : description of processes. Wageningen: Statutory Research Tasks Unit for Nature & the Environment; 2016.
11. Pistocchi A, Groenwold J, Lahr J, Loos M, Mujica M, Ragas AMJ, Rallo R, Sala S, Schlink U, Strebel K, Vighi M, Vizcaino P. Mapping Cumulative Environmental Risks: Examples from the EU NoMiracle Project. Environ Model Assess. 2011 Apr;16(2):119–133.
12. Schriever CA, Liess M. Mapping ecological risk of agricultural pesticide runoff. Sci Total Environ. 2007 Oct 1;384(1–3):264–279. PMID: 17689592
13. Strassemeyer J, Daehmlow D, Dominic AR, Lorenz S, Golla B. SYNOPS-WEB, an online tool for environmental risk assessment to evaluate pesticide strategies on field level. Crop Prot. 2017 Jul;97:28–44.
14. Zhan Y, Zhang M. PURE: a web-based decision support system to evaluate pesticide environmental risk for sustainable pest management practices in California. Ecotoxicol Environ Saf. 2012 Aug;82:104–113. PMID: 22704897
15. Ropke B, Bach M, Frede H. DRIPS—a DSS for estimating the input quantity of pesticides for German river basins. Environ Model Softw. 2004 Nov;19(11):1021–1028.
16. AGIS Lab, University of California, Davis. PUR Web GIS (Internet). (cited 2021 May 3). Available from: http://purwebgis.ucdavis.edu/PURwebGIS.html
17. Maggi F, Tang FHM, la Cecilia D, McBratney A. PEST-CHEMGRIDS, global gridded

maps of the top 20 crop-specific pesticide application rates from 2015 to 2025. Sci Data. 2019 Sep 12;6(1):170. PMCID: PMC6761121
18. California Department of Pesticide Regulation. A Guide to Pesticide Regulation in California. CDPR; 2017.
19. CDPR. California Pesticide Information Portal (CalPIP) (Internet). (cited 2018 Oct 20). Available from: https://calpip.cdpr.ca.gov/main.cfm
20. CDPR. Summary of Pesticide Use Report Data 2017 (Internet). 2019 (cited 2019 Oct 17). Available from: https://www.cdpr.ca.gov/docs/pur/pur17rep/17sum.htm
21. Atwood D, Paisley-Jones C. Pesticide Industry Sales and Usage – 2008-2012 Market Estimates. U.S. Environmental Protection Agency; 2017.
22. DiBartolomeis M, Kegley S, Mineau P, Radford R, Klein K. An assessment of acute insecticide toxicity loading (AITL) of chemical pesticides used on agricultural land in the United States. PLoS One. 2019 Aug 6;14(8):e0220029. PMCID: PMC6684040
23. Xie Y, Luo Y, Singhasemanon N, Goh KS. Regulatory modeling of pesticide aquatic exposures in california's agricultural receiving waters. J Environ Qual. 2018;47(6):1453–1461. PMID: 30512076
24. Halbach K, Möder M, Schrader S, Liebmann L, Schäfer RB, Schneeweiss A, Schreiner VC, Vormeier P, Weisner O, Liess M, Reemtsma T. Small streams-large concentrations? Pesticide monitoring in small agricultural streams in Germany during dry weather and rainfall. Water Res. 2021 Sep 15;203:117535. PMID: 34403843
25. Dubus IG, Brown CD, Beulke S. Sources of uncertainty in pesticide fate modelling. Sci Total Environ. 2003 Dec 30;317(1–3):53–72. PMID: 14630412
26. RStudio Team. RStudio: Integrated Development for R. RStudio; 2020.
27. USGS, USDA. Federal Standards and Procedures for the National Watershed Boundary Dataset (WBD). US Geological Survey Techniques and Methods 11-A3. 2nd ed. 2011.
28. Multi-Resolution Land Characteristics (MRLC) Consortium. National Land Cover Database (NLCD) (Internet). (cited 2019 Jun 6). Available from: https://www.mrlc.gov/data?f%5B0%5D=category%3Aland%20cover&f%5B1%5D=category%3Aurban%20imperviousness&f%5B2%5D=region%3Aconus&f%5B3%5D=category%3Aland%20cover&f%5B4%5D=category%3Aurban%20imperviousness&f%5B5%5D=region%3Aconus
29. USDA. CropScape - NASS CDL Program (Internet). (cited 2018 Mar 19). Available from: https://nassgeodata.gmu.edu/CropScape/
30. CADWR Land Use Viewer (Internet). (cited 2019 Jul 10). Available from: https://gis.water.ca.gov/app/CADWRLandUseViewer/
31. USDA. 2017 Census of Agriculture . USDA; 2019 Apr. Report No.: AC-17-A-51.
32. Agriculture and Environment Research Unit, University of Hertfordshire. PPDB - Pesticides Properties DataBase (Internet). (cited 2018 Oct 20). Available from: https://sitem.herts.ac.uk/aeru/ppdb/en/
33. USEPA. Aquatic Life Benchmarks and Ecological Risk Assessments for Registered Pesticides (Internet). (cited 2022 Jun 8). Available from: https://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/aquatic-life-benchmarks-and-ecological-risk
34. USDA. USDA - National Agricultural Statistics Service Homepage (Internet). (cited 2020 Dec 13). Available from: https://www.nass.usda.gov/

35. USGS. NAWQA Estimated Annual Agricultural Pesticide Use - Pesticide Use Maps (Internet). (cited 2019 Aug 11). Available from: https://water.usgs.gov/nawqa/pnsp/usage/maps/compound_listing.php
36. Baker N, Stone W. Estimated Annual Agricultural Pesticide Use for Counties of the Contimerous United States, 2008-12. USGS; 2015.
37. National Resource Conservation Service (NRCS). Geospatial Data Gateway (Internet). (cited 2019 Jun 26). Available from: https://datagateway.nrcs.usda.gov/
38. Center for Biological Diversity. San Francisco Bay Area and Delta Protection (Internet). (cited 2019 Oct 18). Available from: https://www.biologicaldiversity.org/campaigns/san_francisco_bay_area_and_delta_protection/index.html#
39. State of California Department of Fish and Wildlife. State and Federally Listed Endangered and Threatened Animals of Califonria. State of California Department of Fish and Wildlife; 2020.
40. State of California Department of Fish and Wildlife. State and Federally Listed Endangered, Threatened, and Rare Plants of California. State of California Department of Fish and Wildlife; 2020.
41. De Parisa M, Orlando J, McWayne M, Hladik M. Pesticide Inputs to the Sacramento–San Joaquin Delta, 2015-16: Results from the Delta Regional Monitoring Program. USGS; 2018.
42. Haviland DR, Symmes EJ, Adaskaveg JE, Duncan RA, Roncoroni JA, Gubler WD, Hanson B, Holtz BA, Stapelton JJ, Tollerup KE, Trouillas FP, Zalom FG. UC IPM Pest Management Guidelines: Almond – Publication 3431 (Internet). University of California Integrated Pest Management. (cited 2021 Jun 9). Available from: https://www2.ipm.ucanr.edu/agriculture/almond/

Chapter 3. Scaling Up the Identification of Pesticide Sources and Risk Reduction Targets for Aquatic Environments

Pesticides remain a primary cause of dispersed chemical pollution in surface waters, emphasizing the importance of tools that can identify and prioritize strategies to mitigate risks. To target risk reduction opportunities, we introduce a tool, the Environmental Fate Tool (EFT), which is novel in its ability to, within a single simulation, quantify the aquatic risks for hundreds of pesticides and watersheds across expansive landscapes that encompass tens of thousands of kilometers. The EFT goes further by, within a single simulation, pinpointing spatially explicit source contributions of application sites within watersheds and scaling up analyses to the study extent. The tool is a discretized, mechanistic fate model, unique in its capacity to deliver individual and cumulative pesticide screening ecological risk assessments at various scales, thereby facilitating the development of strategies to safeguard our water resources.

This investigation applied the tool to simulate pesticide concentrations and associated risks for 208 watersheds with agricultural development in a 22,000 km^2 study area within the San Francisco Bay Delta Watershed, California. Risks to various aquatic organisms, including fish, invertebrates, and nonvascular and vascular aquatic plants, were considered. Results demonstrate that from 2016 to 2020, 80% of pesticide risks, as weighted by application area, were concentrated in 9% of the watersheds and were predominantly attributable to applications of lambda-cyhalothrin, imidacloprid, and indaziflam to aquatic taxa investigated per area of pesticide application. Most (81%) of toxicity for pesticide active ingredients considered (290) are predicted for invertebrates, followed by 16% for vascular plants, 3% for nonvascular plants, and 0.3% for fish. Furthermore, across the simulation

period, a consistent trend was observed for applied pesticides—the maximum cumulative risk of pesticides transported to surface waters for each taxonomic group significantly ($p<1E-10$) exceeded that posed by individual pesticides. The maximum cumulative risk observed for any day of the simulation was 370%-820% greater than individual pesticide risk for investigated taxa.

3.1 Introduction

Pesticides profoundly impact global environmental pollution(1–4) and are the predominant cause of aquatic toxicity of dispersed organic chemical pollution in both the United States(2) and Europe(1). However, understanding the specific risks they pose to diverse taxa is challenging, given variations in their use patterns, landscape characteristics, and crop management practices. Assessing pesticide risks becomes particularly difficult due to limited monitoring observations for model calibration, data paucity for environmental parameterization, and insufficient resolution and availability of pesticide use data. Yet, overcoming these challenges is crucial for preserving and restoring environmental health.

Fortunately, geospatial datasets have made significant advancements, particularly in California, offering valuable information on pesticide applications, soil hydrologic properties, climate, and irrigation practices. Despite this wealth of data, existing tools fall short in their ability to fully harness available data to identify risks of the many pesticides used simultaneously at the scale they are registered and managed in the United States and Europe, typically at state, national, or multi-national levels(5,6).

Widely used tools like SWAT(7–9) and HSPF(10–12) in the United States, as well as SYNOPS(13,14) in Europe, support analyses of agrochemical risks over large areas. However, they cannot compare risks for the many pesticides in use within a single

simulation, nor account for risks of pesticide mixtures, which can be significantly higher, especially considering the seasonality of pesticide impacts or longer exposures(15–17). Additionally, these tools do not effectively highlight the sources of pesticide risk in their outputs, such as identifying specific application sites that contribute the highest pesticide risk from runoff and eroded sediments.

The present investigation addresses these limitations by developing the EFT to efficiently prioritize risk reduction needs and opportunities for numerous pesticide application sites managed across large geographic extents. The EFT quantifies pesticide concentrations in environmental media for hundreds of pesticides and watersheds per simulation, as well as thousands of application sites. It also provides risk indices for various aquatic taxa, identifies primary sources of pesticide toxicity at multiple scales, and predicts the number of days concentrations exceed adverse health effect levels. The EFT is part of the Pesticide Mitigation Prioritization Model framework and includes a companion model, the Environmental Release Tool(16), which summarizes hotspots of pesticide-applied toxicity.

By considering large extents, we gain a better understanding of where risks exist; however, limited data availability or resolution for chemical use rates/locations, environmental characteristics, instream hydrology, and climate can increase uncertainty and pose challenges.

For complex fate and transport models, it is common to consider numerous parameters requiring proxy data from other sites, expert judgment, or to use static values for highly variable characteristics such as stream dimensions, suspended sediment organic carbon concentrations, suspended particle radius, burial rate, resuspension rate, etc. Global calibration methods are often used to parameterize such models, which involve fitting the

model parameters such that the output approaches observed data(18). However, this approach is prohibitive of risk modeling in that many surface waters and watersheds have limited or no monitoring data for many of the pesticides in use. The calibration approach also emphasizes global model responses (e.g., predictions at the watershed outlet), which can mask important sources of toxicity(19,20). These sources of toxicity remain hidden because the model is adjusted to match landscape and waterbody parameters in a way that minimizes discrepancies between predicted chemical concentrations in the waterbody and the limited available observations. Observations are highly limited spatially and temporally relative to predictions, and parameterization via global calibrations may not reflect our best understanding of how to represent unique landscape conditions and management practices' effects on the transport of chemicals from specific sites in runoff and eroded sediments.

To overcome the need to perform global calibrations in surface waters for large-scale risk assessment tools, a key aim of the EFT is to understand sources of pesticide risk by quantifying pesticide concentrations in surface runoff, lateral flow, eroded sediment, and benthic sediment based on high-resolution pesticide use reports. The aim is to provide a tool able to evaluate aquatic risks as a calibrated or uncalibrated tool where instream hydrologic data is unavailable or limited. The EFT emphasizes the identification of realistic concentrations in the most vulnerable tributaries within a watershed and predicts intra-waterbody risks from runoff and eroded sediment concentrations, which has important advantages for evaluating risk at scale.

Simulating instream concentrations requires complex data about aquatic compartment dimensions, discharge, and instream processes. These types of data are often unavailable or have severely limited spatial resolution. For instance, discharge, a critical instream

characteristic, has the most extensive temporal coverage. However, in many regions, such as California, discharge is only monitored at approximately one location per 220 km of stream length(21,22). Moreover, 66% of streams in California are dry for a substantial part of the year(22). As a result, obtaining comprehensive and representative data for instream characteristics is challenging.

Another advantage of the EFT's approach, predicting aquatic risks from runoff, lateral flow, and eroded sediment is the ability to explore potential risks to the most vulnerable waterways within each watershed where monitoring data of many pesticides in use are unavailable. During a runoff event in small tributaries, instream concentrations approach those of runoff(23); this is attributable to the waterbodies having lower dilution potential and slower discharge rates. These small waterbodies also have important ecological significance as they can host greater biodiversity(24). By simulating concentrations in runoff and eroded sediment, the EFT facilitates the identification of risks to vulnerable waterways, thereby contributing to more effective risk assessment and management strategies for data-limited aquatic ecosystems.

In this study, we introduce the EFT's development, application, and validation for targeting pesticide sources and risk reduction opportunities at scale. We evaluate the tool's application for subwatersheds of the Bay Delta Watershed (BDW) in California. The BDW study extent encompasses 22,000 km^2 of intensive agriculture in 208 watersheds within ~100 km of the San Francisco Bay Delta (**Figure 1**). The BDW encompasses diverse crops, irrigation practices, soil characteristics, and pesticide use strategies, making it a useful study area. Furthermore, over 90 threatened or endangered species are found in this area(25), and

56% of waterways designated as impaired by pesticides in California are located within waterbodies hydrologically connected to the Bay Delta(26).

The objectives of this investigation of pesticide risks to aquatic taxa in the BDW are as follows: 1) assess the EFT's effectiveness in accurately predicting concentrations in small agricultural water bodies across large geographical areas; 2) identify the specific sources, application sites and pesticides, that contribute the greatest aquatic risks within individual watersheds and across the entire study area; 3) quantify the significance of accounting for pesticide mixtures to understand the frequency of runoff events with concentrations that may cause adverse effects on aquatic organisms.

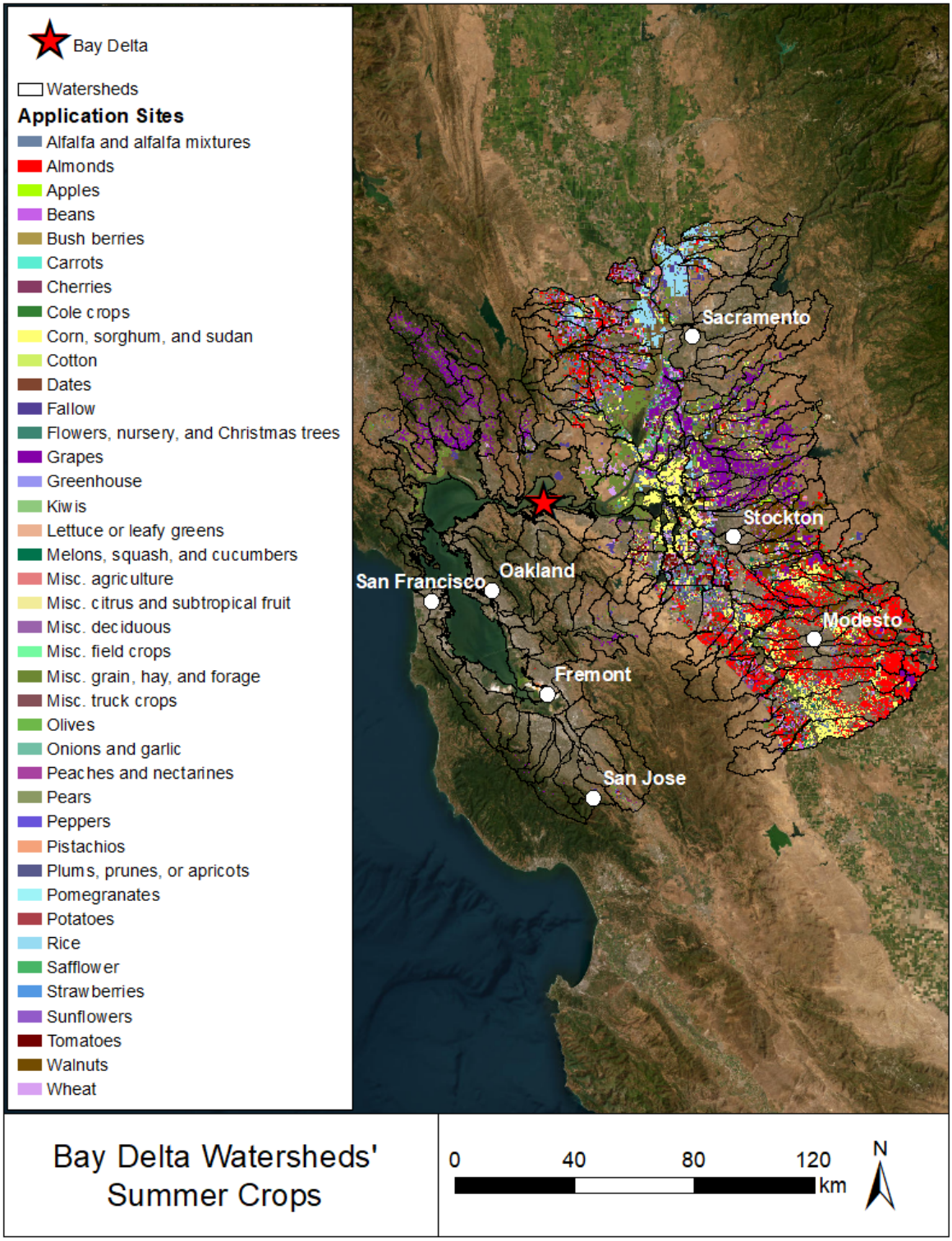


Figure 1. Investigated subwatersheds in the Bay Delta Watershed and their summer crop rotations.

