MODELING AND EVALUATING WASTEWATER-DERIVED PESTICIDES IN SURFACE WATER

by

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ABSTRACT

DENISE ADJIDJONU. Modeling and Evaluating Wastewater-Derived Pesticides in Surface Water. (Under the direction of DR. JACELYN RICE-BOAYUE and DR. MARIYA MUNIR)

Pesticide use has reached alarming levels globally, causing potential risks to human health and the environment. With its high population densities and rapid development, California emerges as one of the country's leading users of pesticides in the country. Recognized point and non-point pathways for pesticides entering surface water include mixed indoor and outdoor applications and treated municipal wastewater effluent, indicating that conventional wastewater treatment plants (WWTPs) treatment processes are inefficient at removing pesticides from effluents. Recent studies have assessed the fate of pesticides in surface water with a limited understanding of watershed characteristics. This project aimed to quantify WWTP discharges, a lesser-known source of pesticide loads, and investigate the potential environmental benefits of their removal. To evaluate WWTP pesticide concentrations, we developed a geospatial model with municipal WWTP discharges, streamflow characteristics, and pesticide loading data to estimate pesticide concentrations within wastewater receiving streams. Next, we set a multimetric Pesticide Vulnerability Index (PVI) to identify the most vulnerable California watersheds to wastewater-derived pesticide loading. Finally, we investigated the environmental benefits of incorporating advanced WWTP processes for pesticide residue removal from treated effluent before surface water discharge using estimated WWTP life-cycle costs.

This work presents an integrated assessment of pesticides in surface water to support source control and mitigation efforts. It highlighted the significance and effects of municipal WWTP pesticide loading in California's urban waterways. In addition, completing this project provided insight into the environmental and economic costs associated with municipal wastewater-derived pesticide mitigation.

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DEDICATION

This doctoral project is dedicated to my beloved family: Ing. Samuel Mensah Adjidjonu, Mrs. Lucy Adjidjonu, my siblings Thelma Adjidjonu (MBA) and Samuel Senanu Adjidjonu. I am truly grateful for your enduring love and support.

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LIST OF ABBREVIATIONS

7Q10	7-day 10-year low flow
AB	Aquatic life benchmarks
AOPs	Advanced oxidation processes
ATPs	Advanced treatment processes
CDPR	California Department of Pesticide Regulation
CBA	Cost-benefit analysis
CFS	Cubic feet per second
CIAWH	California Integrated Assessment of Watershed Health
CWNS	Clean watersheds need survey
DFs	Dilution factors
EECs	Estimated environmental concentrations
GIS	Geographic information systems
HQ	Hazard quotient
HUC	Hydrological unit code
LC	Lethal concentration
LCA	Life-cycle Assessment
LD	Lethal dose
LOC	Level of concern
MGD	Million gallons per day

NCCV	National Climate Change Viewer
NHDPlus	National hydrography data set plus
PAH	Polycyclic aromatic hydrocarbons
PEPS	Primary Effluent Pump Station
PCS	Permit Compliance System
PVI	Pesticide Vulnerability Index
SSO	Strahler Stream Order
SURF	Standardized Urban Riverine Framework
SWAT	Soil and Water Assessment
USDA	U.S. Department of Agriculture
USEPA	U.S. Environmental Protection Agency
USGS	United States Geological Survey
UV	Ultraviolet
VOCs	Volatile organic compounds
WWTPs	Wastewater treatment plants

CHAPTER 1: INTRODUCTION

1.1 URBAN PESTICIDE LOADINGS INTO SURFACE WATER

The primary source of pesticide loads in the US are from agricultural usage, typically diffuse or non-point, covering vast application areas [1]. However, pesticide residues have been detected in municipal wastewater treatment plants (WWTP) effluent, making them a contributor to pesticide loading in urban waterways [3]. Down-the-drain pathways for pesticide loading into municipal WWTPs include indoor use (e.g., pet product applications, laundry, showers, handwashing, etc.) and outdoor use (e.g., gardening, extermination, etc.) pesticides that make it indoors (see Figure 1). Unfortunately, the current design technologies of WWTPs are inefficient in effectively tracing and removing pesticides before their discharge into surface waters [4, 9].

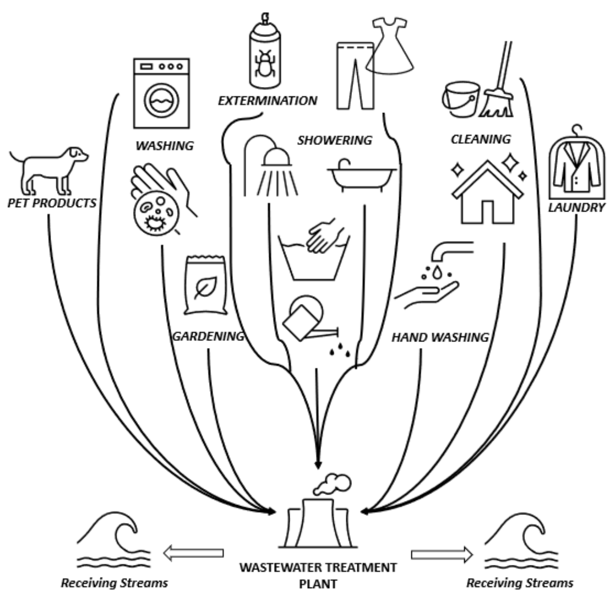

Figure 1: Model of urban pesticide pathways via down-the-drain transport sources to surface waters. Adapted from Sutton et al. (2019) and Xie et al. (2021) [3, 7].

Secondary treatment processes applied to contaminated influents from municipal WWTPs in various California regions have shown only marginal reductions in the effluent pesticide concentration for certain pesticides [4]. That poses a high risk to aquatic life, potentially leading to adverse effects, such as decreased motility and reduced fertility [10, 11]. Therefore, this study considers municipal WWTPs as significant sources of pesticide loading to surface waters and evaluates potential risks posed to aquatic health. Analyzing the potential risks posed by wastewater-derived pesticides further provides valuable insights for mitigating pesticide contamination and safeguarding water quality.

This dissertation also aims to examine potential benefits of improving pesticide removal through advanced wastewater treatment, with a focus on the wider objective of improving water quality and reducing ecological risks. This study focuses on California, however, the findings and insights from this research will have broader implications for other regions grappling with similar pesticide pollution challenges. The outcomes of this research will help stakeholders, policymakers, and water resource managers make informed choices in mitigating the impact of municipal WWTPs as sources of pesticide loading, ultimately leading to cleaner and healthier water environments.