3.2 Methods

To identify risk reduction opportunities, the EFT requires users to delineate their study extent by watersheds, as well as by unique application sites and, optionally, crop rotations. We recommend and use watersheds from the USGS Watershed Boundary Dataset(27). The dataset delineates watersheds using hydrologic unit codes (HUCs), which employ a numeric ordination approach to naming watersheds in consideration of their hydrologic connectivity across various spatial scales. Watershed names also have different lengths that correspond to their resolution. For instance, HUC 2-digit codes cover hundreds of thousands of square kilometers, and HUC 12-digit codes (HUC12) represent subwatersheds of the shorter digit codes (e.g., HUC2), typically spanning tens to hundreds of square kilometers. In our study, we focus on HUC12 watersheds, with an average area of 100 km^2 in California.

3.2.1 Sources

To evaluate the spatiotemporal distribution of pesticides, the EFT enables manual inputs of pesticide use data via text files; or, for California, the tool can autoload pesticide use report data from statewide agricultural applicators(28). The EFT internally hosts the pesticide use data for California. Using an autoload sub-module, the tool aggregates data for the area of interest to the user.

Pesticide use data in the EFT autoload submodule used for this investigation are retrieved by active ingredient (AI) and for the 432 site types that are agricultural from California Department of Pesticide Regulation (CDPR) Pesticide Use Reports(28). The pesticide use reports contain daily time-step pesticide application data by site type at the

County Meridian Township Range Section (2.6 km^2, referred to as Section). Rice and urban applications are excluded from the autoload pesticide use sub-module. Rice applications were not considered owing to their use of water detention mechanisms not simulated by the tool. Urban applications are excluded due to use reports not including household applications, and most professional urban applications being recorded at the county level and at a monthly time-step, which cannot be allocated to a specific watershed or date. Although not accommodated in the autoload feature for pesticide use data, the EFT also supports evaluations in urban and undeveloped lands where users aggregate the required inputs manually.

To identify the contributions of specific application sites to pesticides within a watershed, the EFT adapts the SWAT method of delineating unique land uses, where watersheds are subdivided into Hydrologic Response Units (HRUs)(29). Within each HRU, environmental media characteristics are treated as both homogenous and contiguous. Using this approach, the effects of distinct soil hydrologic behaviors (such as runoff, infiltration, and water storage), as well as application rates on the transport and transformation of pesticides, are accounted for within each HRU.

To delineate HRUs by crop type, county-specific agricultural department crop permitting spatial data (e.g., Kern(30)) and the crop type reported in pesticide use reports could be used to delineate field level data crop use data; however, this data was unavailable for most of our study extent. Accordingly, to assign application data to a specific location within each Section, we employed the 2018 California Department of Water Resources (CADWR) land use surveys(31) to delineate HRUs; the surveys employ satellite imagery and ground truthing surveys. The 2018 dataset was leveraged to delineate fields, although more

recent land use data sets exist due to the year representing conditions in the middle of the simulation period. The CADWR dataset was selected from reviewed land use datasets, which include the CDL(32) and NLCD(33) datasets, due to its provision of the most accurate data, with a median accuracy of 97.5% and positional quality of 8m(34).

For the present investigation, we delineate HRUs by considering fields within a watershed that maintain the same crop rotation patterns throughout the year. Taking into account crop rotations is particularly important in warmer regions like California, where it's frequent to have 2-3 crop rotations within a single field and year. Incorporating crop rotations is crucial as it enables users to grasp the cumulative impacts of pesticide toxicity from specific application sites within a watershed. This approach also allows us to simulate diverse irrigation practices and evaluate the risks linked to fields cultivating multiple crops within a year. In total, 2,794 HRUS were delineated in the study extent.

After delineating watersheds and HRUs for analyses in California, the EFT can autoload pesticide use data from the most recently available pesticide use reports. The autoload feature assigns pesticide use data to watersheds using a relational database developed for the Sections within which pesticide use is reported and watersheds from geospatial intersection analyses.

Section geospatial data is available through the California Pesticide Information Portal(28). To assign pesticide use data within a Section that overlaps multiple watersheds, the applied mass is divided by the area fraction of overlap. Within each watershed, pesticide use can then be assigned to the land uses within the watershed by quarterly crop rotations. If multiple HRUs of a watershed have the same crop rotation within a given quarter, assignment of pesticide application to HRUs is conducted by weighting the total mass of

applied pesticide in the watershed for a given day to the crop types by the cultivation area of each HRU.

The relationship between multiple watershed resolutions is accommodated in the pesticide use autoload feature, which includes HUC12 (~100 km^2), HUC10 (~440 km^2), and HUC8 (~3,600 km^2) watersheds. Pesticide use data for all of California for the most recently available 10-year period is hosted internally and is updated as new data becomes available (latest dataset 2021). To accommodate the assignment of pesticide uses to specific land uses of interest to the user within these watersheds, the tool considers information input for the user's HRUs, which describe which watershed the HRU is located in.

The autoload feature for pesticide use data is only suitable when considering all fields of crop types of interest within a watershed. Where only the analysis of a few fields of a crop type (e.g., grapes) is of interest to the user, the auto-load submodule will still aggregate all pesticide use data for the crop type in the watershed.

Pesticides evaluated in the present investigation were detected in surface water monitoring campaigns in California from 2014-2018(35). Of detected pesticides with available toxicity data, we simulated all forms of their active ingredient (n=290) within California's pesticide use reports.

3.2.2 Irrigation

A submodule for the EFT was developed to simulate irrigation based on methods reported by growers. For the study, irrigation extent accounts for ~600-800% of water received by fields and is a key factor in simulating landscape hydrology for the prediction of the offsite transport of pesticides. To quantify the irrigation water application volume and

frequency from reported methods, the submodule then considers distinct crop evapotranspiration rates, crop growth stages, crop rotations, the soil water holding capacity in each HRU, and plant water stress. These data enable us to predict the variation in irrigation timing and applied volume among diverse crops and for the same crop type across the landscape in the absence of detailed irrigation data, which is rarely available due to proprietary constraints stemming from socioeconomic factors.

For crops, the irrigation methods used are reported by growers to the California State Water Resources Control Board as part of their compliance with the Irrigated Lands Regulatory Program(36). This program oversees agricultural land discharges to mitigate potential water quality impacts and requires reporting irrigation methods per crop by Section (2.6 km^2). Although the program's coverage isn't statewide, it encompasses more than 2 million hectares of agricultural land, involving approximately 40,000 growers and encompassing most of the BDW study extent. To assign irrigation method data to specific HRUs, we conducted a spatial join with reports and the CADWR 2018 land use survey data (by Section). In cases where irrigation methods were not reported for specific areas within the study region, we utilized the nearest neighbor interpolation technique, based on crop types, to predict the irrigation method used for an HRU.

Evapotranspiration and precipitation data employed to predict the irrigated water depth required to alleviate the plant water stress of HRUs is derived from the comprehensive climate monitoring network known as the California Irrigation Management Information System (CIMIS)(37). The stations are operated by the CADWR with the aim of supporting informed irrigation for growers.

Within the CIMIS system, a network of 267 monitoring stations (although not all are currently operational) collects daily weather data. Utilizing this data, we conduct calculations to estimate water loss for each unique HRU and irrigation method to predict irrigation requirements. This involves taking into account several key factors: the specific crop rotations associated with each HRU, the soil's capacity to retain water within the crop's rooting depth, the developmental stages of the crops, and the irrigation methods' typical rate of application and efficiency. Information about crop rotations is derived from the CADWR's land use survey(34), data for the available water capacities of HRU soils are sourced from gSSURGO(38), and the crop rooting depths are derived from the National Resource Conservation Service Irrigation Guide(39). For the developmental stages of crops, crop evapotranspiration coefficients, and method application rates and efficiencies, we consider data from the Basic Irrigation Scheduling Program dataset(40). In cases where coefficients were unavailable, we turn to values provided by the University of California Division of Agriculture and Natural Resources(41,42).

Essential to the prediction of irrigation and impacts to pesticide transport is accounting for the crop water stress. To achieve this aim, evapotranspiration coefficients that relate evapotranspiration data at reference stations to specific crops were used(43). From the reference evapotranspiration observed at monitoring stations, the actual crop evapotranspiration E_a, is calculated as(41):

$$E_a = E * Kc \quad 3.2.1$$

Where E is the evaporation observed at the monitoring station and Kc is the crop evapotranspiration coefficient.

The Kc is calculated for different crop stages, categorized as A, B, C, D, and E. Each stage represents a specific phase in the crop's growth cycle. Stage A to B represent the crop's initial growth stage, the period from planting to about 10% of the crop's full ground shading; stage B to C is the rapid growth phase where crop ground shading is 10% to 75%; stage C to D is the midseason where crop ground shading is greater than or equal to 75% ground shading until the crop begins to have reduced evapotranspiration due to aging(41,42). Finally, stages D to E represent the late season, characterized by a gradual decline in the crop's evapotranspiration coefficient until harvest(41,42). During stages A to B and C to D, constant evapotranspiration rates are applied, meaning the crop coefficient remains stable throughout these phases.

For stages with a dynamic Kc, B to C and D to E, changes are estimated mathematically using a linear representation of Kc where the slope b is calculated using(41,42):

$$b = \frac{Kc_2 - Kc_1}{d} \quad 3.2.2$$

Where Kc_1 is the crop evapotranspiration at the beginning of the growth stage, Kc_2 the crop evapotranspiration at the end of the growth stage, and d the number of days in the growth stage. Using this approach, Kc is calculable for the k^{th} day of the growth stage, d_k, as:

$$Kc = Kc_1 + b * d_k \quad 3.2.3$$

To calculate the frequency of water application required to alleviate plant water stress, irrigation methods are grouped into four primary methods drip, micro-sprinkler, sprinkler, and gravity (i.e., furrow, border strip, and flood). To simulate the irrigation schedule and depth of water applied, we then consider typical application rate, the irrigation method's efficiency, and the amount of water required to replenish the soil to field capacity

down to the rooting depth of the crop. The application rate (mm -h^{-1}) and efficiency, respectively, for the irrigation methods are 11.2 and 0.75 for gravity, 3.2 and 0.75 for sprinkler, 1.75 and 0.8 for micro-sprinkler, and 0.7 and 0.85 for drip(40).

The sub-module triggers irrigation to replenish soil water once the water deficit reaches a level that leads to unfavorable plant stress, referred to as the Management Allowed Deficit, MAD (mm)(44). To estimate the MAD, the sub-module takes into account the soil available water capacity AWC (mm/mm) for the soil depth from the surface to the termination point of the crop's root system, $depth$ (mm). Via consideration of these properties and the fraction of allowable water depletion, frc_{dep}, the MAD is calculated as:

$$MAD = AWC * depth_{root} * frc_{dep} \qquad 3.2.4$$

Provided that we have no site-specific information across the study extent for the frc_{dep}, and commonly the frc_{dep} is 0.5, we use 0.5 for all crops.

To calculate the soil water deficit, *deficit* (mm), at the daily time-step we consider the E_a, irrigated water, $irrig_{depth}$ (mm), and precipitation, $precip$ (mm). We assume most irrigators due not have soil moisture probes and rely on basic water balance calculations where:

$$deficit = defecit_0 + E_a - irrig_{depth} - precip \qquad 3.2.5$$

When crops are irrigated, we assume the soil moisture content is returned to field capacity, FC. To determine the $irrig_{depth}$ when the *deficit* reaches the *MAD*, we consider the effects of the irrigation methods typical efficiency, eff(40):

$$irrig_{depth} = \frac{FC - MAD}{eff} \qquad 3.2.6$$

To consider the application rate, the irrigation sub-module quantifies the frequency of irrigation required for the method's application rate to maintain desirable soil moisture

conditions, and the application rate's effect to runoff (see *Section 3.2.3*). For irrigation methods with low application rates, like drip, the rates are too low to fully replenish the soil water content to field capacity within a 24-hour period if irrigators were to wait until reaching the *MAD*. Instead, our approach assumes that for these methods, irrigation occurs with a frequency that ensures the soil water content can be returned to field capacity during the lower incident solar radiation hours of the day (we assume 12 hours).

When evaluating water application rates and frequency to align with daily evapotranspiration rates for low-volume irrigation methods, another issue can surface. In some cases, the rate and volume of water application required will exceed the soil's infiltration capacity, and runoff would be simulated, even though runoff is unlikely to occur in reality. This discrepancy arises from the fact that the soil's water retention capacity might be inadequate to prevent runoff when the entire field is irrigated. However, low-volume irrigation methods are targeted specifically to the plant root area, and excess water can infiltrate the surrounding field soil without introducing runoff. Provided the fraction of fields that are irrigated is highly variable and insufficient data is available for large extents, the EFT takes a different approach to prevent simulating runoff events from low-volume irrigation methods.

When entering irrigation inputs into the EFT for each HRU, users are required to specify whether the irrigation method employed on the HRU is categorized as a 'runoff' or 'no runoff' method. With this approach, HRUs where irrigation methods are employed that will produce runoff, such as gravity-based methods, the HRU is designated as a 'runoff' site and the generated runoff and eroded sediment is calculated using approaches outlined in *Section 3.2.3*. Conversely, for methods categorized as 'no runoff', the assumption is that any

excess water near the crop rooting zone infiltrates the surrounding soil. To simulate this, the soil water content of the entire field is adjusted to match the field capacity of the HRU's soil. This approach bypasses the need for often difficult-to-obtain data—the fraction of soil irrigated within the crop field—while ensuring a conservative balance of soil water within the field as related to pesticide offsite transport. The approach is conservative in that higher soil water content will induce runoff and sediment erosion for smaller precipitation events than when soils have a lower water content.

3.2.3 Environmental Compartments and Pesticide Transport

The EFT is designed to simulate pesticide concentrations in surface runoff, lateral flow, eroded sediment, and benthic sediment. It's important to clarify that the model does not directly predict pesticide concentrations in the stream water column. This is because such predictions would necessitate detailed information about instream discharge and dimensions, which is often not available(21,22). Instead, our methodology focuses on estimating conservative (higher) concentrations in small water bodies using runoff and eroded sediment concentrations. Our approach is rooted in the fact that pesticide concentrations in small tributaries approach levels similar to runoff concentrations during runoff events(23).

Regarding benthic sediments, we utilize a simplified box model to predict concentrations independently of instream water column characteristics. Despite not accounting for pesticide behavior in the water column of streams, we include benthic sediment in our analysis due to its potential for pesticide accumulation. Sediments have relatively slow advection rates and, for certain pesticide classes, are compartments with slow degradation rates. The specifics of the approach are detailed later in this section.

To predict pesticide behavior in the environment, we consider the following for each active ingredient: physicochemical properties, degradation rates, and physical processes that transport pesticides. Pesticide physicochemical and degradation data were compiled from the Pesticide Properties Database (PPDB)(45). The database is a comprehensive resource of pesticide information derived from European and United States regulatory agencies when available, and where data is unavailable through regulatory agencies, peer-reviewed literature, pesticide property/ecotoxicity prediction tool results, and other resources.

To consider the transport potential of pesticides in each HRU, we account for the unique climate, irrigation activities, soil hydrologic property data, and crop management parameters that affect runoff and eroded sediment. Climate and irrigation datasets are described in *Section 3.2.2*. To obtain soil hydrologic properties, we extracted data from the gridded USDA Soil Survey Geographic Database(38). This comprehensive dataset encompasses various hydrologic and textural properties of soils and was developed by the National Resource Conservation Service. The dataset groups soils into 'mapping units' based on their similarities. When possible, we used area-depth weighted averages for soil characteristics(46). For HRUs that intersect multiple mapping units with different reported values for a soil hydrologic property, the dominant soil characteristic was used. We considered the median value for continuous data, and for categorical data, the value derived from the mapping unit comprising the largest land coverage area within the HRU.

Crop management characteristics were compiled from default parameterizations of the cultivar in the Pesticides in Water Calculator, a model utilized by the USEPA to predict edge of field runoff for California crops(47). Where values are unavailable, we consider data

from the United States Department of Agriculture handbook 'Predicting Rainfall and Erosion Losses'(48).

To predict pesticide concentrations within each HRU, we begin by calculating the daily soil water balance. The EFT model considers two distinct soil layers: the surface soil and the soil up to the crop rooting depth. By default, the surface soil depth is set to 30 cm, and the crop rooting depth is determined based on typical values reported for crops in the National Resource Conservation Service Irrigation Guide(39). The depth of the second layer is the depth of the crop root less the surface soil depth.

The daily soil water content of the surface soil, SW_{surf} (mm), and subsurface layer up to the crop rooting depth, SW_{root} (mm), are calculated by adapting the SWAT water balance approach(29):

$$SW_{surf} = SW_{surf,0} + W_{input} - Q_{surf} - E - W_{perc,surf} \quad 3.3.1$$

$$SW_{root} = SW_{root,0} + W_{perc,surf} - E - W_{perc,root} \quad 3.3.2$$

Where $SW_{surf,0}$ (mm) and $SW_{root,0}$ (mm) are the initial soil water contents of the surface and subsurface layer respectively, W_{input} (mm) is the water received by the HRU (precipitation or irrigation), Q_{surf} is the surface runoff (mm), E (mm) is the evapotranspiration, $W_{perc,surf}$ (mm) is water lost as leachate from the surface soil layer, and $W_{perc,root}$ (mm) is leachate lost in the subsurface layer. For E, the user can opt within the EFT to use crop specific evapotranspiration data required for irrigation inputs (used here and recommended) or use evapotranspiration data directly from the climate dataset.

From the daily water content of the soil layers, surface runoff, lateral flow, leachate, and eroded sediment are calculated. Here, lateral flow describes groundwater movement

down to the crop rooting depth that may return as surface water flow, depending on field slope.

Surface runoff is calculated using the Soil Conservation Service Curve Number Method(49) as:

$$Q_{surf} = \frac{(W_{input} - I_a)^2}{W_{input} - I_a + S} \qquad 3.3.3$$

Where I_a is the initial abstraction (mm), and S the soil water retention parameter (mm). For initial abstraction, we employ the empirically derived relationship to soil water retention where I_a is approximately equal to $0.2S$(49) to represent the initial abstraction.