1.2 RESEARCH SCOPE AND OBJECTIVES

This research was designed to comprehensively assess pesticide risks within the receiving streams of wastewater treatment plants (WWTP) in California. The primary objective was to conduct a thorough evaluation of the extent and nature of pesticide contamination in these aquatic environments. This involved the identification of specific pesticides present within watersheds, their concentrations, and the potential ecological and human health risks associated with their presence. Subsequently, the research aimed to delineate environmentally susceptible watersheds and to identify geographical areas where pesticide contamination may exhibit heightened ecological sensitivity. This involved integrating geographical, hydrological, and climatic data to ascertain the spatial patterns of pesticide occurrence and potential impacts. Furthermore, the study sought to investigate the economic value of implementing advanced wastewater treatment technologies for pesticide removal within the WWTPs. An economic assessment considered the costs and benefits associated with tertiary treatment of pesticides, aiming to provide valuable insights into the feasibility and economic efficiency of advanced treatment methods in reducing risks to aquatic ecosystems posed by pesticides. Geospatial data science is used to explore pesticide transport and fate by simulating the spatiotemporal dynamics of pesticide movement and persistence across watersheds. This integration of climatic and anthropogenic datasets enables us to derive meaningful insights for evidence-based decision-making.

The specific research objectives are: (1) evaluate pesticide risk in municipal WWTP effluent receiving streams based on aquatic health benchmarks; (2) identify watersheds more susceptible to combined pesticide loadings from multiple-point and non-point sources; and (3) investigate monetary valuations for environmental benefits associated with advanced wastewater treatment for pesticide removal. Through these interconnected objectives, this research endeavors to contribute to a comprehensive understanding of pesticide-related environmental risks, facilitate targeted conservation efforts, and inform decision-making processes for sustainable water management practices.

1.2.1 RESEARCH QUESTIONS AND HYPOTHESES

Through completion of the aforementioned research objectives, answers to several research questions will be explored. Specifically, the following questions and their respective hypotheses will be investigated.

RQ1: What are the predicted pesticide concentrations in California WWTP receiving streams under mean annual, mean monthly and low-flow conditions?

> *H1: Pesticide concentrations will temporally increase with decreasing streamflow in WWTP effluent receiving streams.*

RQ2: What are the predicted aquatic benchmark exceedances in California WWTP receiving streams under mean annual, mean monthly and low-flow conditions?

> *H2: The likelihood of benchmark exceedances in California's WWTP receiving streams will vary temporally due to variations in streamflow and be more prominent for pesticides with relatively higher aquatic toxicity and measured environmental concentrations.*

RQ3: What is the spatial distribution of watersheds relatively more susceptible to pesticide loadings from point and non-point sources?

> *H3: California's urban watersheds demonstrate higher susceptibility to pesticide loadings originating from both point and non-point sources.*

RQ4: What is the spatial correlation of the vulnerable watersheds in relation to endangered species?

> *H4: There are statistically significant spatial correlations for hotspots representing pesticide vulnerability and endangered aquatic species across California.*

RQ5: How can environmental benefits associated with upgrading a secondary treatment WWTP to an advanced treatment train for pesticide removal be economically quantified?

H5: Shadow pricing can be utilized as a monetary proxy for the environmental benefits of removing pesticides through advanced wastewater treatment.

1.3 SIGNIFICANCE OF THE STUDY

The intellectual merit of this research lies in recognizing wastewater treatment plants (WWTPs) as significant contributors to pesticide loadings. By developing an approach to integrate the environmental benefits of advanced wastewater treatment for pesticide removal into traditional cost-benefit analyses, this study introduces a new perspective to the field. The results from Chapter 3 highlighted the role of wastewater treatment plants (WWTPs) as a significant point source of pesticides in the municipal sewage system. These findings shed light on the chronic exposure threats posed to invertebrates and other aquatic life in these systems. Chapter 4's results are significant as they provide information on the regions most affected by pesticide contamination, aiding in prioritizing management efforts. Chapter 5's analysis yielded crucial insights into the effectiveness of wastewater treatment measures in reducing pesticide contamination and minimizing the ecological risks associated with WWTP discharges. The outcomes of these studies can inform decision-making and policy development at both the state and national levels. The findings from this project will be disseminated widely through three journal articles, aiming for academic advancement and ensuring broad distribution within the scientific community.

Overall, this research holds intellectual merit by addressing a significant gap in understanding the role of WWTPs in pesticide loadings and their potential environmental impacts. Additionally, its broader impact lies in providing valuable insights to decision-makers and policymakers, enabling them to make informed choices regarding wastewater treatment strategies and environmental protection efforts.

1.4 ORGANIZATION OF DISSERTATION

This dissertation consists of six chapters. Chapter 1 is an introductory chapter providing an overview of pesticide use, fate, and transport in the aquatic environment and the approach taken in this study. Chapter 2 provides a comprehensive literature review on pesticide loadings in surface water and gaps in the literature. Chapters 3, 4, and 5 are presented as research articles addressing the gaps in the literature. Chapters 3 and 4 have been submitted to the California Department of Pesticide Regulation (CDPR) for review. Chapter 3 will be submitted in article format to *Environmental Science and Technology – Water*, and Chapter 4 will be submitted to *SETAC Integrated Modeling and Assessment Journal*. Chapter 5 is being prepared for submission to *Environments*, an internationally recognized and interdisciplinary open-access journal for environmental systems by MDPI. A conclusive summary of the findings, research limitations, and future recommendations are provided in Chapter 6.

CHAPTER 2: LITERATURE REVIEW

This literature review explores the impacts of pesticides discharged from urban areas in aquatic environments and water quality effects in surface waters. Pesticides are commonly used in urban areas and are introduced into the atmosphere through different pathways. Once in the environment, pesticides undergo various chemical transformations, which can affect their persistence and inherent toxicity to aquatic wildlife. Based on available studies, these pesticides pose a significant threat to aquatic wildlife and require prompt action to mitigate their effects.

Other pathways by which pesticides enter urban streams include stormwater runoff [2, 3] and contaminated runoff from landscape maintenance [4]. Aquatic ecosystems, found in urban and agricultural landscapes, provide ecosystem services to humans but remain vulnerable to harmful human activities (e.g., pesticide use) that lead to their contamination [5, 6]. Urban stormwater runoff carries a mixture of contaminants, including organic chemicals like polycyclic aromatic hydrocarbons (PAHs), pesticides, and pharmaceuticals [7, 8]. Recent studies revealed significant concentrations of these organic chemicals, with some individual concentrations exceeding 10,000 ng/L and cumulative concentrations reaching up to 263,000 ng/L during runoff events [8]. This suggests the potential for adverse environmental effects from stormwater runoff. The concentration of organic chemicals was positively correlated with impervious surfaces and highly developed urban catchments. In contrast, inorganic chemical concentrations in stormwater were generally diluted and did not exceed chronic aquatic life criteria [8].