The soil water retention parameter, S, is derived from the observed relationship to the runoff coefficient of soils, CN, which is dependent on the soils hydrologic class and soil cover conditions. We calculate a dynamic soil water retention parameter based on daily soil moisture conditions(29). Provided that antecedent soil moisture condition affects the runoff coefficient, we consider multiple coefficients, the average runoff coefficient (empirically derived), CN_2, and the runoff coefficients at the wilting point and field capacity of soil, CN_1 and CN_3 respectively. CN_1 and CN_3 are calculated, using the SWAT approach(29), as:

$$CN_1 = CN_2 - \frac{20*(100-CN_2)}{(100-CN_2+\exp(2.533-0.0636*(100-CN_2)} \qquad 3.3.4$$

$$CN_3 = CN_2 * \exp(0.00673 * (100 - CN_2)) \qquad 3.3.5$$

The soil water retention parameters under typical conditions, S_2 (mm), at the soil wilting point, S_{max} (mm), and at the soil field capacity, S_3 (mm), are calculated with the runoff coefficient under the respective conditions as(29):

$$S_x = \frac{1000}{CN_x} - 10 \qquad 3.6$$

Values derived for the soil water retention parameter under the soil field capacity and wilting point are used to calculate the soil water retention at the daily time-step, S_t (mm) as(29):

$$S_t = S_{max} * \left[1 - \frac{SW_t}{SW_t + \exp\left(w_1 - w_2 * SW_t\right)}\right] \qquad 3.7$$

Where SW_t (mm) is the soil water content at time *t*, and w_1 and w_2 are the soil water retention shape coefficients. The shape coefficients are based on the amount of water in the soil at field capacity, FC (mm), and the amount of water at soil saturation, SAT (mm) as(29):

$$w_1 = ln\left[\frac{FC}{1 - S_3 * {S_{max}}^{-1}} - FC\right] + w_2 * FC \qquad 3.8$$

$$w_2 = \frac{\left[ln\left[\frac{FC}{1 - S_3 * {S_{max}}^{-1}} - FC\right] - ln\left[\frac{SAT}{1 - 2.54 * {S_{max}}^{-1}} - SAT\right]\right]}{SAT - FC} \qquad 3.3.9$$

To quantify water and pesticides lost in lateral flow, we adopt a 2-dimensional, kinematic storage model approach for subsurface flow(50). The model assumes water has a constant slope across the simulated space for the field length of the HRUs, L (m). The drainable volume of water per unit area of the saturated zone of a soil layer, $SW_{drain,ly}$ (mm)(50), is:

$$SW_{drain,ly} = H_0 * \emptyset_d * L/2 \qquad 3.3.10$$

Where H_0 (mm/mm) is the saturated thickness normal to the slope at the outlet as a fraction of the total thickness and $\emptyset_d$ (mm/mm) is the drainable porosity of the soil. Provided that $SW_{drain,ly}$ is calculated using the difference of SW_{ly} (*Equations 3.3.1 and 3.3.2*) and the soil layer field capacity, FC_{ly} (mm), and $\emptyset_d$ can be quantified from the difference of the soil porosity and porosity at field capacity, we can solve for the unknown value H_0 (mm/mm) as(50):

$$H_0 = \frac{2*SW_{drain,ly}}{1000*\emptyset_d*L} \qquad 3.3.11$$

In which 1000 is a unit conversion factor. Lateral flow, Q_{lat} (mm/day), is then calculable from H_0 and the velocity of flow at the end of the downslope, v (mm/s), as(50):

$$Q_{lat} = 24 * H_0 * v \qquad 3.3.12$$

Where 24 is a unit conversion factor. The velocity of flow is determinable from the saturated hydraulic conductivity, K_{sat} (mm/h), and field slope, $\propto$ (degrees), as(50):

$$v = K_{sat} * \sin(\propto) \qquad 3.3.13$$

In the EFT, the slope input is as the increase in elevation per distance, $slope$ (mm/mm), which is equal to tan($\propto$). For field slopes, tan($\propto$) $\cong$ sin($\propto$)(29); using this approximation, and by combining *Equations 3.3.11* and *3.3.12*, Q_{lat} is calculated as:

$$Q_{lat} = 0.024 * \left[\frac{2*SW_{drain.ly}*K_{sat}*slope}{\emptyset_d*L_{hill}}\right] \qquad 3.3.14$$

To calculate vertical water fluxes in the soil layers, we adopt the approach of Neitsch et al. (2011). The travel time of percolation TT_{perc} (h) is predicted from the water content at saturation in the soil layer, SAT_{ly} (mm), the FC_{ly}, and K_{sat}(29):

$$TT_{perc,ly} = \frac{SAT_{ly} - FC_{ly}}{K_{sat}} \qquad 3.3.15$$

The water loss vertically through the soil as leachate, $Q_{perc,ly}$ (mm), during the time-step, Δt (h), can then be calculated:

$$Q_{perc,ly} = SW_{drain,ly} * \left[1 - exp\left[\frac{-\Delta t}{TT_{perc}}\right]\right] \qquad 3.3.16$$

Leachate from the surface layer transports water and pesticides to the subsurface layer; leachate in the subsurface layer is treated as a loss process, and no effects on groundwater are calculated.

After predicting the soil water balance and loss, sediment erosion is simulated using the Modified Universal Soil Loss Equation (MUSLE)(51). MUSLE predicts erosion from rainfall and runoff as(51):

$$sed = 11.8 * (Q_{surf,musle} * q_{peak} * A)^{0.56} * KFFACT * C * P * LS \quad 3.3.17$$

Where sed (metric tons/day) is the sediment yield, $Q_{surf,musle}$ (mm/ha) the runoff, q_{peak} (m^3/s) the peak runoff rate, A (ha) the area, $KFFACT$ (0.013 metric ton m^2 hr/(m^3-metric ton cm)) the erodibility factor of soil weighted by the coarse fragment factor, C the cover and management factor of the crop rotation, P the support practice factor of the land use, and LS the length-slope factor.

The peak runoff at time t, $q_{peak,t}$ (m^3/s), is calculated using the rational method(29):

$$q_{peak,t} = \frac{C_r * i_t * A}{3.6} \quad 3.3.18$$

Where C_r is the ratio of surface water runoff to rainfall, i_t (mm/h) is the rate at which water is received by the soil for the HRU at time t, and 3.6 is a unit conversion factor. For each HRU, i_t on days with precipitation events is assigned to typical rainfall intensities of the HRU, and for irrigation events, i_t is assigned based on the hourly application rate of the irrigation method.

3.2.4 Pesticide Phase Distribution

The mobility of pesticides in the soil compartment depends on the sorbed and dissolved fraction of the chemical within the compartment. We adopt a linear and instantaneously reversible pesticide sorption model where pesticides in the compartment are instantaneously and homogeneously mixed within the soil. The approach adapts the solid-water distribution coefficient for the compartment, $K_{d,comp}$ (L/mg)(29). The coefficient is

calculable from the organic carbon sorption coefficient, K_{oc} (L/mg), and organic carbon content of the compartment, OC_{comp}, as(29):

$$K_{d,comp} = K_{oc} * \frac{OC_{comp}}{100} \qquad 3.4.1$$

$K_{d,comp}$ represents the ratio of pesticide present in the sorbed phase and is equal to the quotient of the concentration of pesticides in the sorbed C_{sorbed} (kg pesticide/kg), and dissolved phase, C_{diss} (mg/L), and can also be expressed as:

$$K_{d,comp} = \frac{C_{sorbed}}{C_{diss}} \qquad 3.4.2$$

To calculate the mobile phase of a pesticide during a runoff event, we begin by defining the relationship between the pesticide mass in the soil layer, $pst_{s,ly}$ (kg/ha), and concentrations in the dissolved and sorbed phases of the soil layer as:

$$pst_{s,ly} = 0.01(C_{diss,ly} * SAT_{ly} + C_{sorbed,ly} * \rho_s * depth_{ly}) \qquad 3.4.3$$

Where 0.01 is a conversion factor, SAT_{ly} (mm) is the water content of the soil layer at saturation, ρ_s (Mg/m^3) is the density of the soil, and $depth_{ly}$ (mm) is the depth of the soil layer. Substituting with *Equation 3.4.2,* we can derive a relationship between the mass of pesticide and concentration with only the dissolved phase concentrations as:

$$pst_{s,ly} = 0.01(C_{diss,ly} * SAT_{ly} + C_{diss,ly} * K_{d,ly} * \rho_s * depth_{ly}) \qquad 3.4.4$$

Loss of pesticides in the dissolved phase at time-step *t* is dependent on the water phase available for transport in each soil layer, $w_{avail,ly}$ (mm) and is calculated as:

$$\frac{dpst_{s,ly}}{dt} = 0.01 * C_{diss,ly} * w_{avail,ly} \qquad 3.4.5$$

The water phase available for transport is the sum of flowing water in surface runoff, Q_{surf} (mm), lateral flow of the layer, $Q_{lat,ly}$ (mm), and percolate of the layer, $Q_{perc,surf}$ (mm):

$$w_{avail,surf} = Q_{surf} + Q_{lat,surf} + Q_{perc,surf} \qquad 3.4.6$$

$$w_{avail,root} = Q_{lat,root} + Q_{perc,root} \quad 3.4.7$$

From the pesticide mass in soil layer, $pst_{s,ly}$ (kg/ha), the pesticide concentration in soil-solution is calculable by rearranging *Equation 3.4.4*:

$$C_{diss,ly} = \frac{pst_{s,ly}}{0.01*(SAT_{ly}+K_{d,ly}*\rho_s*depth_{ly})} \quad 3.4.8$$

To quantify the change in pesticide mass in the soil layer for a time-step, we combine *Equations 3.4.5* and *3.4.8*:

$$\frac{dpst_{s,ly}}{dt} = \frac{pst_{s,ly}*w_{avail,ly}}{SAT_{ly}+K_{d,ly}*\rho_s*depth_{ly}} \quad 3.4.9$$

Integrating, we can calculate the amount of pesticide present in the soil layer at time *t,* $pst_{s,ly,t}$ (kg/ha):

$$pst_{ly,t} = pst_{ly,0} * exp\left[\frac{-w_{avail,ly}}{SAT_{ly}+K_{d,ly}*\rho_s*depth_{ly}}\right] \quad 3.4.10$$

The amount of pesticide available for transport in the water phase, $pst_{avail,ly}$ (kg/ha), is then calculated by subtracting the final mass of the pesticide by the initial mass:

$$pst_{avail,ly} = pst_{ly,0}\left[1 - exp\left[\frac{-w_{avail,ly}}{SAT_{ly}+K_{d,ly}*\rho_s*depth_{ly}}\right]\right] \quad 3.4.11$$

Using the pesticides present in the mobile water phase of the soil, the concentrations of pesticides in the dissolved phase of the surface soil and the subsurface, $C_{flow,ly}$(kg pst/ha-mm), can be calculated. Using an upper limit of concentration of the pesticide's solubility, pst_{sol} (mg/L):

$$C_{flow,ly} = min\begin{bmatrix} pst_{avail,surf}/w_{avail,ly} \\ pst_{sol}/100 \end{bmatrix} \quad 3.4.12$$

Where 100 is a unit conversion factor. The loss of pesticide in surface runoff, pst_{surf} (kg pst/ha), is then:

$$pst_{surf} = C_{flow,surf} * Q_{surf} \qquad 3.4.13$$

In lateral flow and leachate of soil layers, $pst_{lat,ly}$ (kg/ha) and $pst_{perc,ly}$ (kg/ha) respectively, pesticide loss from soil is:

$$pst_{lat,ly} = C_{flow,ly,} * Q_{lat,ly} \qquad 3.4.14$$

$$pst_{perc,ly} = C_{flow,ly} * Q_{perc,ly} \qquad 3.4.15$$

To predict eroded sediment concentrations, an expression to calculate $C_{sorbed,ly}$ is required. First, we rearrange *Equation 3.4.2* to solve for $C_{diss,ly}$, and substituting in *Equation 3.4.3*:

$$pst_{s,ly} = 0.01(\frac{C_{sorbed,ly}}{K_{d,ly}} * SAT_{ly} + C_{sorbed,ly} * \rho_s * depth_{ly}) \qquad 3.4.16$$

Then solve for $C_{sorbed,ly}$:

$$C_{sorbed,ly} = \frac{100 * K_{d,ly} * pst_{ly}}{SAT_{ly} + K_{d,ly} * \rho_s * depth_{ly}} \qquad 3.4.17$$

Next, the pesticide concentration of eroded sediment, C_{sussed} (kg pesticide/kg), is calculated using the pesticide enrichment ratio in surficial sediments, ε:

$$C_{sussed} = C_{sorbed,ly} * \varepsilon \qquad 3.4.18$$

ε is estimated by adopting a relationship of enrichment to the concentration of eroded sediment(52):

$$\varepsilon = 0.78 * (C_{sed,surf})^{-0.2468} \qquad 3.4.19$$

The mass of pesticides transported via eroded sediment, pst_{sussed} (kg pesticide/ha) is then:

$$pst_{sussed} = 0.001 * \frac{sed}{A} * C_{sussed} \qquad 3.4.20$$

Where 0.001 is a conversion factor.

The EFT provides the user the option to predict benthic concentrations of pesticides for risk screening, where pesticides may accumulate due to the slow rate of advection relative

to the water column and slow rates of degradation for some pesticide classes in the compartment. In keeping with the aim to provide pesticide risk information for waterbodies with limited or no data describing compartment characteristics, the EFT employs a simple-box sub-model with flow through. The model is designed to simulate concentrations in surficial sediments, where the sorbed pesticides are instantaneously and homogeneously mixed within the compartment. For pesticide influx to the compartment, in addition to eroded sediment, we consider dispersion between runoff transported over the edge of field benthic sediment. Loss processes considered in the benthic sediment include advective sediment loss, resuspension, burial, degradation, and dispersion of sorbed pesticides to overlying runoff. We assume a constant surficial sediment compartment volume, and the advection, resuspension, or burial of sediment on day *t* is equal to sediment entering the waterbody.

The mass of pesticides in benthic sediment, pst_{sed} (kg), is the sum of pesticides in the dissolved and sorbed phases, represented as:

$$pst_{sed} = C_{pw} * V_{pw} + C_{sed\ solid} * V_{sed\ solid} * \rho_{sed\ solid} \qquad 3.4.21$$

Where C_{pw} (kg/m^3) is the concentration of pesticide in porewater of sediment, V_{pw} (m^3) is the volume of porewater in sediment, $C_{sed\ solid}$ (kg pesticide/kg) is the concentration of pesticide sorbed to sediment solids, $V_{sed\ solid}$ (m^3) is the volume of sediment solids, and $\rho_{sed\ solid}$ (kg/m^3) the density of sediment solids. Adopting the relationship between the sorbed and dissolved phase in *Equation 3.4.2* into *Equation 3.4.21* and rearranging, we can calculate the concentration in porewater as:

$$C_{pw} = \frac{pst_{sed}}{(V_{pw} + V_{sed\ solids} * K_{d,sed} * \rho_{sed\ solid})} \qquad 3.4.22$$

Considering the relationship between the dissolved and sorbed phase (*Equation 3.4.2*), $C_{sed\ solid}$ can be represented as:

$$C_{sed\ solid} = C_{pw} * K_{d,sed} \qquad 3.4.23$$

The transfer of pesticide from runoff entering the ditch into benthic sediment via dispersion, γ, is estimated using a mass transfer coefficient approach adopted by the United States Environmental Protection Agency in the Variable Volume Water Model(53). The mass transfer coefficient approach represents all pesticide exchange processes that create an equilibrium between the overlaying water and sediment. The approach is used to quantify a first-order mass transfer coefficient for data-limited water bodies and is derived from a boundary layer exchange model, Ω, calculated as:

$$\Omega = \frac{A_{sed}D}{V_{sed}\Delta x} \qquad 3.4.24$$

Where A_{sed} (m^2) is the area of sediment, D (m^2/s) is the overall water column-benthic dispersion coefficient, V_{sed} (m^3) is the total volume of sediment and pore water, and Δx (m) is the boundary layer thickness. The first-order water-benthic mass transfer coefficient, α (m^3/s), is:

$$\alpha = \frac{\Omega}{(V_{pw}+pst_{sed}*K_{d,sed})} \qquad 3.4.25$$

From α, the pesticide mass exchange between runoff entering the waterbody and sediment is calculated:

$$\gamma = \alpha\left(C_{flow,surf} - C_{pw}\right) * 86{,}400 \qquad 3.4.26$$

Where 86,400 is a unit conversion factor. The mass of pesticide in sediment is calculated as:

$$pst_{sed} = pst_{sed,0} + pst_{sussed} * f_{dep} + \gamma - C_{pst,sed,t-1} * sed \qquad 3.4.27$$

Where f_{dep} is the fraction of sediment deposited.

f_{dep} is input for each HRU by the user. The actual f_{dep} ranges dependent on instream dimensions and flow are commonly unavailable, and the EFT employs a constant

f_{dep} throughout the simulation period. To estimate the f_{dep} of an HRU, we use the sediment settling velocity and travel time of the sediment along the edge of field water body length. By treating the sediment particles as Brownian, particle interaction negligible, and that frictional force compensates the external force of gravity, the particle velocity, v_s(m/s), is calculated as(54):

$$v_s = \frac{1}{6\pi\mu r} * F_{ext} \qquad 3.4.28$$

Adopting Stokes' Law, the external force acting on the particle due to gravity within a viscous fluid(54):

$$F_{ext} = \frac{4}{3} g * \pi * r^3 * (\rho_{sussed} - \rho_{water}) \qquad 3.4.29$$

Substituting *Equation 3.4.29* in *Equation 3.4.28*:

$$v_s = \frac{2}{9} * \frac{\rho_{sussed} - \rho_{water}}{\mu} * g * r^2 \qquad 3.4.30$$

Where ρ_{sussed} (kg/m^3) is the density of suspended solids, ρ_{water} (kg/m^3) is the density of water, μ (kg/m-s) the dynamic viscosity of water, g (m/s^2) the acceleration due to gravity, and r (m) the particle radius. By default, we consider a particle radius of 62.5 μm(55) and a suspended sediment density of 1400 kg/m^3.

To determine the amount of solids that settle onto the bottom layer, we consider a method that calculates retention time within the edge of field water body, factoring particle settling characteristics(56,57). Notably, data describing the dimensions, discharge, and instream characteristics are commonly unavailable for edge-of-field water bodies. In our study, we evaluate the retention time, denoted as T_{sussed} (s), and consider a typical runoff event to have a depth of 2 mm. This runoff flows into a trapezoidal water body situated at the field's edge. The water body at the edge of the fields is assumed to have the shape of a right-

trapezoidal prism with 2:1 side slope, a base width of 0.5 m, a surface width of 1m, a depth of 1 m, 100 m in length, and has a wetted perimeter of 1.65 m due to a flow height of 0.1 m. The flow velocity can be deduced using Manning's equation, considering a channel slope of 2% and a Manning's coefficient of 0.4 for its small hydraulic radius(58). With this data, we can anticipate the portion of sediments that will settle in the water body to predict the settled fraction of settled sediments in the waterbody(57).

For a ditch in steady-state flow where the change in sediment across the stream length is based on a first-order deposition constant(57), the relationship of the difference in concentration of suspended sediments entering the waterbody, $C_{sussed,in}$ (kg/m^3), the final concentration of suspended sediment leaving the channel, $C_{sussed,out}$ (kg/m^3), and the suspended sediment concentration after sedimentation has reached equilibrium, $C_{sussed,e}$ (kg/m^3) is:

$$\frac{C_{sussed,out}-C_{sussed,e}}{C_{sussed,in-C_{sussed,e}}} = exp\left(-\frac{v_s * T_{sussed}}{L_{chn}}\right) \qquad 3.4.29$$

$$TT_{sussed} = \frac{L_{chn}}{flow} \qquad 3.4.30$$

Where L_{chn} (m) is the length of the channel. f_{dep} is thus equal to:

$$f_{dep} = 1 - \exp\left(-\frac{v_s * T_{sussed}}{L_{chn}}\right) \qquad 3.4.31$$

For our assumptions of typical stream dimensions and runoff events, the fraction of settled solids in the neighboring water body is 0.42.

To account for the mass of pesticide loss within the soil or sediment compartment, degradation is represented as a first-order process, with a rate constant, $k_{deg,comp}$. The pesticide present within a compartment after considering degradation for each day since the application, pst_{comp} (kg), is calculated as:

$$pst_{comp} = pst_{comp,0} * \exp(-k_{deg,comp} * days) \quad 3.4.32$$

For the mass of the pesticide to reach half of the initial concentration, we can substitute the pesticide mass in *Equation 3.4.28* as:

$$0.5 * pst_{comp,0} = pst_{comp,0} * \exp(-k_{deg,comp} * pst_{HL50,comp}) \quad 3.4.33$$

We can then solve for $k_{deg,comp}$:

$$k_{deg,comp} = \frac{0.693}{pst_{HL50,comp}} \quad 3.4.34$$

The mass of pesticide in the soil layers and sediment at the end of the time-step in the surface soil, $pst_{s,surf,end}$ (kg), subsurface soil, $pst_{s,root,end}$ (kg), and sediment, $pst_{sed,end}$ (kg) after consideration of pesticide degradation is:

$$pst_{surf,end} = (pst_{s,surf,0} + pst_{app} - pst_{surf} - pst_{lat_{surf}} - pst_{perc,ly} - pst_{sed}) * \exp(-k_{deg,soil}) \quad 3.4.35$$

$$pst_{root,end} = (pst_{s,root,0} + pst_{app} - pst_{lat_{ly}} - pst_{perc,ly} - pst_{sed}) * \exp(-k_{deg,soil}) \quad 3.4.36$$

$$pst_{sed,end} = (pst_{sed,0} + pst_{sussed} * f_{dep} + \gamma - C_{pst,sed,t-1} * sed) * \exp(-k_{deg,sed}) \quad 3.4.37$$

3.2.5 Risk

To identify risks, we adopt the risk quotient, RQ, which summarizes potential risks to a species under investigation. RQ is employed to predict when environmental concentrations introduce harm by United States and European Environmental Agencies(59,60). The RQ of the i^{th} pesticide in the j^{th} HRU for the k^{th} taxa is:

$$RQ_{i,j,k} = \frac{C_{i,j}}{T_{i,k}} \quad 3.5.1$$

Where $C(\mu g/L)$ is the pesticide concentration and T ($\mu g/L$) is the toxicity threshold. Adapting the cumulative toxicity approach(61,62), the cumulative risk quotient, RQ_{cum} is calculable for *n* pesticides as:

$$RQ_{cum,j,k} = \sum_{i=1}^{n} \frac{C_{i,j}}{T_{i,k}} \qquad 3.5.2$$

Although the cumulative addition approach does not capture synergistic or antagonistic interactions of pesticides, for studies with hundreds of pesticide mixtures, the method has been observed to predict mortality within a factor of 2 for 90% of samples(63–65). Given the effectiveness of the cumulative addition approach and the presence of substantial data gaps regarding pesticide mixture interactions(66), we incorporated the approach in the EFT.

For the present evaluation, we evaluate acute risks in the water column (<96 h) to fish, invertebrates in the water column, nonvascular aquatic plants, and vascular aquatic plants. Ecotoxicological thresholds considered include half-maximal effect or lethal concentrations to the sample population, the EC50 and LC50, as available in the PPDB(45) for the water column. Where ecotoxicological endpoints were missing, we employed effect thresholds from the United States Environmental Protection Agency (USEPA) Aquatic Life Benchmarks Database[60,61]. Additionally, where USEPA benchmarks were more conservative than the PPDB, USEPA benchmarks were used. Where endpoints were still unavailable for AI forms, endpoints of another of the base AI forms were used (e.g., 2-4 D esters).

Available literature considers that the most acute risk in a pesticide mixture can be represented by the pesticide introducing the greatest toxicity within a sample(38,68). However, the types of pesticides and frequency of applications vary throughout the year, especially for crop rotations, and single-sample toxicity is not representative of the variation in risks that may be observed(15,17,67). To quantify the significance of accounting for all

pesticides introduced to the water column to understand risks to aquatic compartments, the maximum RQ_{cum} of watersheds observed on any simulation day was compared to the maximum RQ observed for any individual pesticide. Significance was tested using a one-way, paired t-test, a method commonly used to compare predictions relative to observed data(69). For the analysis, we consider the maximum risk quotient observed for any individual pesticide to be the prediction of risk and the cumulative risk quotient the observed (actual) risk.

In addition to evaluating the risk quotients of different taxa, the EFT computes a risk index, RI (ha^{-1}). This index is specifically designed to consolidate risk impacts for the source under investigation at various extents and for diverse taxa. This consolidation results in a singular index for a pesticide, application site type, or watershed of interest, which can be summarized at various time-steps (daily, monthly, annual, or over the simulation period). The index is weighted based on the size of the HRUs which comprise the extent the RI is summarized for. This approach ensures large HRUs which may have a higher applied mass due to a greater cultivation area are not penalized more than smaller HRUs. The RI is determinable for the i^{th} pesticide and k^{th} taxonomic group for n HRUs for a given day, month, or simulation as:

$$RI_{i,k} = \sum_{j=1}^{n} \frac{C_{i,j}}{T_{i,k} * A_j} \quad 3.5.3$$

The RI for the j^{th} HRU and k^{th} taxonomic group for p pesticides is:

$$RI_{j,k} = \sum_{i=1}^{p} \frac{C_{i,j}}{T_{i,k} * A_j} \quad 3.5.4$$

The net risk index of the m investigated taxa, RI_{net} (ha^{-1}) for the i^{th} pesticide in n HRUs in the study extent is calculated as:

$$RI_{net,i} = \sum_{j=1}^{n} \sum_{k=1}^{m} \frac{C_{i,j}}{T_{i,k} * A_j} \quad 3.5.5$$

Similarly, for the j^{th} HRU for p pesticides in the study extent:

$$RI_{net,j} = \sum_{i=1}^{p} \sum_{k=1}^{m} \frac{C_{i,j}}{T_{i,k} * A_j} \quad 3.5.6$$

To summarize an index of risk over the simulation period for all pesticides, HRUs, and taxa, we calculate the RI_{net} as:

$$RI_{net} = \sum_{j=1}^{n} \sum_{i=1}^{p} \sum_{k=1}^{m} \frac{C_{i,j}}{T_{i,k} * A_j} \quad 3.5.7$$

It's important to highlight that the RIs are not suited for evaluating specific risks to aquatic organisms. Instead, their purpose lies in pinpointing regions where relatively higher toxic loads per unit area are introduced to water bodies per application area for various species.

Furthermore, the absence of toxicity data for certain active ingredient(s) within specific taxonomic group(s) can result in elevated RIs in certain areas where only pesticides with known toxicity endpoints for all taxa considered are used. This elevation occurs in comparison to regions where applied pesticides lack toxicity data, leading to a negatively skewed RI. For this investigation, toxicity data for fish and invertebrates is available for all pesticides considered, for nonvascular plants data is available for 92% of pesticides, and for vascular plants 77%. While the increased occurrence of missing data for aquatic plants introduces a negative bias to risk indices in some application sites and watersheds, they are included to provide an index of risk for all evaluated taxa based on the best available information.

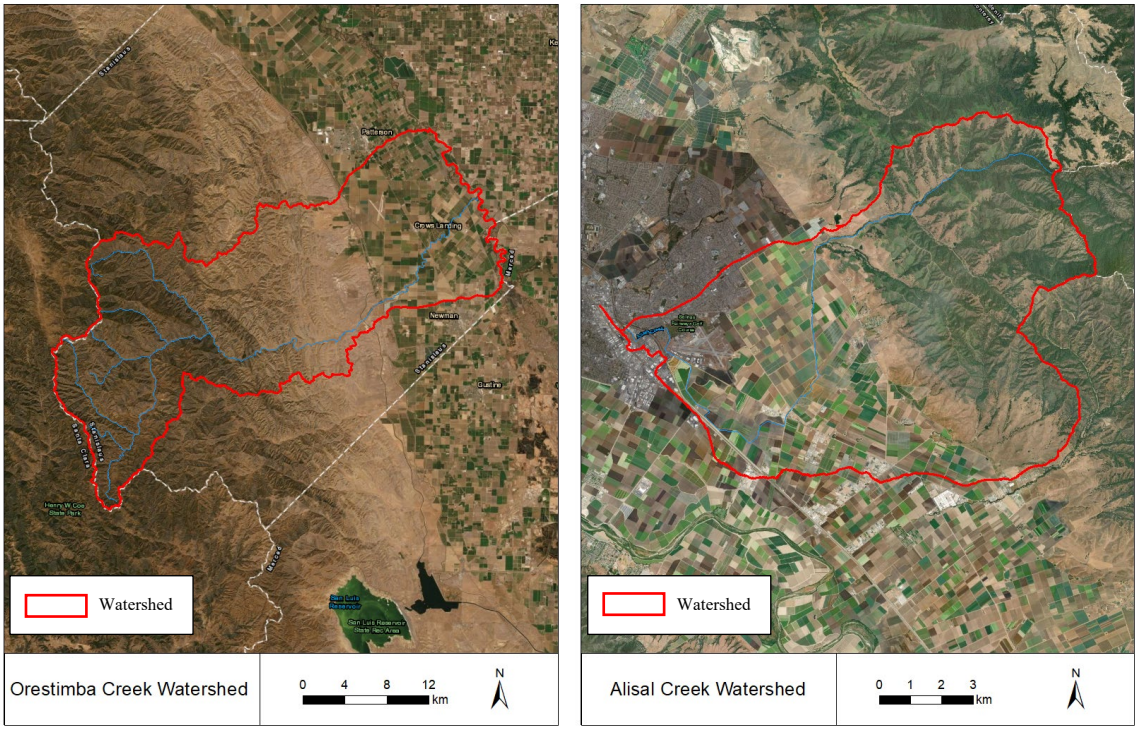
3.2.6 Validation

The EFT was developed to facilitate risk assessment across large extents with high-resolution pesticide use and environmental characteristic data and limited instream data. Here, we evaluate tool accuracy for predicting aquatic risks as an uncalibrated tool. By examining the EFT's performance as an uncalibrated tool, we can gain a clearer understanding of its accuracy when applied in regions where there is limited or no in-stream data available for calibration purposes.

Validation efforts compared predictions of the EFT in runoff and benthic sediment to observed data in surface water and benthic sediment of water bodies with monitoring data available in the CDPR Surface Water Database(35). Although the EFT does not calculate the instream dilution of runoff, we hypothesized that in small waterbodies predominantly impacted by agriculture, the tool could reasonably predict maximum concentrations of pesticides in the water body and acute risks by assuming no dilution since they are runoff-dominated.

Validation was performed in water bodies unaffected by urban influences, including agricultural creeks and ditches. The assessment of agricultural creeks focused on the Orestimba and Alisal Watersheds, spanning the period from 2011 to 2020 (refer to **Figure 2**). These watersheds were chosen for their lack of upstream impacts from developed land. Furthermore, validation was also carried out in agricultural ditches across the entire BDW study area, as shown in **Figure 1**.

Figure 2 (a and b). The validation study watersheds of the **a)** Orestimba Creek and **b)** the Alisal Creek.



Within the Orestimba and Alisal Creeks, we evaluated pesticide concentrations in the dissolved phase, which represents the most bioavailable form. The available monitoring data for dissolved pesticide concentrations in these creeks were then compared against the concentrations predicted by the EFT model.

In the case of the agricultural ditches spanning the BDW study area, only samples representing the whole water column (dissolved and sorbed phase) were available for validation. These samples were compared against the EFT's projections of whole water concentrations for the years 2016 to 2020.

Due to the significantly larger number of application sites and watersheds being evaluated in comparison to the Orestimba and Alisal Watersheds, a narrower time frame of 5 years was chosen for the BDW study. Opting for a 10-year analysis would have exceeded the available RAM in RStudio for standard operating systems, and our objective was to furnish

default simulation data for the EFT to support investigations within this ecologically important area.

For each validation study area, a validation dataset comprised all observations of a pesticide within a watershed. In the Orestimba and Alisal watersheds, 49 validation datasets were available in the water column for 44 active ingredients and 17 validation datasets were available for benthic sediment for 11 pesticides with diverse physicochemical properties(35). In the case of filtered water samples diverse physicochemical parameters were observed, with ranges of 0.001 to 100,000 mg/L for solubility, 1.6 to 283,707 mL/g for K_{oc}, and 0.4 to 500 days for soil half-lives(45). In sediment, pesticide physicochemical parameter ranges include for solubility 0.001-60 mg/L, Koc 609-307,558 mL/g, soil half-lives 18.4-175 days, and sediment half-lives 10.4-161 days(45).

Additionally, we evaluated all available agricultural ditch observations within the water column and benthic sediment in watersheds across the study extent. For water columns in agricultural ditches, 23 validation datasets were available for 15 pesticides(35). In the benthic sediment of the agricultural ditches' 11 validation datasets were available for 6 pesticides(35). Pesticide physicochemical properties across the BDW study extent were also diverse. For whole water samples, solubility varied from 0.001 to 100,000 mg/L, Koc ranged from 28.3 to 283,707 mL/g, and soil half-lives spanned from 6.2 to 229 days(45). In ditch benthic sediment ranges in solubility spanned 0.001 to 0.33 mg/L, Koc values ranged from 5,000 to 307,558 mL/g, soil half-lives were between 21.9 and 175 days, and sediment half-lives spanned from 17 to 161 days(45).

In all validation scenarios for surface water, we considered only validation datasets with more than 2 observations. In sediment, where substantially fewer monitoring data are available, all validation datasets were considered.

To select metrics of accuracy for chemical concentrations, careful consideration must be made. Metrics can penalize errors differently across predicted magnitudes. Yet, typical environmental concentrations of pesticides vary by orders of magnitude, as do the environmentally relevant concentrations at which ecotoxicological impacts occur; a common range is parts per trillion to parts per one hundred. Additionally, the data required to parameterize fate and transport models are compiled from unique sources whose data availability, scale, and support units for field observations range widely. For instance, climate stations are tens to hundreds of miles apart and pesticide application data is available at the field level. Accuracy measures independent of the scale of analysis are thus required (e.g., relative errors)(68).

We sought metrics that hold significance when dealing with data that spans various orders of magnitude, and exhibit symmetry concerning the mean, treating errors of over and underpredictions with equal bias. Another desired quality was the ability to help gauge the tool's capability to predict concentrations at the upper end of the observed data spectrum, which holds substantial importance for the health of various species. Selected metrics include log-transformed accuracy ratios and signed symmetric percent bias(68).

The accuracy ratio of median, maximum, and 99th percentile predictions for a pesticide, Q_{perc}, is calculable from their respective percentiles X as:

$$Q_{perc} = \frac{percentile(predicted\ concentration,\ X)}{percentile(observed\ concentration,\ X)} \quad 3.6.1$$

The accuracy of median predictions evaluates the EFT's ability to predict typical conditions. The accuracy of maximum predictions helps to understand the model's ability to predict the most hazardous concentrations observed for chemicals and to evaluate the reliability of predicted ranges. For the 99th percentile of predictions, we compared it to the maximum observed concentration. This was conducted to evaluate if 99th percentile predictions more accurately predict observed maxima, provided predicted concentrations encompass each day of the simulation period, and observations do not.

When considering accuracy ratios, it is useful to produce a log-transformed accuracy ratio, R. The log transformation ensures the metric is symmetric for over and under-predictions(68). R is calculable from paired observed concentrations and as:

$$R = \exp\left(\left|log_e\left(Q_{perc}\right)\right|\right) \qquad 3.6.2$$

Log-transformed accuracy ratios are helpful for comparing the error of individual prediction and observation pairs. However, due to the EFT predicting irrigation schedules which produce runoff, and the actual schedules being unknown, we do not compare observed data to predicted concentrations at the daily time-step (for single prediction and observation pairs). Instead, we evaluate the accuracy ratio of median, maximum, and 99th percentile predictions for the simulation period.

Considering the log-transformed accuracy ratios, we can calculate the symmetric percentage bias metric, which is interpreted similarly to the mean absolute error percentage but penalizes under and over-predictions equally. This measure also uses a sign function to indicate whether the predictions are typically over or under(68). We calculate the signed symmetric percentage bias of the percentiles, ζ_{perc}, of predictions as:

$$\zeta_{perc} = 100 * sign\left(\text{median}(log_e(Q_{perc})\right) * (\exp\left(\left|median(log_e(Q_{perc}))\right| - 1\right)$$

3.6.3

When comparing predictions to observations, our analysis considered predicted data with concentrations surpassing the median limit of quantification (LOQ) of observations. This decision was driven by the model's ability to predict concentrations that are below the level at which pesticides can be detected in monitoring campaigns.