2.1 PESTICIDE USE, FATE AND TRANSPORT IN THE ENVIRONMENT

Pesticides are classified by their chemical compositions (i.e., organophosphates, pyrethroids, phenylprazoles, etc.) and have various applications in agricultural, industrial, residential, and commercial settings in the US [7, 12]. According to the most recent study of pesticide use tracking by Xie et al. [3], California accounts for nearly 20% of the country's total pesticide use, with significant estimated urban (indoor and outdoor) applications based on mass consumer data. Their applications stem from gardens, laundry and bathroom cleansers, pet products, and other domestic collections. These are directly channeled down the drain to waste streams and exhibit limited removals in WWTP effluent [9, 13].

Due to increased population growth and urban developments, farming and domestic activities produce new emerging contaminants (i.e., pesticides) [7, 14]. Older organophosphates (e.g., chlorpyrifos, diazinon) are gradually being replaced by phenylpyrazoles (e.g., fipronil), pyrethroids (e.g., permethrin, cypermethrin, bifenthrin), and neonicotinoids (e.g., imidacloprid) in urban and household usage, but not without consequences to non-targeted species [15, 16]. Since fipronil is less toxic than organophosphates, it is widely used for pesticide control [17], residential and veterinary practice, and agricultural purposes [18, 19]. Imidacloprid is one of the most commonly used neonicotinoids globally, with applications in lawn and landscape maintenance, outdoor structural pest control, and pet treatments for ticks and fleas [4, 20]. Synthetic pyrethroids have been widely used to control various pests in agriculture, public health, and residential settings [21, 22]. However, these chemicals can harm non-target aquatic organisms entering aquatic environments.

Studies have shown that synthetic pyrethroids can have toxicological impacts on these aquatic organisms. The toxicity of synthetic pyrethroids to non-target aquatic organisms can vary based on species, life stage, and exposure duration [22, 23]. Some observed toxicological impacts include acute mortality, impaired growth and reproduction, altered behavior, and biochemical disruptions in aquatic organisms [22]. Additionally, certain species, such as fish, may be more susceptible to synthetic pyrethroids' toxic effects than others [24]. Therefore, it is crucial to carefully consider synthetic pyrethroids' usage and potential environmental consequences to protect non-target aquatic organisms in aquatic ecosystems.

Maximum human exposure levels for pesticides, such as pyrethroids, neonicotinoids, and phenylpyrazoles, are established by the U.S. Environmental Protection Agency (EPA). These benchmarks are set as reference doses or concentrations where adverse effects are not expected, especially for sensitive groups i.e., children and older humans [23]. Reference doses range from a few hundred micrograms per liter up to 100,000 µg/L, depending on the pesticide being analyzed [23]. Prolonged exposure, even below these benchmarks, is linked to neurodevelopmental issues, endocrine disruption, and increased cancer risk [22].

Since pesticides are classified as volatile organic compounds (VOCs) due to their high vapor pressure and low water solubility, they readily vaporize in the atmosphere during application [12]. Water remains one of the primary transport channels for pesticides through sewers and watersheds [25]. Hence, pesticides are transported to streams and groundwater via seepage, runoff, and recharge from agricultural and urban land, leading to contamination [26]. Seasonal events strongly affect the movement of pesticides to and within surface waters and influence the accumulation of pesticide residues in bed sediment and aquatic biota [27, 28].

Recent surveys of urban streams in California indicate higher levels of imidacloprid concentrations during the wet season (October to April) and lower levels during the dry season (May to September) [23, 29]. Other surveys of effluent-dominated streams in southern California detected fiproles and their degradates during low flow conditions [30, 31]. Some recent studies in

California have highlighted the occurrence of several pesticide residues within treated municipal wastewater effluent at levels hazardous to aquatic organisms, especially during low-flow conditions. Urban stormwater and wastewater effluent have also been associated with higher levels of detection during seasonal changes such as droughts within California [23, 32]. With increased concentrations, pesticide persistence is more likely to exceed aquatic thresholds and impair surface water quality [33]. The fate of these pesticides from point and non-point sources, especially down the watershed, is therefore of utmost importance due to their inherent toxicity to the environment.

A recent study has revealed that concentrations of 21 commonly found pesticides vary significantly, ranging from five (5) orders of magnitude [34]. The research found that some pesticides, including carbendazim, pentachlorophenol, and diuron, were measured at concentrations exceeding 1,000 ng/L, much higher than those previously reported in stormwater runoff from residential and commercial areas. These pesticides have been associated with adverse effects on aquatic organisms. The levels of atrazine, metolachlor, dithiopyr, diuron (DCPMU), imidacloprid, and fipronil were found at concentrations ranging from 3 to 300 ng/L. The study also showed that imidacloprid, commonly used in home and garden applications, has been increasingly detected in urban streams. Furthermore, many concentrations of imidacloprid and fipronil exceeded the U.S. Environmental Protection Agency's (EPA) chronic aquatic life benchmark for invertebrates [34]. Based on these factors, this study intends to investigate the ecological effects of wastewater-derived pesticides from these combined sources on the aquatic environment.

2.2 BACKGROUND INFORMATION FOR THE PESTICIDE SUITE UTILIZED IN THIS STUDY

Various classes of pesticides, such as fipronil, bifenthrin, imidacloprid, permethrin, and chlorpyrifos, have been extensively studied for their effects on water-based organisms. These pesticides are classified as pyrethroids, neonicotinoids or phenylpyrazoles based on their chemical composition and neurotoxicity to aquatic organisms. The US EPA classifies the toxicity of chemicals based on their metabolites and associated health impacts, ranging from class I to IV. [48]. For our study, our target pesticides were selected due to their detections in down-the-drain effluents and sludge. This chapter discusses the effect of each down-the-drain pesticide and their acute and chronic toxic effects on aquatic life.

2.2.1 FIPRONIL

Fipronil, classified as a phenylpyrazole, is a World Health Organization (WHO) level II hazardous insecticide that kills insects by targeting the central nervous system and destroying the glutamate chloride channels and gamma-aminobutyric acid receptors. Since fipronil and its metabolites are widespread, their exposure channels vary substantially. Unfortunately, these pesticides do not always precisely meet their targets (e.g., insects, pests), making their toxicological impacts more widespread on non-targeted species such as humans, fishes, crustaceans, and other aquatic life [11, 35]. Existing and evolving clinical toxicological studies have found that these pesticides are associated with cellular genomic mutations, with subsequent resultant impact on increased risk of apoptosis, hypospadias, and developmental testicular abnormalities among aquatic organisms [11, 36]. The residue from fiproles bioaccumulates in shrimps, crustaceans, and fishes, increasing public health and safety concerns, as seafood is a popular source of protein globally [11, 18, 37]. Recent studies have also discovered that fipronil and its metabolites are associated with mitochondrial dysfunctions, DNA damage, and micronuclei formation among aquatic organisms. While evidence suggests pesticide impacts vary according to the type of aquatic creature, there is a consensus that these chemicals may hamper and potentially halt exposed organisms' survival and growth factors.

2.2.2 BIFENTHRIN

Bifenthrin is a third-generation synthetic pyrethroid insecticide with extremely high ecological persistence in the environment [40]. Bifenthrin has been found to cause deleterious health impacts on the survival of fishes and other aquatic life forms. Target organisms are killed through the destruction of their nervous system, mainly through disruption of sodium channels at the nerve cell endings, eventual depolarization of presynaptic terminals, and a halt in the production of ATPase [40]. This biochemical damage on target organisms may also occur in non-target organisms when these pesticides get into water bodies and other sensitive ecological environments. While there are toxicological studies of bifenthrin's impact on fishes, amphibians, and invertebrates, few available research studies have been consistent in discoveries. For example, in one experimental study, fishes (*clarias batrachus spp*) were exposed to 5.093µg/l, 4.659µg/l, 3.893µg/l, and 3.464µg/l for 24, 48, 72, and 96h period. The researchers discovered that none of the unexposed fishes died during the experimental period, however deaths were recorded among the treatment group even though the mortality rate varied. Additionally, the period of exposure and dose amount were significantly correlated [41]. A different study investigated the impact of dietary exposure to bifenthrin and fipronil on swimming performance in juvenile Chinook Salmon (*Oncorhynchus tshawytscha*) [40]. The researchers reported that fishes exposed to bifenthrin and fipronil mixtures had significantly reduced swimming performance. In conclusion, bifenthrin and its combination with fipronil may induce negative metabolic processes among aquatic organisms.

2.2.3 IMIDACLOPRID

There is consistent toxicological evidence of the impact of imidacloprid on ecosystem health [42]. Freshwater organisms such as amphibians, fishes, and invertebrates are most susceptible. In temperate and sub-tropical environments, exposure of freshwater bodies to imidacloprid has been known to induce a cyanobacterial bloom. Researchers found that the most significant ecosystem response to imidacloprid was recorded among *Gerris sp*., *Diaptomus sp.*, and *Brachionus quadridentatus* [42]. In their study, imidacloprid caused the population decline of the larger zooplankton species (*Diaptomus sp.* and *Ostracoda*), caused an elevated rotifer abundance, and shifted the phytoplankton community to a graze-resistant gelatinous cyanobacteria dominated ecosystem. Apart from the freshwater environment's exposure to the imminent threat, public health was also a vital issue for the researchers, as human food sources are directly linked to freshwater bodies.

2.2.4 PERMETHRIN

Permethrin is a pyrethroid chemical that is classified as level II (moderately) or level III (slightly toxic), depending on its formulation [45]. Therefore, the US EPA has flagged it as a ‘restricted use pesticide’ due to its toxic impact on fish. However, since most restrictions are focused on active pesticide ingredients and not on their formulations, most of these products are given to public consumption, thereby posing a threat to aquatic life (invertebrates, amphibians, fishes) and other non-target organisms [46]. An earlier study investigated the acute toxicity of permethrin on guppies *Poecilia reticulata*, and the result showed that the biochemical and behavioral responses were more noticeable at higher doses [46]. At the highest concentration (525µg/l), the loss of equilibrium, hanging vertically in the water, rapid gill movement, erratic swimming, and sudden swimming motion in a spiral manner became markedly observable for the researchers, indicating the toxic impacts of permethrin. These lethal impacts are similar for amphibians, crustaceans, and other aquatic organisms [17]. Given these aquatic creatures' sensitivity to permethrin being discharged from WWTPs into freshwater bodies, this pesticide undoubtedly poses a critical danger to these species, the ecosystem, and public health in general.

2.2.5 CHLORPYRIFOS

Chlorpyrifos is one of the most familiar organophosphate pesticides widely used in agriculture, feed crops, cattle ear tags, golf course turf, industrial plants, and vehicles, non-structural wood treatments including processed wood products, fence posts, and utility poles, and to control public health pests such as mosquitoes and fire ants [6, 35, 47]. Similar to many other pesticides, exposed aquatic creatures may suffer adverse outcomes such as dysfunction of steroid metabolism, reduced opercular movement, disruption of the hepatic system, behavioral alterations, respiratory stress, epithelial hyperplasia, hydropic degeneration, erratic swimming, delayed metamorphosis, curling of secondary lamellae, degeneration & necrosis of renal tubules, and constriction of the glomerulus [35]. In one study, the larvae of common toads were exposed to six different concentrations of chlorpyrifos (1-500 µg/l), and bio-responses were recorded [52]. Observation showed that the exposed toads displayed reduced swimming activity, growth impairment, and delayed metamorphosis.

Based on the literature reviewed, it is evident that the pesticides chosen for the study, when discharged into surface waters, have the potential to impact aquatic life through chronic exposure. These chemicals can disrupt the normal physiological functions of aquatic organisms, impair reproduction, growth, and development, and even cause mortality. Pesticides can also indirectly affect higher trophic levels in food chains, leading to ecological imbalances and cascading effects on ecosystems. There can be potential risks to public health if pesticides contaminate drinking water sources or recreational waters [53].

2.3 WWTP PESTICIDE REMOVAL EFFICIENCY

WWTPs have been established as point sources for pesticide loadings into surface waterbodies due in part to their inadequacy to remove pesticide residuals from influents [9, 13]. In the US, most WWTPs employ primary and secondary treatment processes in wastewater management before discharge, but pollutant removal rates vary based on the prospective influent concentrations and chemical characteristics [4, 32]. With the rapid developments in wastewater treatment, Fatta-Kassinos et al. [93] analyzed advanced treatment processes (ATPs) for contaminants of emerging concern (CECs) such as pesticides. They found that membranes, ozone, adsorption, and advanced oxidation processes (AOPs) are the most viable for WWTP applications. ATPs are concerned with removing dissolved and suspended trace contaminants, such as pesticides, which are not reduced significantly by conventional secondary treatment processes [94]. ATPs have been shown to produce less sludge and show rapid reactions for neutralizing contaminants on a large scale. Several pilot studies have been conducted to assess ATPs' efficacy for pesticide removal (Table A4 in Chapter 7 Appendix). The specific results depend on the type of pesticide, the treatment method used, and the conditions of the treatment process [95].

Overall, the concerns about pesticides from urban discharge highlight the need for robust monitoring programs, analytical tools like the Surface Water database (SURF), and applying vulnerability indices to address the issue effectively.