3.3 Results

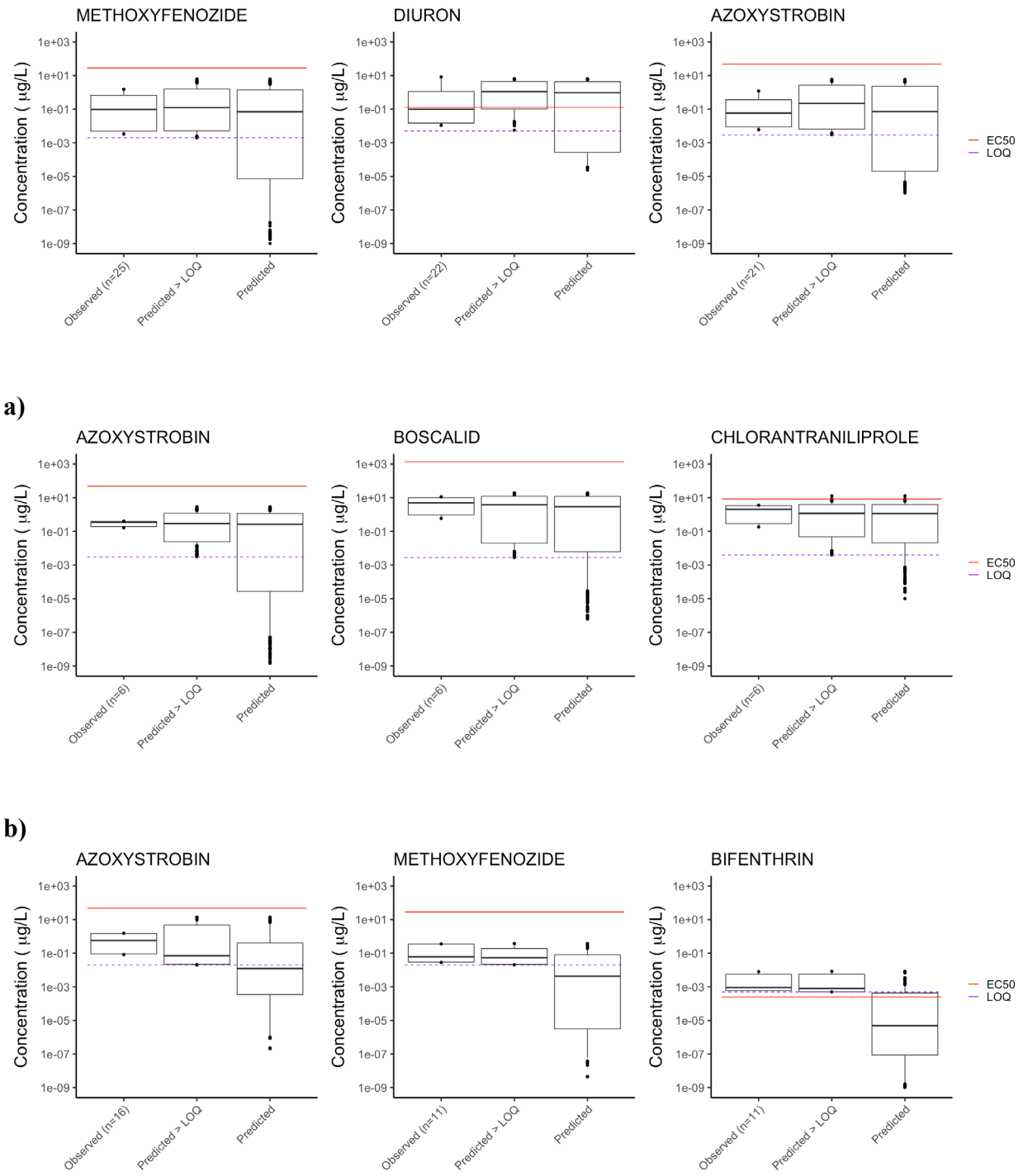
3.3.1 Predicted Environmental Concentrations – Validation

To evaluate the model's ability to predict aquatic risks, we compared predictions of pesticide concentrations in runoff and eroded sediment in two investigations. First, we focused on creeks which receive runoff from agricultural land within the Orestimba and Alisal and second, we examined predictions of pesticide concentrations in agricultural ditches across the BDW study extent.

The evaluation of the EFT predictions for dissolved concentrations of pesticides in the Orestimba and Alisal Creeks revealed the symmetric signed bias of median pesticide concentrations (ζ_{med}) and 99th percentile (ζ_{99}) predictions to be 35% and 140% respectively. The majority of the predicted median concentrations fell within a factor of 3.1 of the observed data and 0.14 µg/L of the observed median, demonstrating good agreement between typical predictions and observations (**Figure 3 (a-b)** and **Table 1**). Typical prediction bias of pesticide median concentrations was comparable to the bias of a study evaluating concentrations of chlorpyrifos and diazinon with SWAT in the Orestimba watershed, whose percent bias was 25% and 35%, respectively(20).

Examining the 1 in 10-year maximum predicted concentration accuracy of pesticides for the simulation period, the symmetric signed percent bias, ζ_{max}, was 356%. Taking into account that the model predicts concentrations for every day of the simulation period while observations are based on substantially more restricted temporal extents, this level of agreement is reasonable. Relative to a study demonstrating SWAT to be an effective model for simulating concentrations over large extents for a single pesticide, atrazine, the EFT was able to capture 78% of the observed maximum concentrations of the 44 pesticides investigated, while SWAT captured 50% of observed maximum for atrazine(69). Moreover, the magnitude of bias of maximum predictions for the pesticides evaluated was similar to that observed for atrazine, -369%. However, it's important to note that the SWAT model generally produced predictions that were lower than the actual maximum concentrations. The EFT predictions were also in line with the standards set by the USEPA. The EFT predictions were also within the range of what the USEPA deems acceptable, an order of magnitude to be acceptable(70). This acceptable range is notably broad, and this can be attributed to the wide variety of environmental concentrations encountered, as well as the numerous environmental processes at play.

Results of predicted medians in agricultural ditches demonstrated improved agreement relative to the Orestimba and Alisal Creeks which receive runoff from undeveloped and agricultural lands (**Figure 2**). The ζ_{med} of predictions was -1.04%, with most predictions within a factor of 2.6 and 0.01 μg/L of observed (**Figure 3 (c)** and **Table 2**). For 99th percentile and maximum predictions, close agreement was also observed, with symmetric signed percent biases of 173% and 212% respectively.



c)

Figure 3 (a-b). Dissolved predicted and observed concentrations of pesticides within the **a)** Orestimba Creek**, b)** Alisal Creek. Whole water concentration **c)** within agricultural ditches across the BDW study extent. From left to right in each boxplot, we depict the observed concentrations, predicted concentrations above the median limit of quantification for the pesticide, and all predicted concentrations. Of the pesticides evaluated, the pesticides with the greatest number of observations are shown.

Table 1. Comparison between observed and predicted environmental concentrations (PECs) in the dissolved phase for the Orestimba and Alisal Creeks; pesticides with risk quotients (RQ) greater than one are in bold.

Pesticide	Watershed	n	EC50 (ppb)	Median Observed (ppb)	Max Observed (ppb)	Median PEC (ppb)	99th Percentile PEC (ppb)	Max PEC (ppb)	Observation RQ	99th Percentile PEC RQ	Max PEC RQ
acetamiprid	Alisal	5	10.5	0.074	0.227	0.0182	0.214	0.46	0.0216	0.0204	0.0438
azoxystrobin	Alisal	6	49	0.339	0.405	0.288	1.74	2.88	0.00827	0.0356	0.0588
boscalid	Alisal	6	1340	4.88	11.2	3.79	14.9	19	0.00836	0.0111	0.0142
chlorantraniliprole	**Alisal**	6	8.3	2.02	3.55	1.18	6.14	12.6	0.428	0.74	1.52
chlorthal-dimethyl	Alisal	6	4600	0.309	4.6	0.533	3.36	5.21	0.001	0.000731	0.00113
clothianidin	Alisal	6	11	0.449	1.34	0.817	6.53	9.95	0.122	0.593	0.904
cyantraniliprole	Alisal	3	10.2	0.0222	0.049	0.0454	0.92	2.58	0.0048	0.0902	0.253
cyprodinil	Alisal	6	16	0.0648	0.111	0.0296	0.631	1.14	0.00694	0.0395	0.0713
dimethomorph	Alisal	6	1000	0.188	0.427	0.253	2.91	3.79	0.000427	0.00291	0.00379
dinotefuran	Alisal	5	790	0.0664	0.22	0.101	1.89	4.96	0.000278	0.0024	0.00628
diuron	**Alisal**	6	0.13	0.0259	6.21	0.755	3.99	4.14	47.8	30.7	31.8
fenamidone	Alisal	6	24.5	0.109	2.83	0.0348	0.768	1.33	0.116	0.0313	0.0541
flonicamid	Alisal	6	49000	0.0371	8.12	0.0412	1.91	6.06	0.000166	3.89E-05	0.000124
fludioxonil	Alisal	5	24	0.0814	0.121	0.0097	0.0227	0.0246	0.00504	0.000946	0.00103
fluopicolide	Alisal	6	29	0.388	1.97	0.723	3.28	3.92	0.0679	0.113	0.135
flupyradifurone	Alisal	3	67700	0.882	1.23	1.18	13.8	25	0.0000182	0.000204	0.000369
fluxapyroxad	Alisal	6	466	0.0484	0.214	0.271	1.06	1.28	0.000459	0.00227	0.00274
imidacloprid	**Alisal**	6	0.385	0.429	4.18	3.22	18.5	33.7	10.9	48	87.6
mandipropamid	Alisal	6	2500	0.458	4.45	0.0279	0.787	1.45	0.00178	0.000315	0.00058
methoxyfenozide	Alisal	6	28.5	0.281	0.524	0.0948	1.7	3.56	0.0184	0.0596	0.125
myclobutanil	Alisal	6	240	0.34	0.84	0.0802	0.827	1.41	0.0035	0.00345	0.00589
oxyfluorfen	Alisal	6	0.29	0.119	0.221	0.0237	0.127	0.22	0.762	0.438	0.76
penthiopyrad	Alisal	3	145	0.0247	0.122	0.015	0.247	0.477	0.000841	0.00171	0.00329
piperonyl butoxide	Alisal	3	240	0.0341	0.328	0.0078	0.114	0.134	0.00137	0.000474	0.000557
prometryn	**Alisal**	5	1.04	0.141	0.448	0.111	0.926	1.89	0.431	0.891	1.82
propiconazole	Alisal	6	21	0.163	0.652	0.0225	0.159	0.279	0.031	0.00758	0.0133
propyzamide	Alisal	6	760	0.167	0.468	0.428	8.38	19.2	0.000616	0.011	0.0252
pyrimethanil	Alisal	6	1200	0.0203	0.291	0.0588	1.43	2.41	0.000243	0.00119	0.00201
tebuconazole	Alisal	3	144	0.169	3.24	0.0193	0.234	0.263	0.0225	0.00162	0.00183
tetraconazole	Alisal	4	310	0.0167	0.0231	0.162	0.355	0.368	0.0000745	0.00115	0.00119
thiamethoxam	**Alisal**	6	17.5	1.42	4.37	0.94	9.56	22.4	0.25	0.546	1.28
triadimefon	Alisal	3	800	0.508	1.5	0.0211	0.112	0.187	0.00188	0.00014	0.000234
azoxystrobin	Orestimba	21	49	0.059	1.2	0.22	4.47	5.97	0.0245	0.0911	0.122
diazinon	**Orestimba**	5	0.105	0.0171	0.284	0.0298	0.795	2.61	2.7	7.58	24.8
dimethoate	**Orestimba**	9	21.5	0.0192	1.95	0.0711	18.8	27.7	0.0907	0.873	1.29
diuron	**Orestimba**	22	0.13	0.0987	8.32	1.12	5.52	6.53	64	42.5	50.2
flubendiamide	Orestimba	16	27.4	0.0152	0.927	0.0171	0.163	0.179	0.0338	0.00594	0.00655
glyphosate	Orestimba	3	11900	0.48	1.2	0.0868	1.77	5.47	0.000101	0.000149	0.00046
hexazinone	**Orestimba**	17	7	0.0116	0.16	1.59	18.4	20	0.0229	2.64	2.86
imidacloprid	**Orestimba**	14	0.385	0.0309	0.159	0.287	2.12	4.88	0.413	5.51	12.7
methoxyfenozide	Orestimba	25	28.5	0.0957	1.52	0.125	3.6	6.22	0.0533	0.126	0.218
metolachlor	**Orestimba**	14	8	0.0205	0.184	0.404	29	45.1	0.023	3.63	5.64
metribuzin	Orestimba	3	8.1	0.0428	0.0594	0.258	6.06	7.26	0.00733	0.749	0.896
norflurazon	Orestimba	15	9.7	0.0169	0.696	0.258	2.65	2.75	0.0718	0.273	0.283
oryzalin	Orestimba	7	13	0.131	0.49	0.237	2.22	2.97	0.0377	0.171	0.228
pendimethalin	Orestimba	5	4	0.0141	0.0245	0.0675	1.11	1.57	0.00613	0.279	0.392
propiconazole	Orestimba	6	21	0.0144	0.446	0.0506	0.579	0.849	0.0212	0.0276	0.0404
pyraclostrobin	Orestimba	4	1.5	0.00923	0.0137	0.0065	0.13	0.138	0.00913	0.0867	0.0922
simazine	**Orestimba**	16	6	0.0296	2.91	0.556	6.97	8.11	0.485	1.16	1.35

Table 2. Comparison between observed and for predicted environmental concentrations (PECs) in whole water for agricultural ditches across the study extent; pesticides with risk quotients (RQ) greater than one are in bold.

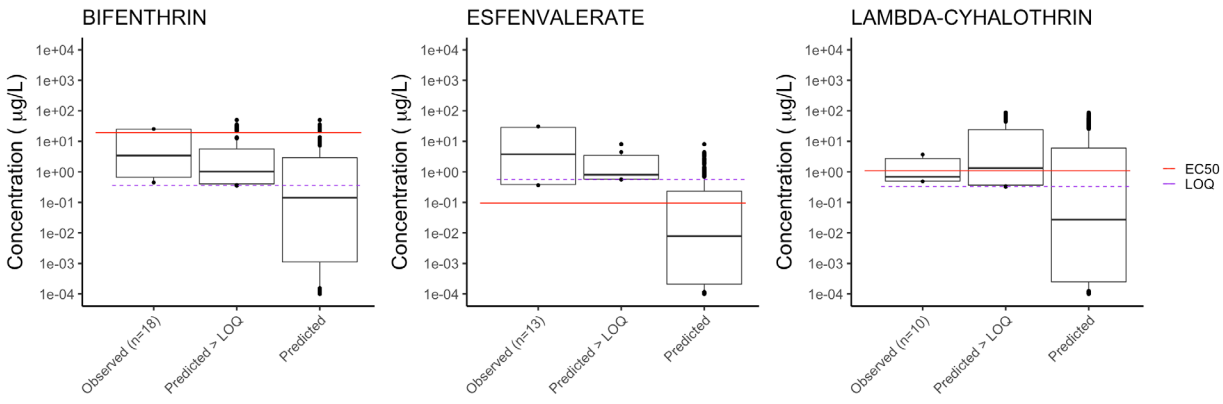
Pesticide	Watershed	n	EC50 (ppb)	Median Observed (ppb)	Max Observed (ppb)	Median PEC (ppb)	99th Percentile PEC (ppb)	Max PEC (ppb)	Observation RQ	99th Percentile PEC RQ	Max PEC RQ
azoxystrobin	HUC180201630302	16	49	0.571	1.54	0.0704	9.36	14.1	0.0314	0.191	0.288
bifenthrin	**HUC180201630302**	5	0.0002	0.0008	0.0019	0.0008	0.00659	0.00837	7.71	26.7	33.9
chlorantraniliprole	HUC180201630302	8	8.3	0.0216	0.141	0.134	2.63	2.85	0.017	0.317	0.344
hexazinone	HUC180201630302	3	7	0.02	0.02	0.104	1.04	1.1	0.00286	0.148	0.157
methoxyfenozide	HUC180201630302	11	28.5	0.061	0.357	0.0537	0.346	0.378	0.0125	0.0121	0.0133
metolachlor	**HUC180201630302**	5	8	0.022	0.304	0.172	15.7	32.7	0.038	1.96	4.09
oxyfluorfen	**HUC180201630302**	3	0.29	0.16	0.41	0.169	2.45	2.52	1.41	8.45	8.68
propiconazole	HUC180201630302	6	21	0.0345	0.277	0.101	1.02	1.15	0.0132	0.0484	0.0546
bifenthrin	**HUC180400020202**	9	0.0002	0.001	0.006	0.0033	0.113	0.23	24.3	459	931
glyphosate	HUC180400020202	3	11900	13	21	30.6	949	1170	0.00176	0.0797	0.0982
simazine	HUC180400020202	4	6	1.29	2.5	3.45	3.6	3.6	0.417	0.599	0.6
bifenthrin	**HUC180400020205**	8	0.0002	0.004	0.02	0.001	0.0141	0.0378	81.1	57	154
chlorpyrifos	**HUC180400020205**	8	0.04	0.071	0.5	0.0245	0.0727	0.0732	12.5	1.82	1.83
dimethoate	HUC180400020205	4	21.5	0.79	3.3	0.272	6.22	7.75	0.153	0.289	0.36
diuron	**HUC180400020205**	5	0.13	0.85	76	0.559	0.715	0.715	585	5.5	5.5
lambda-cyhalothrin	**HUC180400020205**	8	4E-05	0.003	0.006	0.0012	0.0219	0.0376	150	548	940
oxyfluorfen	**HUC180400020205**	5	0.29	0.18	0.3	0.177	0.305	0.305	1.03	1.05	1.05
pendimethalin	**HUC180400020205**	6	4	0.3	4.7	0.299	1.26	1.3	1.18	0.314	0.324
lambda-cyhalothrin	**HUC180400020405**	4	4E-05	0.004	0.01	0.0021	0.0689	0.0745	250	1720	1860
bifenthrin	**HUC180400030901**	9	0.0002	0.003	0.07	0.0009	0.0187	0.0227	284	75.9	92
lambda-cyhalothrin	**HUC180400030901**	6	4E-05	0.002	0.003	0.0011	0.00389	0.00478	75	97.2	119
diuron	**HUC180400121105**	5	0.13	1.1	5.1	2.01	11	11.2	39.2	84.6	85.9
bifenthrin	**HUC180400510304**	11	0.0002	0.0009	0.008	0.0008	0.00804	0.00827	32.5	32.6	33.5

For benthic sediment evaluations, we also conducted separate validation efforts for the Orestimba/Alisal watersheds and the BDW study extent, although the same sample types were available. Separate validations were conducted owing to creeks in the Orestimba and Alisal watersheds receiving runoff from both large undeveloped areas and agricultural development (**Figure 2**), while the agricultural ditches evaluated across the study extent predominantly receive agricultural runoff.