2.4 ECONOMIC MODELING OF WASTEWATER TREATMENT

Municipal WWTP processes can be improved with more efficient technology to comply with the aquatic standards for effluent discharge and water reuse. Dealing with these upgrades implies increased capital costs (new equipment, new reagents) and annual costs, which must be sufficiently differentiated. ATPs have short- and long-term environmental benefits (e.g., removal of pesticide elements), which need to be adequately quantified as they have no market value [103]. These costs are typically analyzed using traditional cost-benefit analyses (CBA) [104] or life-cycle assessments (LCA) [105]. Several studies for the economic valuation of these environmental benefits have been conducted and have served as a valuable indicator of the feasibility of subsequent wastewater treatment projects [103, 105, 106]. Additionally, the profits and losses associated with WWTP upgrade implementation could be a function of socio-economic influence [107], where limiting pesticide usage from human applications would significantly reduce the aquatic risk posed as opposed to just upgrading wastewater processes.

2.5 MONITORING ECOLOGICAL RISKS POSED BY PESTICIDES

Monitoring the presence and levels of pesticides in aquatic environments is essential for assessing their potential risks. This requires regular sampling and analysis of water bodies to determine the concentrations of pyrethroids and their breakdown products. To address the potential risks associated with pesticide use, regulatory agencies, such as the United States Environmental Protection Agency (EPA), have established aquatic life benchmarks and ecological risk assessments for registered pesticides [54, 55]. These benchmarks guide assessing the potential impacts of pesticides on aquatic organisms and ecosystem health. However, ongoing research and monitoring efforts are necessary to enhance our understanding of long-term effects and potential synergistic interactions between pyrethroids and other pollutants. A critical consideration in assessing environmental effects is the acute toxicity of the pesticides, which is measured as the amount or concentration of a toxicant required to kill 50 percent of the animals in a test population [56]. This measure is the LD50 (lethal dose 50) or LC50 (lethal concentration 50). LD50 and LC50 values are a basis for comparing the toxicities of different active ingredients and formulations containing the same active ingredient [56, 57].

2.6 CURRENT MONITORING AND MITIGATION OF PESTICIDE LOADINGS

Pesticide contamination of the aquatic environment has been a long-standing concern in the United States due to its adverse effects on aquatic and human health. In recognizing the risks associated with pesticide discharges, monitoring programs are in place to assess the presence and concentrations of pesticides in surface waters. Monitoring helps identify the sources, distribution patterns, and trends of pesticide contamination, enabling targeted mitigation efforts [64]. Many organizations have developed plans to manage aquatic watersheds for monitoring and reducing pesticide loadings. For example, the USDA's Natural Resources Conservation Service (NRCS) has developed a comprehensive conservation plan for the Chesapeake Bay watershed that includes BMPs, regulations, and monitoring programs to address pesticide loadings [67]. Since non-point sources of pesticides remain diffuse, pesticide use reporting and origin monitoring practices vary across the nation and may not be publicly available [68].

State and local monitoring surveys of surface and groundwater have been conducted by the US Geological Survey (USGS) National Water Quality Assessment (NAWQA) program to analyze pesticide loads [73]. The program has collected and analyzed water samples from over 3,000 sites nationwide for dissolved pesticides such as fipronil and its degradates. The USGS has also implemented a national program to monitor pesticides in streams in agricultural and urban areas [23]. These surveys indicate the presence of pesticide analytes in waterbed sediments and aquatic creatures' tissues but have significant time requirements and depend on specific hydrologic conditions. They are also limited in scale due to seasonal changes and ecological and anthropogenic variations, i.e., agricultural vs urban land use.

In the US, state and federal agencies spend $470 million annually on pesticide control and regulation [64]. In 1972, the Clean Water Act (CWA) was enacted by the US Congress to spearhead campaigns that regulate the discharge of pollutants from point sources such as WWTPs in meeting new aquatic quality standards [7]. However, no specific policies regulate pesticide usage and discharge into surface waters [68]. In the absence of federally mandated use reporting, the California Department of Pesticide Regulation (CDPR), under the auspices of the EPA, regulates and monitors pesticide use across the state. California has publicly accessible pesticide use reports (PUR) that inform water quality assessments of pesticide loading to urban waterways [71].

2.7 WATERSHED HEALTH, VULNERABILITY, AND ASSESSMENT

Watershed vulnerability refers to the susceptibility of a geographic area or region characterized by a defined watershed boundary to adverse environmental, hydrological, or anthropogenic changes or stressors [81]. This definition is based on watershed characteristics and the hydrological conditions that factor into the degree of pesticide vulnerability [63]. Factors contributing to watershed vulnerability may include climate variability, land use changes, pollution, and population growth. Because vulnerability is a function of the interaction of watershed characteristics and the imposed contaminant, selected pesticide loadings can be assessed across a region with known spatial traits. This approach is one of three ways to assess vulnerability: a) index-based, b) process-based, which approximates contaminant fate and transport, and c) statistical-based, which uses numerical simulations.

Established index-based methodologies for vulnerability assessment include the AVI [82-84], DRASTIC [84-88], California Integrated Assessment of Watershed Health (CIAWH) [89], GOD and SINTACS [82, 90]. However, these approaches depend on how the selected variables are weighed. Therefore, these methods need to be validated either through statistical methods [72] or through comparison with actual observed conditions [91, 92].

The California EPA conducted an integrated index-based assessment of watershed health at state and regional levels in a report titled the California Integrated Assessment of Watershed Health (CIAWH) [89]. This report used metrics such as hydrologic data, water quality, habitat characteristics, and biological data, for a holistic relative assessment of healthy watersheds across the state. The CIAWH methodology was incorporated into this study to assess pesticide vulnerability within California's watersheds.

More recent spatial tools such as Geographic Information Systems (GIS) and SWAT have been successfully incorporated into vulnerability assessment models [74, 91, 92]. Geospatial models such as Arc SWAT incorporate multiple criteria related to hydrology, land use, climate, ecology, and other historical attributes into geographic frameworks for visualization [75]. The framework is then validated by statistical correlation and regression methods (e.g., fuzzy logic, analytical hierarchy, multiple linear regression) or by comparison with real-world conditions [72, 76]. Based on the analysis results, inferences about the complex relationships between watersheds and their immediate environments can be made. GIS plays a vital role in watershed modeling for pesticide transport, providing a powerful framework for integrating spatial data and analyzing the dynamic interactions within complex environmental systems [75]. For pesticide transport modeling, GIS incorporates multiple geospatial layers such as land use, soil types, and hydrological features to develop comprehensive watershed models. The application of Getis Ord Gi* statistics allows for the identification of spatial clusters or hotspots of pesticide concentrations [73, 75]. Getis Ord Gi* assesses the degrees of spatial autocorrelation, and pinpoints areas with statistically significant high or low concentrations of pesticides. This analysis helps identify localized patterns of pesticide transport within watersheds and offers insights into areas of potential environmental susceptibility. Hotspot analysis further examines spatial patterns by highlighting statistically significant clusters of high or low values [74]. For pesticide transport, hotspot analysis helps to identify regions where concentrations are higher in order to guide resource allocation for monitoring and management efforts. By leveraging these GIS techniques, watershed modeling becomes a more precise and informed process, thereby enhancing our understanding of pesticide transport dynamics and facilitating targeted strategies for mitigating environmental impacts.

With the advancement of geospatial tools and remote sensing, geospatial modeling is helpful in site optimization, index-based analyses, and watershed vulnerability to pesticides. Wolfram et al. [77] assessed 32 pesticides and six (6) degradants potential risks in the US using a spatiotemporal model, which found that smaller watersheds demonstrate higher pesticide exceedances when compared to larger ones.

2.8 SUMMARY OF RESEARCH NEEDS

The concerns raised about pesticides from urban discharge highlight several gaps in our knowledge that must be addressed. First, there is a need to understand WWTP discharge threats to aquatic life from exposure. This need is partially addressed by analyzing the concentrations of commonly used pesticides like fipronil, bifenthrin, imidacloprid, permethrin, and chlorpyrifos in WWTP effluent. That will provide a comprehensive understanding of the extent of pesticide contamination and its potential impacts on ecosystems.

Additionally, we prioritized watersheds most likely to be impacted by pesticide discharges from multiple sources. By applying vulnerability indices, this study can help assess the potential risks of pesticide contamination in different aquatic ecosystems. These indices consider factors such as the sensitivity of the ecosystem, the exposure pathway, and the potential impacts on ecological processes. By applying vulnerability indices, we can prioritize areas that are most at risk and allocate resources for targeted mitigation and management strategies.

Furthermore, our study aims to incorporate the benefits of advanced treatment into current decision-making practices. We take the shadow price approach, which models the environmental benefit from upgrading a secondary WWTP to remove target pesticides. By doing so, this study considers not only the costs but also the broader ecological advantages, ensuring more sustainable and ecologically responsible water management practices.

Through this research, we can take significant steps towards reducing the adverse effects of pesticide runoff on aquatic creatures. This research work will provide valuable insights into the extent of pesticide contamination in different aquatic environments, the ecological impacts associated with pesticide runoff, and practical risk assessment and management strategies. Ultimately, these efforts will contribute to the protection of public health, the preservation of aquatic ecosystems, and the sustainable management of pesticide contamination.

CHAPTER 3: ASSESSING THE THREAT OF DOWN-THE-DRAIN PESTICIDES FROM WASTEWATER TREATMENT PLANT DISCHARGES: A CALIFORNIA CASE-STUDY

*Submitted to California Department of Pesticide Regulations for internal review in preparation for submission to *Environmental Science and Technology - Water*

3.1 ABSTRACT

Prior literature has shown that WWTPs' conventional and advanced treatment processes do not adequately remove pesticides from effluents. An in-depth assessment of the WWTPs' contributions to pesticide loading in surface waters was conducted in this study. A GIS-based spatial model of 165 WWTPs in California was created to measure the buffering capacity of each receiving stream under multiple streamflow conditions. These capacities were categorized by region, dilution factor, and Strahler Stream Order (SSO) across the state. The study found that under mean annual, mean monthly, and low flow conditions, 90th percentile concentrations of bifenthrin, cypermethrin, fipronil, imidacloprid, and permethrin, were 0.0022 µg/L, 0.0021 µg/L, 0.05 µg/L, 0.1741 µg/L, and 0.022 µg/L, respectively. More than 50% of these WWTP sites were found to discharge to streams with SSO of 2 and lower, indicating lower buffering capacity, and vice versa. These values were then compared to stipulated aquatic benchmarks (AB) for each pesticide. Overall, bifenthrin and cypermethrin showed the most AB exceedance (84%), with fipronil showing the least AB exceedance (71%) under mean annual conditions. In addition, we have identified watersheds where the habitats of endangered invertebrates intersected with WWTP discharge sites that do not meet pesticide safety thresholds, with at-risk watersheds located mainly in the San Diego basin, Central Valley, and Central Coast. Among 41 watersheds with endangered invertebrate habitats overlapping WWTP surface water discharges, 36 had at

least one discharge site where a pesticide safety limit was exceeded. This study can be utilized to enhance our understanding of effluent-driven pesticide contamination and inform policy measures to protect endangered species in California's streams.

3.2 INTRODUCTION

The release of pesticide residues from agricultural and urban activities into surface water poses a threat to both freshwater and marine aquatic ecosystems[1-5]. Agricultural sources are well established as a contributor to pesticide pollution, however, less is known for wastewater-derived pesticides. Over the years, pesticide concentrations from urban activities have been purported to have similar contributions to surface water contamination, often at thresholds that exceed federal aquatic health benchmarks[6-8]. Pesticides such as fipronil and neonicotinoids have been detected within wastewater effluents due to down-the-drain loadings from domestic home use, gardening, etc. [9] paired with poor removal from conventional treatment [10, 11]. Point sources such as municipal WWTPs typically focus on the removal of organic matter and macro-pollutants and less on pollutants of emerging concern, i.e., pesticides [12]. Sources and pathways for down-the-drain pesticides have been identified through conceptual models that center on routes for laundry, human waste, and cleaning [13]. Pyrethroids such as permethrin, fipronil, and imidacloprid are the main components of general indoor pest control and spot flea/tick treatment products[9, 14]which have been identified in WWTP effluent [14].

Recent studies have shown that pesticides persist even after undergoing primary, secondary, and even tertiary WWTP processes[9, 15]. This was highlighted in a recent study by Supowit et al. that found fipronil and its degradants resistant to removal despite undergoing such processes [16]. The authors' study of 13 California WWTPs also found that imidacloprid had insufficient removal from WWTP effluent. Another study by Parry and Young [17] found that under secondary treatment, increased settling time in the wastewater treatment process was unlikely to completely alleviate pyrethroid (bifenthrin, cypermethrin, and permethrin) presence in the treated effluent. The insufficient removal of these pesticides after primary and secondary effluent treatment processes has led to a significant proportion of receiving waters exceeding aquatic benchmarks (AB) [18-20] due to downstream accumulation over time. Some notable pesticides that are consistently detected and exceed federal aquatic toxicity thresholds include bifenthrin, permethrin, and other pyrethroids [21-24], which raise ecological concerns for the public. A recent study by Budd et al. [18] found that pyrethroid concentrations of California surface waters receiving urban runoff frequently exceeded chronic benchmarks after initial treatment. In addition, many surface water samples from the California Central Coast have tested above the recommended benchmarks for bifenthrin, chlorpyrifos, fipronil, and permethrin [25-27]. These pesticides that remain in the WWTP effluent pose a threat to aquatic organisms when they exceed toxicity thresholds that have been set up by the Environmental Protection Agency (EPA) [13, 22, 24, 28].