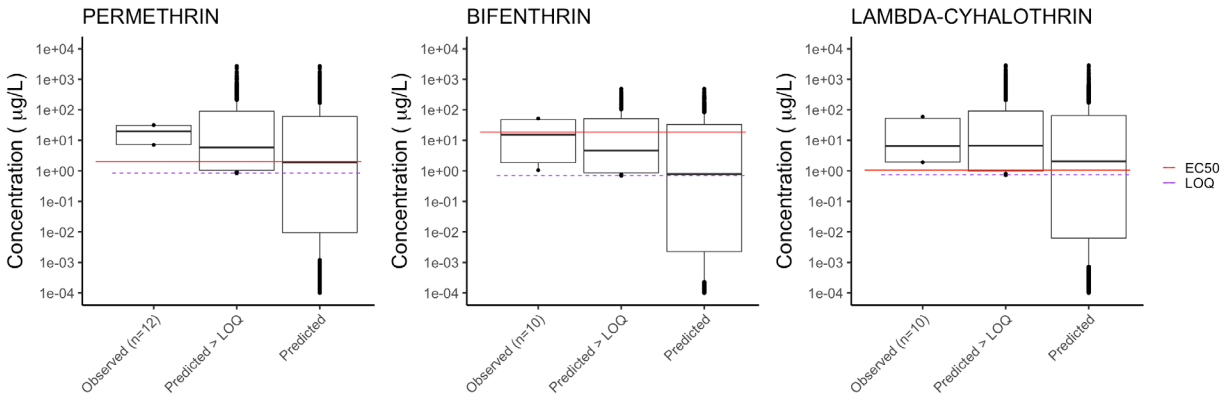
Analyzing predictions for the benthic sediment, we observed a ζ_{med} of -28.8%, and ζ_{99} of 255%. Most of the median predicted concentrations align with observed data and were within a factor of 2.4 and 1.4 µg/kg. Notably all but one validation dataset observation range

was encompassed by predictions, demonstrating considerable agreement, see **Figure 4 (a-b)** and **Table 3**.

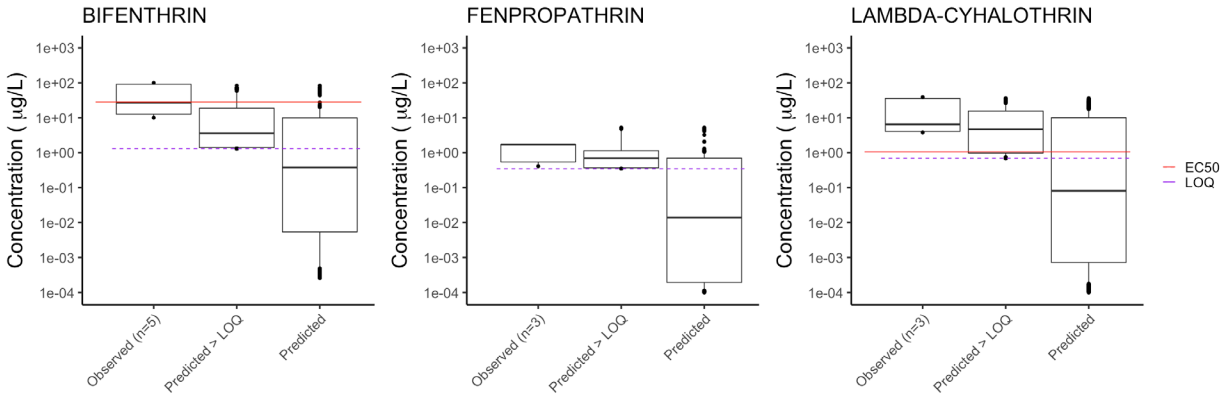
However, when we examined the 1 in 10 year predicted maximum concentrations of the simulation period, a ζ_{max} of 1030% was observed. This indicates that for most pesticides, there was a difference greater than an order of magnitude for maximum predicted concentrations when compared to the observed maximum. The typical accuracy of these predictions exceeds the USEPA criteria of acceptability of an order of magnitude (1000%) and demonstrates the benthic sediment edge-of-field submodule predictions to be overly conservative for agricultural streams. It's worth noting that for pesticides with high partitioning coefficients for organic carbon, like lambda-cyhalothrin, observed concentrations in California's agricultural ditches have fallen within the range of the maximum predicted concentrations, parts per one thousand, during the simulation period and monitoring data may not have captured peak concentrations(35). The reason for the greater inaccuracy of predictions in stream sediments, compared to surface water, could be linked to the slow mixing of ditch sediments and stream sediments compared to the water column of ditches and streams.



a)



b)



c)

Figure 4 (a-c). Concentrations of pesticides observed and predicted in benthic sediments within **a)** the Orestimba Creek, **b)** the Alisal Creek, and **c)** agricultural ditches across the study extent. Of the pesticides evaluated, we illustrate the three pesticides in each area with the greatest number of observations. From left to right, the observed concentrations, predicted concentrations above the median limit of quantification for the pesticide, and all predicted concentrations.

The ζ_{med} of EFT predictions was -62.7%, and the ζ_{99} for pesticides was 162%. The EFT demonstrated a tendency to underpredict sample medians, however, close agreement was observed with most prediction medians within a factor of 1.6 of and 1.5 µg/kg of observed concentrations. Furthermore, recall that we considered validation datasets with as few as one observation in sediment due to data paucity, which may account for the under

prediction of observed medians. For the 1 in 5-year maximum predicted concentrations of agricultural ditch sediments, predictions were agreeable relative to observed, with a ζ_{max} of 184%, see **Figure 4(c)** and **Table 3**.

Table 3. Validation datasets for benthic sediment predicted environmental concentrations (PECs) for the Orestimba and Alisal Creeks, as well as agricultural ditches across the study extent.

Pesticide	Watershed	n	Median Observed (ppb)	Max Observed (ppb)	Median PEC (ppb)	99th Percentile PEC (ppb)	Max PEC (ppb)
bifenthrin	HUC180400	4	6.15	66	4.44	56.7	70.6
cypermethrin	HUC180400	2	1.23	2.1	0.65	5.38	6.37
fenpropathrin	HUC180400	3	1.7	1.7	0.697	4.73	5.26
lambda-cyhalothrin	HUC180400	3	6.5	39	4.67	26.3	36.4
bifenthrin	HUC180400	5	27	100	3.61	58.4	82.4
cyfluthrin	HUC180400	1	1.5	1.5	1.87	4.03	4.23
lambda-cyhalothrin	HUC180400	2	3.8	4.5	2.34	12.7	25.5
permethrin	HUC180400	2	3.3	5.2	3.1	41.5	45
bifenthrin	HUC180400	1	6.4	6.4	3.83	16.8	18.2
bifenthrin	HUC180400	1	2.6	2.6	4.26	86.4	100
lambda-cyhalothrin	HUC180400	1	28	28	2.71	17.2	34.1
bifenthrin	Orestimba	18	3.41	25.5	1.02	12.4	51
chlorpyrifos	Orestimba	5	1.1	6.01	1.74	44	77.3
cyfluthrin	Orestimba	1	0.57	0.57	0.443	2.6	3.09
diazinon	Orestimba	2	2.05	3	2.61	47.2	120
dicofol	Orestimba	1	9.65	9.65	0.123	17.1	17.6
esfenvalerate	Orestimba	13	3.79	31	0.801	4.44	8.17
lambda-cyhalothrin	Orestimba	10	0.69	3.7	1.33	44.1	89.2
permethrin	Orestimba	4	0.46	0.71	1.09	6.99	8.05
bifenthrin	Alisal	10	15.4	52	4.64	104	488
chlorpyrifos	Alisal	3	5.2	9.75	14.6	455	1250
chlorthal-dimethyl	Alisal	1	33.5	33.5	62.6	1160	5790
cyfluthrin	Alisal	4	3.09	7.19	1.03	11.5	30.2
cypermethrin	Alisal	5	5.36	14.9	2	18.5	59.6
esfenvalerate	Alisal	4	0.883	10.5	1.69	33	162
fenpropathrin	Alisal	6	2.93	25.9	1.5	31.9	97.1
lambda-cyhalothrin	Alisal	10	6.49	59.6	6.63	212	2880
permethrin	Alisal	12	19.8	31.8	5.82	212	2750

3.3.2 Aquatic Risks and Sources

In the analysis of aquatic risks for the BDW, three metrics were taken into account, the RQs, days of exceedance, and RIs. The RQ reflects the ratio between the water body concentration and toxic concentration. RQs exceeding one indicate concentrations surpassing

adverse effects for aquatic organisms on specific days. The days of exceedance, a metric that tallies the days when concentrations within an HRU surpass the adverse effect concentration, quantifies the number of events where concentrations in HRUs pose risks to aquatic life (RQ>1). The RI consolidates risk impacts for the diverse sources or taxa under investigation simultaneously and is weighted based on the size of the analysis area. Importantly, while RQs and exceedance days reveal specific risks, RIs offer a comparative perspective and can highlight the relative magnitude of impact that may exist to numerous sources and target taxa simultaneously.

We begin by exploring the RI_{net} for the analysis period, which provides a high-level overview of which sources per cultivated hectare contributed the greatest risk to fish, water column invertebrates, nonvascular and vascular aquatic plants for the simulation period. We observed that for the water column, 80% of the RI_{net} was concentrated in 9% of the watersheds (**Figure 5(a)**). The RI_{net} for all pesticides, application sites, and watersheds predicted the greatest proportion of impact to investigated taxa, from greatest to least, for water column invertebrates (81%), vascular plants (16%), nonvascular plants (3%), and fish (0.3%).

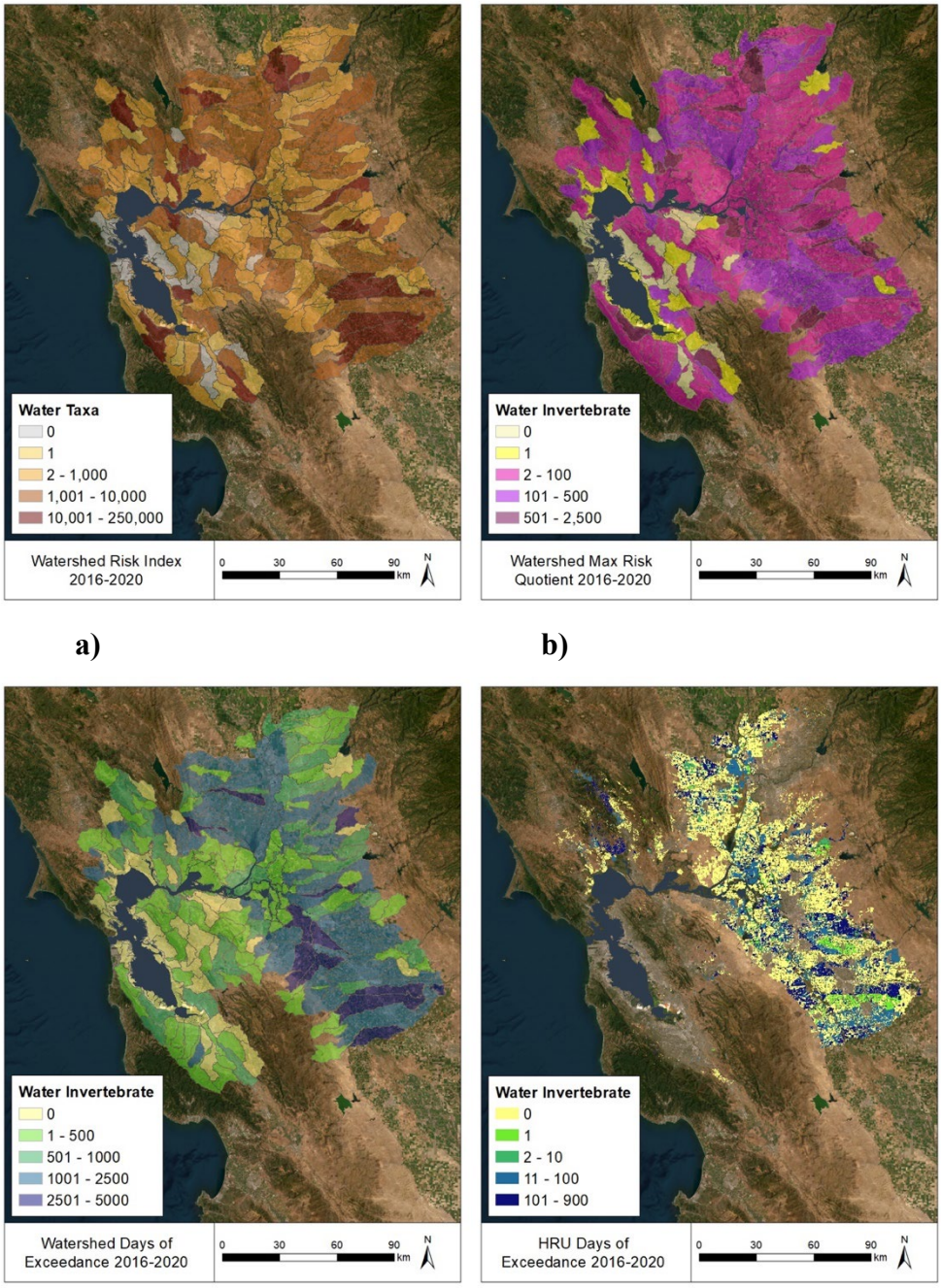


Figure 5 (a-d). a) The net risk index (RI_{net}) for all investigated taxonomic groups fish, invertebrates, nonvascular and vascular aquatic plants; **(b-d)** illustrate example spatial insights that can be gleaned from the study extent for specific taxonomic groups, using invertebrates in the water column as an example. For the simulation period 2016-2020, **b)** portrays maximum risk quotients predicted for invertebrates by watershed, **c)** highlights the sum of days of exceedance observed in watersheds, and **d)** displays HRU specific days of exceedance across the study extent.

In terms of direct indices of risk, RQs and exceedance events, the results demonstrated a consistent pattern across the taxonomic groups investigated within the water column. The order of impact, from the highest impacted taxonomic group to the least, mirrored what was observed for the RI_{net} (invertebrate > vascular plants > nonvascular plants >fish). Summaries of risk indices and quotients for the BDW study extent can be reviewed in **Table 4**, details for exceedance events can be reviewed in **Table 5**, and the spatial distribution of risk for all pesticide RQs and exceedance events for the highest impacted taxonomic group, water column invertebrates, can be viewed in **Figure 5**. It's important to note that the EFT's reporting of exceedance events is comprehensive, covering each HRU for every day of the simulation period. Consequently, the number of exceedance events may surpass the total number of days in the simulation period.

Table 4. Pesticides contributing to 99% of the net risk index (RI_{net}) over the simulation period (2016-2020) in surface waters of the BDW study extent, and their maximum predicted risk quotient (RQ) on any day of the simulation.

Pesticide	Max RQ Fish	Max RQ Water Invertebrate	Max RQ Nonvascular Plant	Max RQ Vascular Plant	RI_{net} (ha^{-1})	RI_{net} (% of Total)	RI_{net} (Cummulative % of Total)
lambda-cyhalothrin	9.85	3,570	0.0286	0.281	59,900	51.80%	51.80%
imidacloprid	0.00381	821	0.0316	0	19,000	16.50%	68.30%
indaziflam	0.0403	0.00171	0.0226	890	9,830	8.52%	76.80%
diuron	0.214	1.61	52.3	1090	6,910	5.98%	82.80%
fenpropathrin	1.49	1080	0.0261	0.00164	6,600	5.71%	88.50%
bifenthrin	0.849	258	0.000219	0.000193	4,560	3.95%	92.50%
oxyfluorfen	0.111	0.154	38.1	33.5	1,500	1.30%	93.80%
methiocarb	1.51	49.4	0.0617	0	1,030	0.89%	94.60%
flumioxazin	0.0147	0.00616	20.4	48.4	1,010	0.88%	95.50%
simazine	0.334	2.14	178	15.9	825	0.71%	96.20%
hexazinone	0.00189	0.00341	36.9	6.91	525	0.46%	96.70%
chlorpyrifos	11.1	249	0.071	0.0188	488	0.42%	97.10%
diazinon	0.297	127	0.00361	0	390	0.34%	97.50%
esfenvalerate	0.117	19.6	0.00149	0.000968	295	0.26%	97.70%
mcpa, dimethylamine salt	0.0102	5.46	3.07	3.78	247	0.21%	97.90%
paraquat dichloride	0.000274	0.00274	4.14	0.0231	229	0.20%	98.10%
pendimethalin	0.166	0.0816	2.86	0.914	199	0.17%	98.30%
carbaryl	1.03	134	0.19	0.0083	185	0.16%	98.50%
cyfluthrin	0.639	10.9	0.0109	0.0259	175	0.15%	98.60%
permethrin	0.375	44.8	0.0336	0.0462	166	0.14%	98.70%
s-metolachlor	0.0462	0.0406	7.1	2.7	145	0.13%	98.90%
(s)-cypermethrin	0.0448	31.2	0.000131	0.0054	144	0.13%	99.00%

Table 5. Pesticides contributing to 99% of the net risk index (RI_{net}) in agricultural ditches of the BDW study extent, and their predicted exceedance events to investigated taxa.

Pesticide	Fish	Water Invertebrate	Nonvascular Plant	Vascular Plant	All	% of Total	Cummulative % of Total
lambda-cyhalothrin	242	78,651	0	0	78,893	16.31%	16.31%
imidacloprid	0	29,502	0	0	29,502	6.10%	73.38%
indaziflam	0	0	0	28,366	28,366	5.86%	79.24%
bifenthrin	0	28,010	0	0	28,010	5.79%	85.03%
diuron	0	63	3,055	18,394	21,512	4.45%	89.48%
chlorantraniliprole	0	496	0	0	496	0.10%	89.58%
oxyfluorfen	0	0	11,113	9,978	21,091	4.36%	93.94%
dimethoate	0	163	0	0	163	0.03%	93.97%
fenpropathrin	4	4,541	0	0	4,545	0.94%	94.91%
chlorpyrifos	243	3,873	0	0	4,116	0.85%	95.76%
dinotefuran	0	0	0	0	0	0.00%	95.76%
flumioxazin	0	0	1,632	3,617	5,249	1.09%	96.85%
simazine	0	15	3,208	264	3,487	0.72%	97.57%
hexazinone	0	0	2,463	39	2,502	0.52%	98.09%
esfenvalerate	0	2,420	0	0	2,420	0.50%	98.59%
paraquat dichloride	0	0	1,781	0	1,781	0.37%	98.96%
diazinon	0	1,474	0	0	1,474	0.30%	99.26%
thiamethoxam	0	39	0	0	39	0.01%	99.27%
s-metolachlor	0	0	786	160	946	0.20%	99.46%
clothianidin	0	3	0	0	3	0.00%	99.46%
methomyl	0	89	0	0	89	0.02%	99.48%
carbaryl	1	507	0	0	508	0.11%	99.59%
diflubenzuron	0	501	0	0	501	0.10%	99.69%
permethrin	0	425	0	0	425	0.09%	99.78%
chlorothalonil	367	67	258	0	692	0.14%	99.92%
2,4-d, dimethylamine salt	0	0	0	3	3	0.00%	99.92%
oryzalin	0	0	69	301	370	0.08%	100.00%

Alongside predicted risks, an assessment of observed concentrations obtained from monitoring campaigns within the study area revealed an RQ > 1 for agricultural ditches in the study region. This was evident in 14 out of the 23 observations present in the validation datasets. The EFT accurately predicted observed exceedances, with the exception of pendimethalin. Additionally, the EFT predicted another pesticide to surpass health benchmarks, metolachlor, which was not observed in monitoring data.