Water quality monitoring for WWTP pesticide loadings involves tracking sample concentrations at strategic discharge locations upstream and downstream of the effluent sources [10, 20, 29, 30]. These studies compare detection concentrations in surface waters to stipulated exceedance benchmarks to mitigate the threats of pesticides to the environment. Prior studies have been conducted to monitor pesticide concentrations in California's surface waters, however, the majority of them have been conducted within specific regions of California [30-32], or in specific watersheds and their associated WWTPs [27, 33-35]. Consequently, these catchment scale studies allow for high spatial variability and temporal resolution but are restricted to a few substances at a time [6]. More comprehensive pesticide modeling efforts have been generated by the California Department of Pesticide Regulation (CDPR) through the use of Pesticide Use Reports (PUR) and the Surface Water Database (SURF) [20, 28]. Xie et al.'s [9] statewide California study of municipal WWTP pesticide loadings utilized available annual PUR and sales data to highlight down-the-drain discharge within urban regions, with fipronil, imidacloprid, and pyrethroids showing significant amounts from indoor and outdoor household usage. With the introduction of these WWTP-derived pesticides from inefficient treatment, hazardous bioaccumulation is evident in aquatic creatures exposed to effluent loads [28, 36-40]. These pesticide monitoring models therefore help to identify specific WWTPs for the implementation of more stringent treatment standards or upgrades through advanced treatment technologies to mitigate their ecological impacts [41, 42]. Furthermore, very few studies connect seasonal and streamflow-related changes (low flow, mean annual flow, etc.) in watersheds and their impact on pesticide detection levels in California [21, 43, 44]. Therefore, assessing statewide WWTP effluent contributions towards pesticide loading into California's urban streams in varying environmental conditions is essential since these contaminants could have potential adverse effects on aquatic life and other biodiverse ecosystems.

The main aim of this study is therefore to assess the ecological threat of pesticides from California WWTP sources through a geospatial model under varying streamflow conditions. Effluent loads were examined under low, mean annual, and mean monthly streamflow conditions to provide foresight on each receiving stream's buffering potential. Exceedance analyses indicated the most impacted streams through a comparison of estimated dilution factors (DF) to aquatic benchmarks (AB) of selected pesticides. Additionally, we identified watersheds where endangered species intersect with effluent-receiving streams that fail to provide sufficient dilution to meet pesticide safety thresholds. This study can be utilized to enhance our understanding of effluent-driven pesticide contamination, guide the improvement of wastewater treatment levels, and inform policy measures to protect aquatic ecosystems in California's streams.

3.3 METHODS AND MATERIALS

3.3.1 CASE-STUDY SITE

California is an ideal region for conducting research on the fate and transport of pesticides within wastewater treatment systems. This choice is justified by the state's unique geographic and demographic characteristics[45]. The presence of densely populated urban areas in California is a significant driver for wastewater treatment challenges [46]. These urban areas encompass diverse households with various pesticide-related needs[9, 13]. As a consequence, pesticide residues have been detected in treated sludge, highlighting the pressing need for comprehensive investigation [10, 46]. Furthermore, California's distinct ecosystems are home to protected and endangered aquatic species, adding another layer of significance to the research. The extensive usage of pesticides and their subsequent discharge into treated wastewater can pose a considerable threat to these fragile aquatic ecosystems [47]. Understanding the dynamics of pesticide fate and transport in the context of California is crucial for developing effective management strategies that mitigate the adverse impacts on aquatic ecosystems. California's combination of diverse urban populations and its rich tapestry of aquatic ecosystems make it a compelling focal point for pesticide fate and transport research.

3.3.2 DATA COLLECTION AND MINING

For this study, in-stream dilution factors for treated municipal WWTP discharges were estimated by developing a geospatial model with WWTP location and attribute data incorporated from multiple sources. Location data for WWTP discharges to surface water were collected and estimated from the EPA's Clean Watershed Needs Survey (CWNS) 2012 database [48]. This database is a comprehensive set of data that compiles all the relevant information regarding all publicly owned wastewater treatment and collection facilities across California. The CWNS 2012 contains all the contact and location information for each facility, as well as the population served, facility design flow capacities, and effluent volume data. These attributes are continuously updated by the EPA to reflect current trends. Based on the CWNS 2012 data, the WWTPs are categorized based on their discharge methods. Of the 828 wastewater treatment facilities in California, 165 WWTPs with discharge to surface water were extracted and compiled for verification. 107 of these facilities reported centralized treatment systems while 58 reported decentralized treatment systems (see Figure A1 in the Appendix). Each facility and the discharge location(s) were visually verified via Google Maps. The facility discharge locations were verified with the National Pollutant Discharge Elimination System (NPDES) reports, which contain information on which permits have been issued to each wastewater facility [49, 50]. This database also provides documented geographic locations for each discharge outlet as well as the facility's classification. For each missing data, the Permit Compliance System (PCS) database was used for further verification [51]. Finally, any other missing data was obtained with a Google search for the facility's website. In total, 165 WWTPs were visually verified under discharge to surface waters.

3.3.3 GEOSPATIAL MODEL BUILDING

Hydrologic data was obtained from the National Hydrology Dataset Plus Version 2 (NHDPlus V2) [52, 53]. This hydrologic data is a geospatial framework that combines the National Hydrography Dataset (NHD), the National Elevation Dataset (NED), and the Watershed Boundary Dataset (WBD). This framework was developed in 2012 by the EPA in conjunction with the USGS to serve as a simulation of real-world flowlines. The NHDPlus V2 data is based on an 8-digit hydrologic unit (HUC8), which represents each subbasin within the state of California. Each subbasin contains a delineated watershed that indicates where water flows out of. The NHDPlus V2 also reports the SSO classification which defines each stream size based on the hierarchy of tributaries[54]. The NHDPlus V2 dataset for California was extracted and spatially joined to the WWTPs attributes in ArcGIS Pro.2.9.5 to locate discharge sites. The spatial model was divided according to the California Regional Water Control Boards for each region in the state [20, 55]. Due to turbulence associated with estuary mixing, WWTP discharge points in Region 2 (San Francisco Bay Area) and the Pacific Ocean were removed from the dataset. Figure 2 shows the initial map generated from the spatial joining of WWTPs attributes and the NHDPlus V2 dataset.

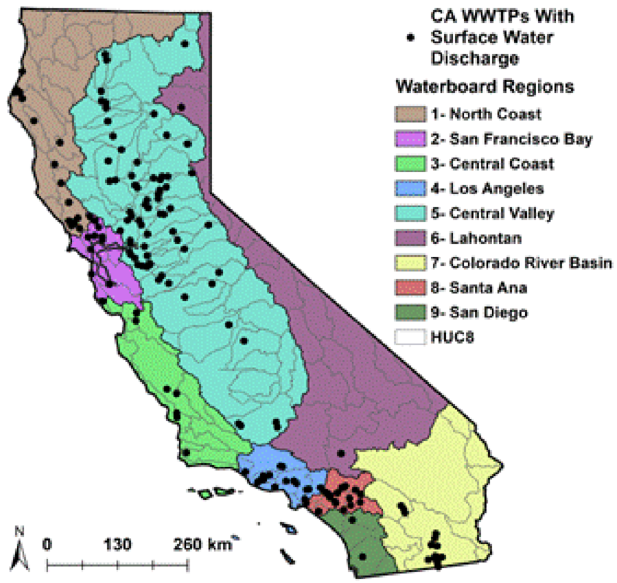

Figure 2: California Watershed Map showing WWTPs discharge locations spatially joined to NHDPlus V2 streamlines and classified by region. Region 2 (San Francisco) and ocean discharges were excluded from this dataset due to turbulence.