A key aim of the development of the EFT was to enable the simultaneous evaluation of the many pesticides in use. To explore the significance of accounting for cumulative risks

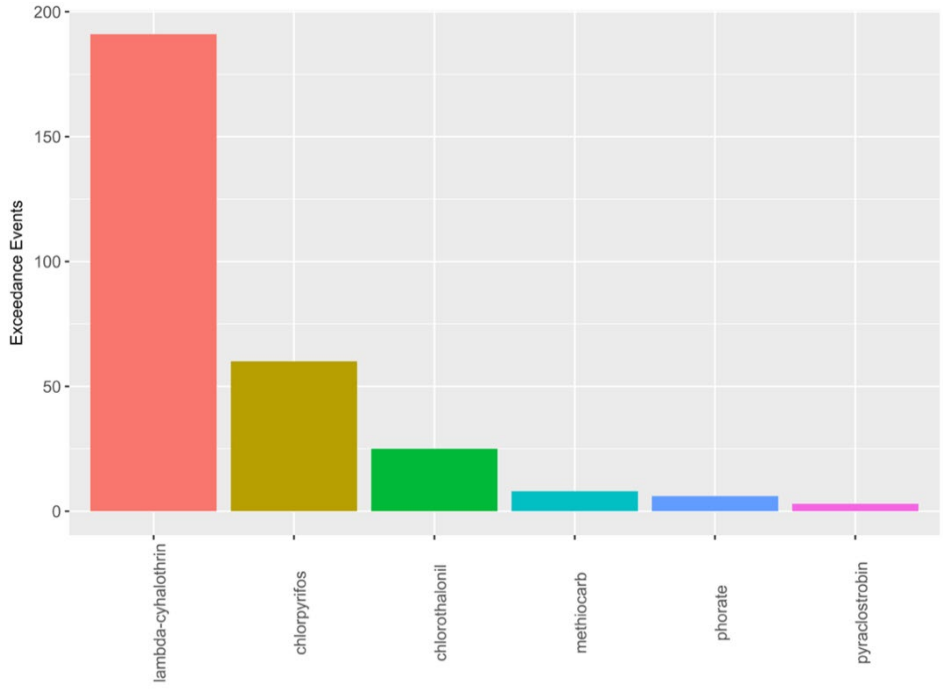
in runoff, we compared the predicted maximum RQ_{cum} to the maximum RQ of individual pesticides in watersheds across the study extent. Results of the analysis, a one-way, paired t-test (α=0.95), demonstrated that for each taxonomic group, the maximum RQ_{cum} was significantly greater than the individual pesticide maximum RQs (p-value < 1E-10, df=207). For 50% of watersheds, the maximum RQ_{cum} for fish, invertebrates, nonvascular and vascular aquatic plants was greater than the maximum RQ of any pesticide by 370%, 540%, 690%, and 820%, respectively.

Finally, to evaluate the importance of leveraging tools like the EFT to address the issue of unobservable pesticide risks due to limitations in analytical sensitivity, we explore the frequency with which monitoring data are unable to capture aquatic health benchmarks considered in this investigation. When examining all pesticide monitoring data employed for validation purposes in the BDW, 42% of samples had a LOQ above the health benchmark. This indicates that the monitoring campaigns might have overlooked identifying aquatic risks that were actually present had the concentrations on the specific monitoring day not been as high. Additionally, when reviewing all sample analyses of pesticides within agricultural ditches in California from 2016-2020, a notable portion—2,356 out of 12,447 (~20%)—in the CDPR SURF database exhibited LOQ values surpassing effect thresholds. For the highest impact pesticide of the investigation, lambda-cyhalothrin (see **Table 4 and 5**), 100% of sample LOQs were greater than the effect threshold (USEPA Aquatic Life Benchmark for invertebrates(71)), and risks could go undetected in any of the samples analyzed.

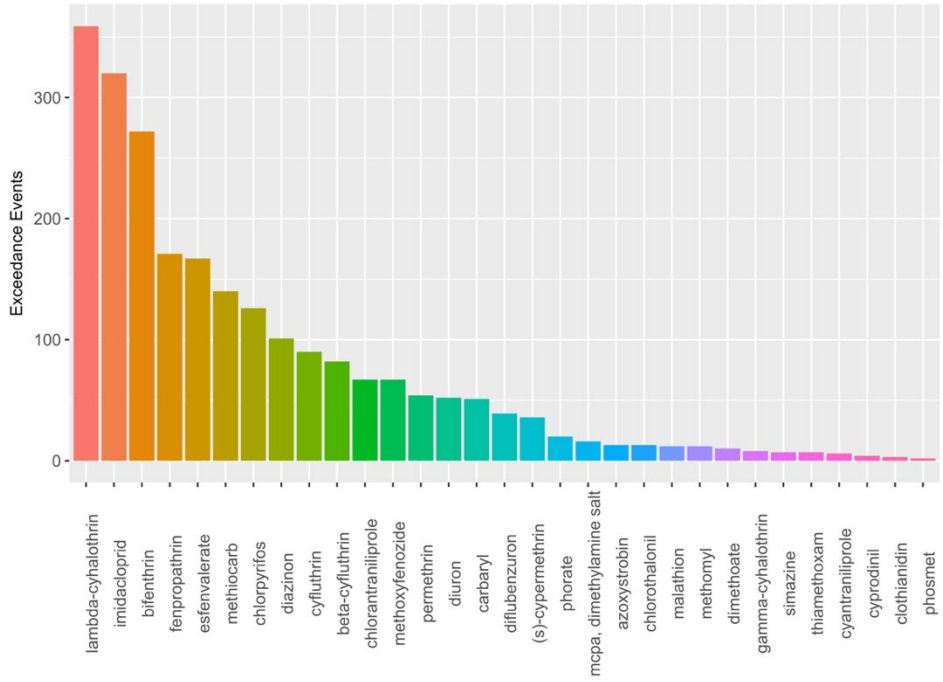
3.3.3 Sources

Within the study area, our observations revealed that a substantial proportion of toxicity was attributed to a relatively small number of sources. Among different application site types, we found that 80% of the overall risk to aquatic taxa in the water column stemmed from merely 10% of the site types (**Table 6**). Similarly, among the pesticide-active ingredients applied during the simulation period, a mere 2.5% accounted for 80% of the RI_{net}, lambda-cyhalothrin, imidacloprid, indaziflam, and bifenthrin. Three of the four highest-impact active ingredients (RI_{net}) were insecticides and were most toxic to invertebrates in the water column. The fourth, indaziflam, is an herbicide that is most toxic to vascular plants. The relative rank of pesticides by impact varied, depending on the metric considered, yet pesticides predicted to have a relatively high or low impact were consistent across evaluated risk metrics (**Table 4 and 5**).

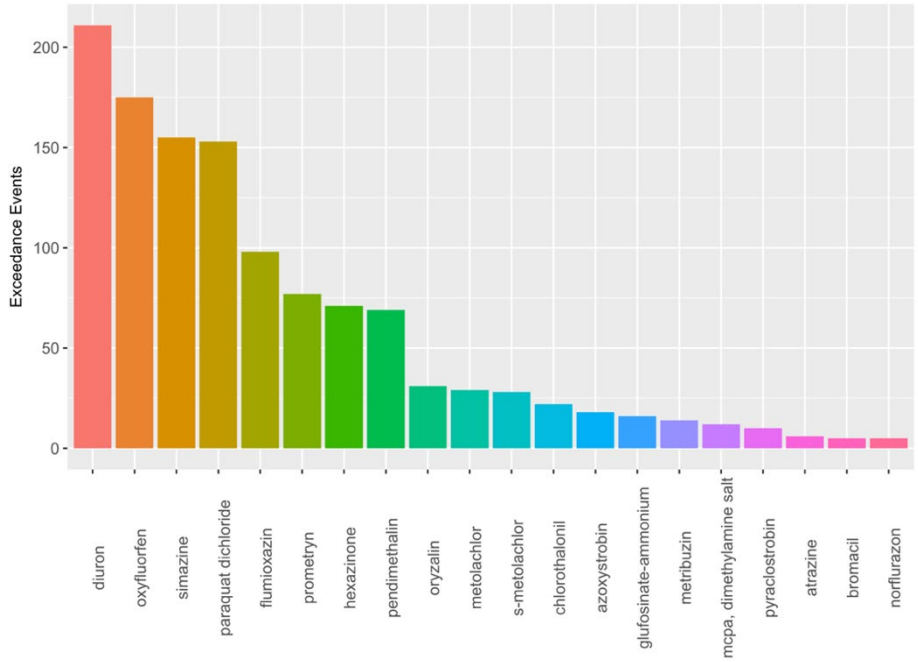
In terms of applied active ingredients, our observations highlighted that lambda-cyhalothrin triggered the highest number of exceedance events in any HRU for water column invertebrates and fish (**Figure 6**). However, the remainder of high-impact pesticides for invertebrates and fish differed. Similarly, for aquatic nonvascular and vascular aquatic plants, the greatest number of exceedance events observed in any HRU were attributable to the same active ingredient, diuron, while the remainder of high-impact pesticides differed.


Exceedance Events
200
150
100
50
0
lambda-cyhalothrin
chlorpyrifos
chlorothalonil
methiocarb
phorate
pyraclostrobin

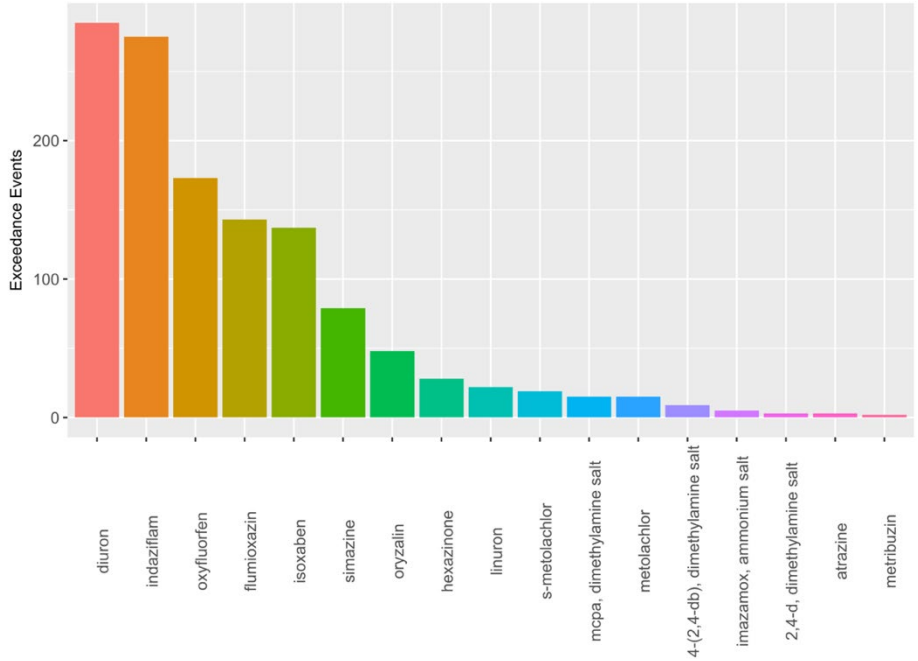
a)


Exceedance Events
300
200
100
0
lambda-cyhalothrin
imidacloprid
bifenthrin
fenpropathrin
esfenvalerate
methiocarb
chlorpyrifos
diazinon
cyfluthrin
beta-cyfluthrin
chlorantraniliprole
methoxyfenozide
permethrin
diuron
carbaryl
diflubenzuron
(s)-cypermethrin
phorate
mcpa, dimethylamine salt
azoxystrobin
chlorothalonil
malathion
methomyl
dimethoate
gamma-cyhalothrin
simazine
thiamethoxam
cyantraniliprole
cyprodinil
clothianidin
phosmet

b)



c)



d)

Figure 6. The maximum number of exceedance events for each taxonomic group evaluated within any Hydrologic Response Unit (HRU) across the study area; only pesticides with exceedance events are shown. This count is provided for **a)** fish, **b)** water invertebrates, **c)** nonvascular plants, and **d)** vascular plants.

With respect to application site types, we observed that per application area, the site type flowers/nursery/Christmas trees contributed the greatest RI_{net}. However, in the review of exceedance events for any of the investigated taxa, the greatest number were observed for alfalfa, walnuts, grapes, and almonds; this is likely attributable to their greater area of cultivation.

The Environmental Release Tool(16), a complementary tool to the EFT in the Pesticide Mitigation Prioritization Model, also predicts the relative environmental impact of application sites and pesticides using the same pesticide use reports as the EFT but only considers applied toxicity. The applied toxicity is defined as the amount of pesticide introduced into the environment, adjusted for its toxicity to the priority species of the investigation. Notably, for the BDW study extent and investigated taxonomic groups in this investigation, the Environmental Release Tool identifies nut orchards and alfalfa as the most significant application sites in terms of impact, in alignment with the EFT. Similarly, the pesticides lambda-cyhalothrin and bifenthrin are predicted as having the highest environmental impact when their applied toxicity is considered, as is also predicted by the EFT. The Environmental Release Tool was also able to predict 50% of the top ten predicted high-impact sites and 40% of the top ten high-impact pesticides. Although it's crucial to simulate how specific pesticides behave in the environment to predict aquatic risks, these results emphasize the importance of data on the sources of toxicity in enhancing our grasp of aquatic threats.

Table 6. Sources of risk by site type, ordered by greatest to least for their net risk index (RI_{net}) to taxa residing in the water column. Additionally, we summarize the number of exceedances of risk quotients for the site type in any HRU, calculated at the daily time-step.

Site Type	RI Fish	RI Water Invertebrate	RI Nonvascular Plant	RI Vascular Plant	RI_{net}	Exceedance Fish	Exceedance Water Invertebrate	Exceedance Nonvascular Plant	Exceedance Plant Vascular
Flowers, nursery, and Christmas trees	188	56,100	344	850	57,500	209	4,566	346	1,207
Alfalfa and alfalfa mixtures	54	13,800	801	4,890	19,500	2	27,063	3,368	9,007
Grapes	48	2,290	1,190	9,090	12,600	139	12,780	10,183	21,836
Almonds	18	2,890	588	2,390	5,890	434	19,409	7,393	12,697
Misc. grain, hay, and forage	7	1,940	137	128	2,210	0	8,341	24	28
Cherries	4	2,020	19	61	2,110	1	7,829	125	1,388
Wheat	7	1,780	19	15	1,820	0	5,542	20	2
Misc. truck crops	3	1,340	75	46	1,470	0	1,021	204	99
Walnuts	4	1,060	53	220	1,340	61	26,001	1,981	11,072
Greenhouse	3	1,180	3	109	1,290	0	320	0	134
Olives	2	932	18	71	1,020	0	209	7	437
Misc. field crops	2	974	4	4	984	0	170	0	0
Melons, squash, and cucumbers	2	780	3	9	794	0	1,157	13	23
Apples	3	641	16	86	745	6	1,873	28	319
Corn, sorghum, and sudan	3	656	40	26	725	0	3,818	304	120
Plums, prunes, or apricots	4	500	16	50	571	16	1,566	144	784
Fallow	2	433	18	79	531	0	1,179	91	384
Tomatoes	2	319	33	13	367	0	3,541	492	119
Pistachios	1	338	2	20	361	0	792	0	474
Peaches and nectarines	2	240	6	17	265	0	2,424	0	168
Beans	1	172	10	11	193	0	946	113	49
Cole crops	0	104	1	1	107	0	737	0	0
Sunflowers	1	81	12	5	99	0	398	102	13
Misc. deciduous	1	31	4	8	44	0	16	0	18
Peppers	0	38	1	0	38	0	459	1	0
Potatoes	1	30	1	3	35	7	513	0	71
Onions and garlic	0	25	2	2	29	0	390	0	0
Pears	0	18	1	8	26	0	763	15	225
Pomegranates	0	15	3	2	21	0	0	0	0
Strawberries	0	12	0	0	12	0	4	0	0
Misc. agriculture	0	4	2	4	10	0	22	13	19
Carrots	0	0	2	8	10	0	0	0	26
Bush berries	0	3	0	3	7	0	91	0	141
Safflower	0	3	0	1	5	0	103	0	14
Misc. citrus and subtropical fruit	0	0	0	0	0	0	0	0	0
Kiwis	0	0	0	0	0	0	0	0	0
Cotton	0	0	0	0	0	0	0	0	0
Lettuce or leafy greens	0	0	0	0	0	0	0	0	0

3.4.0 Discussion

When working on a large scale, it is common to encounter limited or no data on the instream characteristics of waterbodies and observed concentrations of the numerous pesticides in use, which are essential for calibration purposes. In response, the EFT was developed and evaluated for accuracy in predicting pesticide concentrations in surface water environments vulnerable to pesticide impacts (smaller systems predominantly impacted by

agriculture) from runoff, lateral flow, and eroded sediment concentrations. Relative to the widely used model SWAT (7–9), which has been employed in over 2,000 peer-reviewed publications and has nearly 70,000 citations(72), similar observations in accuracy for predicting the range of environmental concentrations in watersheds dominated by agricultural runoff were observed for a calibrated simulation at the watershed level(20), and as an uncalibrated large multi-watershed simulation(69) (see *Section 3.3.1*). However, the EFT has important advantages that enable users to understand the risks of hundreds of pesticides within a single simulation, analyze cumulative risks, and identify primary sources of pesticide risks at large scales where many required data describing instream characteristics are unavailable.

Validation efforts undertaken for the EFT revealed predictions to have close agreement for the range of concentrations observed in surface water and sediment validation datasets. The majority of median predictions in runoff and benthic sediment of agricultural ditches in the BDW study extent were within 0.01 ug/L and 1.5 µg/kg of surface waters and sediments, respectively. Furthermore, regarding high-impact pesticides like lambda-cyhalothrin and bifenthrin, which exhibit low toxicity thresholds, the EFT was able to predict median concentrations within 0.002 ug/L or less of observed. The accuracy demonstrates the EFT to be capable of facilitating pragmatic assessments of even very low environmental concentrations at which these compounds elicit harmful effects(45,71) – effects that presently elude detection within standard monitoring campaigns.

The EFT also offers potential assistance in monitoring efforts by addressing a key challenge: capturing the most impactful runoff events. Traditional monitoring often struggles in this regard due to uncertainties surrounding the timing of these events and the substantial

resources required for planning and funding monitoring campaigns. Consequently, campaigns are frequently scheduled as routine activities, potentially leading to the oversight of peak runoff occurrences(73). Moreover, resource constraints frequently hinder comprehensive analyses of the array of pesticides that could be present. Additionally, the quantification of pesticides in suspended sediments and bed sediment is carried out at much lower frequencies, resulting in an incomplete picture of pesticide risks in these environments(74).

Given these challenges with monitoring and observations of pesticides in aquatic environments, the EFT emerges as a valuable tool to support risk assessment. It achieves this by not only predicting environmental concentrations, but via producing results that inform the prioritization of monitoring and mitigation efforts. The EFT conveys essential risk information regarding the number of days where pesticide concentrations surpass levels associated with adverse health effects across diverse watersheds. It also identifies specific pesticides and application sites that have the most significant impact on aquatic environments. Notably, the tool stands out for its unique ability to highlight the cumulative risks posed by the multitude of pesticides entering surface waters and sediments. This is of importance because, over the simulation period, the cumulative maximum risk quotient, compared to that of individual pesticides, was typically more than half an order of magnitude higher for the investigated taxa. Through these functions, the EFT offers a strategic means to prioritize monitoring initiatives and risk reduction opportunities.

Approaches that may be taken to apply tool knowledge to reduce pesticide risks in aquatic ecosystems include consideration of chemical alternatives or prioritizing locations for the integration of practices to reduce contaminant burdens, such as detention ponds. To

illustrate the EFT's ability to support decisions for chemical alternatives for mitigating high-impact pesticide risks, consider the case of pesticide applications on almond orchards in the BDW. Bifenthrin was identified by the EFT to be the primary contributor to the RI_{net} for the analysis period. On almond orchards, bifenthrin is frequently used to combat mite infestations. Utilizing the results generated by the EFT in combination with an available chemical alternatives database, such as that of the University of California Agricultural and Natural Resources(75), an alternative such as bifenazate can be chosen that effectively targets mites while posing a lower aquatic risk. Bifenazate requires similar application frequencies, yet if all applications of bifenthrin were displaced by bifenazate for the BDW study area and simulation period, at the recommended application rate, aquatic risks would be reduced by 106-fold for fish and ~28,000-fold for aquatic invertebrates per treated hectare.

The EFT can prove a valuable asset to risk assessments; however, the tool has important limitations. The EFT is not designed to predict risks in waterbodies not dominated by agricultural runoff or chronic pesticide risks, which are key components of a comprehensive risk assessment. The tool is designed to understand risks in vulnerable waterways, sources of risk, and the frequency with which acute risks to diverse taxa may occur from pesticide loads introduced in runoff, lateral flow, and eroded sediment. Moreover, some classes of pesticides are moderately to highly volatile or ionizable, which require consideration of additional processes that contribute to the presence of these chemicals in the environment, which are not currently considered. However, many pesticides in use are non-ionizable and have low volatility, which includes insecticides with the highest reported toxicity in the USEPA Aquatic Life Benchmarks database(71), as well as the most widely

used active ingredient classes of insecticides pyrethroids, neonicotinoids, and organophosphates.

3.5 Conclusion

Assessing the impacts of pesticides across the diverse and dynamic conditions found in agricultural landscapes is essential, especially as new use strategies or information about their toxicity becomes available. The EFT is designed for conducting high-resolution risk analyses of pesticides over extensive areas, helping to understand existing and potentially unknown concerns related to their transport, persistence, and risk in aquatic environments. Furthermore, predictive tools like the EFT play a crucial role in supporting monitoring campaigns. This is particularly important for understanding the risks posed to non-target aquatic organisms which share high sensitivity with pests targeted by widely used pesticides but for whose effect levels currently remain undetectable in most monitoring campaigns, such as for pyrethroids. The tool aids in identifying areas where pesticides may have a significant impact on various species and determines the main sources of risk. In regions where risks are prevalent, the EFT serves as a strategic resource for conducting more detailed risk assessments, prioritizing the implementation of management practices, and focusing mitigation strategies.

3.6 References

1. Malaj E, von der Ohe PC, Grote M, Kühne R, Mondy CP, Usseglio-Polatera P, et al. Organic chemicals jeopardize the health of freshwater ecosystems on the continental scale. Proc Natl Acad Sci USA. 2014 Jul 1;111(26):9549–54.
2. Bradley PM, Journey CA, Romanok KM, Barber LB, Buxton HT, Foreman WT, et al. Expanded Target-Chemical Analysis Reveals Extensive Mixed-Organic-Contaminant Exposure in U.S. Streams. Environ Sci Technol. 2017 May 2;51(9):4792–802.
3. Tang FHM, Lenzen M, McBratney A, Maggi F. Risk of pesticide pollution at the global scale. Nat Geosci. 2021 Mar 29;
4. Mullin CA, Frazier M, Frazier JL, Ashcraft S, Simonds R, Vanengelsdorp D, et al.

High levels of miticides and agrochemicals in North American apiaries: implications for honey bee health. PLoS One. 2010 Mar 19;5(3):e9754.
5. U.S. Congress. The Code of Laws of the United States of America. Title 7 2012.
6. European Commission. DIRECTIVE 2009/128/EC. 2009.
7. Srinivasan R, Ramanarayanan TS, Arnold JG, Bednarz ST. Large area hydrologic modeling and assessment part ii: model application. J Am Water Resources Assoc. 1998 Feb;34(1):91–101.
8. Arnold JG, Srinivasan R, Muttiah RS, Williams JR. Large area hydrologic modeling and assessment part i: model development. J Am Water Resources Assoc. 1998 Feb;34(1):73–89.
9. Wang R, Yuan Y, Yen H, Grieneisen M, Arnold J, Wang D, et al. A review of pesticide fate and transport simulation at watershed level using SWAT: Current status and research concerns. Sci Total Environ. 2019 Jun 15;669:512–26.
10. USEPA. Hydrological Simulation Program - FORTRAN (HSPF) (Internet). (cited 2020 Feb 10). Available from: https://www.epa.gov/ceam/hydrological-simulation-program-fortran-hspf
11. Xie H, Lian Y. Uncertainty-based evaluation and comparison of SWAT and HSPF applications to the Illinois River Basin. J Hydrol (Amst). 2013 Feb;481:119–31.
12. A. Saleh and B. Du. Evaluation of SWAT and HSPF within BASINS program for the Upper North Bosque River Watershed in central Texas. Transactions of the ASAE. 2004;47(4):1039–49.
13. Strassemeyer J, Daehmlow D, Dominic AR, Lorenz S, Golla B. SYNOPS-WEB, an online tool for environmental risk assessment to evaluate pesticide strategies on field level. Crop Prot. 2017 Jul;97:28–44.
14. Gutsche V, Rossberg D. SYNOPS 1.1: a model to assess and to compare the environmental risk potential of active ingredients in plant protection products. Agriculture, Ecosystems & Environment. 1997 Jul;64(2):181–8.
15. Curchod L, Oltramare C, Junghans M, Stamm C, Dalvie MA, Röösli M, et al. Temporal variation of pesticide mixtures in rivers of three agricultural watersheds during a major drought in the Western Cape, South Africa. Water Research X. 2020 Jan 1;6:100039.
16. Parker N, Larsen A, Banerjee P, Keller AA. Leveraging high spatiotemporal resolution data of pesticides applied to agricultural fields in California to identify toxicity reduction opportunities. PLOS Water. 2023 Aug 9;2(8):e0000124.
17. Hernández AF, Gil F, Lacasaña M. Toxicological interactions of pesticide mixtures: an update. Arch Toxicol. 2017 Oct;91(10):3211–23.
18. Doherty J. Model-Independent Parameter Estimation (PEST). Watermark Numerical Computing; 2002.
19. Yen H, Bailey RT, Arabi M, Ahmadi M, White MJ, Arnold JG. The role of interior watershed processes in improving parameter estimation and performance of watershed models. J Environ Qual. 2014 Sep;43(5):1601–13.
20. Luo Y, Zhang M. Management-oriented sensitivity analysis for pesticide transport in watershed-scale water quality modeling using SWAT. Environ Pollut. 2009 Dec;157(12):3370–8.
21. California Department of Water Resources. Stream Gages Help Californians Better Understand Water Resources (Internet). 2020 (cited 2023 Feb 22). Available from:

https://water.ca.gov/News/Blog/2020/July/Stream-Gages-Help-Californians-Better-Understand-Water-Resources
22. Surface Water AMbient Monitoring Program. Extent of California's Perennial and Non-Perennial Streams. Califronia Water Resources Control Board; 2011.
23. Halbach K, Möder M, Schrader S, Liebmann L, Schäfer RB, Schneeweiss A, et al. Small streams-large concentrations? Pesticide monitoring in small agricultural streams in Germany during dry weather and rainfall. Water Res. 2021 Sep 15;203:117535.
24. Lorenz S, Rasmussen JJ, Süß A, Kalettka T, Golla B, Horney P, et al. Specifics and challenges of assessing exposure and effects of pesticides in small water bodies. Hydrobiologia. 2017 Jun;793(1):213–24.
25. Center for Biological Diversity. San Francisco Bay Area and Delta Protection (Internet). (cited 2019 Oct 18). Available from: https://www.biologicaldiversity.org/campaigns/san_francisco_bay_area_and_delta_protection/index.html#
26. State Water Resources Control Board. 2014 and 2016 Clean Water Act Section 303(d) and 305(b) Integrated Report — Statewide (Internet). State Water Resources Control Board. 2018 (cited 2019 Mar 11). Available from: https://https://www.waterboards.ca.gov/water_issues/programs/tmdl/integrated2014_2016.shtml
27. USGS, USDA. Federal Standards and Procedures for the National Watershed Boundary Dataset (WBD). US Geological Survey Techniques and Methods 11-A3. 2nd ed. 2011.
28. CDPR. California Pesticide Information Portal (CalPIP) (Internet). (cited 2018 Oct 20). Available from: https://calpip.cdpr.ca.gov/main.cfm
29. Neitsch SL, Arnold JG, Williams JR. Soil & Water Assessment Tool (SWAT) – Theoretical Documentation Version 2009. Temple, Texas: Blackland Research Center, Texas A&M; 2011 Sep.
30. Kern County Department of Agriculture and Measurement Standards. Kern County Spatial Data (Internet). (cited 2021 May 14). Available from: http://www.kernag.com/gis/gis-data.asp
31. California Department of Water Resources. Land Use Surveys (Internet). (cited 2019 Jun 6). Available from: https://water.ca.gov/Programs/Water-Use-And-Efficiency/Land-And-Water-Use/Land-Use-Surveys
32. USDA. CropScape - NASS CDL Program (Internet). (cited 2018 Mar 19). Available from: https://nassgeodata.gmu.edu/CropScape/
33. Multi-Resolution Land Characteristics (MRLC) Consortium. National Land Cover Database (NLCD) (Internet). (cited 2019 Jun 6). Available from: https://www.mrlc.gov/data?f%5B0%5D=category%3Aland%20cover&f%5B1%5D=category%3Aurban%20imperviousness&f%5B2%5D=region%3Aconus&f%5B3%5D=category%3Aland%20cover&f%5B4%5D=category%3Aurban%20imperviousness&f%5B5%5D=region%3Aconus
34. CADWR Land Use Viewer (Internet). (cited 2019 Jul 10). Available from: https://gis.water.ca.gov/app/CADWRLandUseViewer/
35. CDPR. Surface Water Database (Internet). (cited 2018 Oct 20). Available from: https://www.cdpr.ca.gov/docs/emon/surfwtr/surfcont.htm
36. State Water Resources Control Board. Irrigated Lands Regulatory Program (Internet).

2019 (cited 2019 Jun 17). Available from: https://www.waterboards.ca.gov/water_issues/programs/agriculture/
37. California Department of Water Resources. CIMIS (Internet). (cited 2021 May 11). Available from: https://cimis.water.ca.gov/Default.aspx
38. gSSURGO Soil Survey Staff. Gridded Soil Survey Geographic (gSSURGO) Database for California. 2021 Oct 20;
39. National Resource Conservation Service. National Engineering Handbook - Irrigation Guide. 1997;Part 652.
40. Snyder R, Orang M, Bali L. Basic Irrigation Scheduling Program (BISe) (Internet). 2014 (cited 2022 Feb 8). Available from: https://biomet.ucdavis.edu/irrigation-scheduling/
41. Snyder RL, Lanini BJ, Shaw DA, Pruitt WO. Leaflet 21427–Using reference evapotranspiration (ETo) and crop coefficients to estimate crop evapotranspiration (ETc) for agronomic crops, grasses, and vegetable crops. University of California Division of Agriculture and Natural Resources; 1987.
42. Snyder RL, Lanini BJ, Shaw DA, Pruitt WO. Leaflet 21428–Using reference evapotranspiration (ETo) and crop coefficients to estimate crop evapotranspiration (ETc) for trees and vines. University of California Division of Agriculture and Natural Resources; 1987.
43. Pereira LS, Allen RG, Smith M, Raes D. Crop evapotranspiration estimation with FAO56: Past and future. Agricultural Water Management. 2015 Jan;147:4–20.
44. Merriam J. A Management Control Concept for Determining the Economical Depth and Frequency of Irrigation. Transactions of the ASABE. 1966;
45. Agriculture and Environment Research Unit, University of Hertfordshire. PPDB - Pesticides Properties DataBase (Internet). (cited 2018 Oct 20). Available from: https://sitem.herts.ac.uk/aeru/ppdb/en/
46. Wieczorek ME. USGS Data Series 866: Area- and Depth-Weighted Averages of Selected SSURGO Variables for the Conterminous United States and District of Columbia (Internet). United States Geological Survey. 2014 (cited 2021 Nov 30). Available from: https://dx.doi.org/10.3133/ds866
47. USEPA. Models for Pesticide Risk Assessment - Pesticide Science and Assessing Pesticide Risks (Internet). (cited 2020 Jul 8). Available from: https://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/models-pesticide-risk-assessment
48. Wischmeier WH, Smith DD. Predictiong Rainfall Erosion Losses–A Guide to Conservation Planning. Science and Education Administration–US Department of Agriculture; 1978.
49. Soil Conservation Service United States Department of Agriculture R. Urban Hydrology for Small Watersheds TR-55. United States Department of Agriculture; 1986 Jun.
50. Sloan PG, Moore ID. Modeling subsurface stormflow on steeply sloping forested watersheds. Water Resour Res. 1984 Dec;20(12):1815–22.
51. Williams J. The EPIC model. In: Singh VP, editor. Computer models of watershed hydrology. Water Resources Publications; 1995. p. 909–1000.
52. Menzel RG. CREAMS, A field Scale model for chemicals, runoff, and erosion from agricultural management systems. Knisel WG, editor. 1980.

53. Young D. The Variable Volume Water Model Revision B . USEPA; 2019 Sep. Report No.: USEPA/OPP 734S16002.
54. Dhont J, editor. Sedimentation. An introduction to dynamics of colloids. Elsevier; 1996. p. 443–93.
55. Ellison CA, Savage BE, Johnson GD. Suspended-sediment concentrations, loads, total suspended solids, turbidity, and particle-size fractions for selected rivers in Minnesota, 2007 through 2011. Scientific Investigations Report. 2014;
56. Huber W, Cannon L, Stouder M. BMP Modeling Concepts and Simulation. Lai F, editor. United States Environemntal Protection Agency Water Supply and Water Resources Division; 2006.
57. Krajewski A, Sikorska-Senoner AE. Suspended sediment routing through a small on-stream reservoir based on particle properties. J Soils Sediments. 2021 Mar;21(3):1523–38.
58. USDA. Open Ditches for Drainage - Design, Construction and Maintenance. National Engineering Handbook. 1971.
59. USEPA. Technical Overview of Ecological Risk Assessment: Risk Characterization – Pesticide Science and Assessing Pesticide Risks (Internet). (cited 2020 Jan 30). Available from: https://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/technical-overview-ecological-risk-assessment-risk
60. European Environment Agency. Ecological Risk Assessment (Internet). 2016 (cited 2020 Feb 3). Available from: https://www.eea.europa.eu/publications/GH-07-97-595-EN-C2/chapter6h.html
61. Sprague JB, Ramsay BA. Lethal levels of mixed copper–zinc solutions for juvenile salmon. J Fish Res Bd Can. 1965 Feb;22(2):425–32.
62. Bliss CI. The toxicity of poisons applied jointly. Ann Applied Biology. 1939 Aug;26(3):585–615.
63. Nowell LH, Norman JE, Moran PW, Martin JD, Stone WW. Pesticide Toxicity Index--a tool for assessing potential toxicity of pesticide mixtures to freshwater aquatic organisms. Sci Total Environ. 2014 Apr 1;476–477:144–57.
64. Belden JB, Gilliom RJ, Lydy MJ. How well can we predict the toxicity of pesticide mixtures to aquatic life? Integr Environ Assess Manag. 2007 Jul;3(3):364–72.
65. Deneer JW. Toxicity of mixtures of pesticides in aquatic systems. Pest Manag Sci. 2000 Jun;56(6):516–20.
66. Belden JB, Brain RA. Incorporating the joint toxicity of co-applied pesticides into the ecological risk assessment process. Integr Environ Assess Manag. 2018 Jan;14(1):79–91.
67. Bundschuh M, Goedkoop W, Kreuger J. Evaluation of pesticide monitoring strategies in agricultural streams based on the toxic-unit concept--experiences from long-term measurements. Sci Total Environ. 2014 Jun 15;484:84–91.
68. Morley SK, Brito TV, Welling DT. Measures of model performance based on the log accuracy ratio. Space Weather. 2018 Jan;16(1):69–88.
69. Winchell MF, Peranginangin N, Srinivasan R, Chen W. Soil and Water Assessment Tool model predictions of annual maximum pesticide concentrations in high vulnerability watersheds. Integr Environ Assess Manag. 2018 May;14(3):358–68.
70. USEPA. Risk Assessment Guidance for Superfund (RAGS): Part B (Internet). United States Environmental Protection Agency. (cited 2023 Jun 1). Available from:

https://www.epa.gov/risk/risk-assessment-guidance-superfund-rags-part-b
71. USEPA. Aquatic Life Benchmarks and Ecological Risk Assessments for Registered Pesticides (Internet). (cited 2022 Jun 8). Available from: https://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/aquatic-life-benchmarks-and-ecological-risk
72. SciSpace (Internet). (cited 2023 Sep 17). Available from: https://typeset.io/
73. Stehle S, Knäbel A, Schulz R. Probabilistic risk assessment of insecticide concentrations in agricultural surface waters: a critical appraisal. Environ Monit Assess. 2013 Aug;185(8):6295–310.
74. Hladik ML, Kuivila KM. Assessing the occurrence and distribution of pyrethroids in water and suspended sediments. J Agric Food Chem. 2009 Oct 14;57(19):9079–85.
75. University of California Agriculture and Natural Resources. UC IPM Statewide Integrated Pest Management Program (Internet). (cited 2023 Aug 31). Available from: https://ipm.ucanr.edu/

3.7 Acknowledgements

This project was funded by the California Sea Grant Delta Science Fellowship

SEADSR4/183BCA/416701/440000.