Following the initial geospatial verifications, temporal variation was modeled in multiple stages: extreme low-flow events (7Q10), monthly variation (low vs. high monthly streamflow average) and predicted future conditions. The low-flow (7Q10) analysis represents a drought event that has a 10-year recurrence, however past research has demonstrated that seasonal streamflow conditions can also have a significant impact on dilution factors [44]. From the datasets, March and October were identified as the minimum and maximum monthly conditions based on California's wet and dry seasons. Based on the spatial connections, the DF of each stream was calculated under the following conditions: mean monthly streamflow, low flow, and annual flow using Equation 1.

3.3.4 AQUATIC HEALTH BENCHMARK EXCEEDANCE

This analysis is based on the Strahler Stream Order (SSO) and the Dilution Factor (DF) of each stream to determine safety thresholds for selected pesticides. The SSO is a hierarchy of tributaries within each watershed that is classified from 1-10, with 1 symbolizing headwater and ranks of 2 and higher signaling larger tributaries that emanate from convergences. Based on the corresponding stream volume sizes, a lower SSO value indicates that each stream under review is more susceptible to streamflow variations compared to larger streams, and vice versa [56-58]. For this study, SSO values less than zero (0) (i.e., minor streams, unknown classifications) were discarded from the dataset to ensure streamlined calculations. The DF is a ratio that measures the flow of each receiving stream compared to the watershed effluent flow. The DF for each receiving stream was calculated using the following equation:

$$DF = \frac{Q_r + Q_w}{Q_w}, \qquad (1)$$

Where Q_w represents each WWTP present design flow, Q_r is the streamflow of the receiving stream under low/average streamflow conditions. Low-flow estimates were then calculated using data available from gaged waterbodies in iSTREEM and incorporated to generate 7Q10 (low-flow) values [59]. Due to limitations in the iSTREEM dataset, the 7Q10 calculations were estimated for 107 WWTP discharge sites. This portion of the analysis did not account for seasonal fluctuations with streamflow and assumed a constant steady flow for each outlet.

To evaluate the potential ecological effects of the unmitigated effluent discharge, specific discharge site concentrations were compared with the EPA’s Aquatic Life Benchmarks (AB) [60, 61]. Based on the WWTP discharge point DF, acute and chronic benchmark values were assessed for aquatic creatures' exposure to pesticides. The acute benchmarks are calculated based on the lethal concentration level that results in a 50% mortality (LC50) of the most sensitive species divided by a safety factor of 10 [25, 62]. For the purpose of this study, the lowest benchmark value for acute and chronic exposure was used to evaluate potential toxicity for the most commonly detected pesticides in urban streams. The aquatic benchmark (AB) estimation of the most persistent pesticides found within receiving stream effluents was collated from the California Department of Pesticide Regulation (CDPR) database and additional monitoring data from prior studies. The pesticide concentrations were calculated from the estimated environmental concentrations (EECs) set to the median and 90th percentile of measured environmental concentrations reported by CDPR. Based on the data available and the calculations made, selected pesticides of concern for the exceedance analysis in this study include bifenthrin, cypermethrin, imidacloprid, fipronil, and permethrin. Table 1 shows the selected pesticide concentrations and their estimated AB for our exceedance analysis. These estimations help assess the impact of streamflow changes due to climate change in pesticide concentrations within wastewater-impacted streams in California. The minimum required DF for each selected pesticide to meet the AB was calculated and assessed against the calculated DF for each stream. The required DF for each pesticide was calculated using the following equation:

$$DF_{req.} = \frac{Q_{median\ or\ 90th\ percentile}}{AB} \qquad (2)$$

where $Q_{median\ or\ 90th\ percentile}$ is the median or 90th effluent concentration of pesticide, and AB is the reported aquatic benchmark. The concentrations of the selected pesticides (bifenthrin, cypermethrin, permethrin, fipronil, imidacloprid) at each WWTP outlet were estimated using equation 3. These concentrations were calculated based on the assumption that the effluents to the receiving streams come from secondary treatment WWTPs, which is the most common wastewater treatment level in California [58], [67].

$$Conc._{pest.} = \frac{C_{90th\ percentile} \times DF_W}{DF_{req.}} \qquad (3)$$

where $C_{90th\ percentile}$ is the 90th percentile effluent concentration of selected pesticide (µg/L), $DF_{req.}$ is the required dilution factor for selected pesticides (without safety factor), DF_W is the estimated dilution factor under varying conditions.

Table 1: Selected pesticides with estimated aquatic benchmarks and required DF. Non-detects were not factored into pesticide concentrations for this study.

Pesticide	**Classification**	**WW Effluent Pesticide Concentrations**		**Aquatic Benchmark (µg/L)[a]**	**DF Required (w/ SF)[b]**	**DF Required (w/o SF)[c]**
		Median (µg/L)	90th Percentile (µg/L)			
Bifenthrin	Pyrethroid	0.001	0.0022	0.00005	440.0	44.0
Cypermethrin	Pyrethroid	0	0.0021	0.00005	418.0	41.8
Fipronil	Phenylpyrazole	0.021	0.05	0.011	45.5	4.5
Imidacloprid	Neonicotinoid	0	0.1741	0.01	174.1	17.4
Permethrin	Pyrethroid	0	0.0220	0.0042	52.3	5.2

[a]EPA OPP Aquatic Life Benchmarks (ug/L) for chronic exposure for sensitive aquatic invertebrates

[b]Minimum dilution factor required to meet the aquatic benchmark (based on 90th percentile effluent conc.) with a safety factor of 10

[c]Minimum dilution factor required to meet the aquatic benchmark (based on 90th percentile effluent conc.) with no safety factor applied

Hazard quotients were calculated for each pesticide by Equation (4), based on estimated environmental concentrations (EECs), modeled as the median and 90th percentile reported values, and aquatic life benchmarks (AB) for chronic exposure to invertebrates. The dilution factor required to meet the hazard quotient for each pesticide was estimated using Equation (5), where HQ_{eff} is the hazard quotient for each pesticide in the municipal effluent, and LOC is the level of concern considering a recommended safety factor of 10 (0.1) or 1. These values formed the basis of an exceedance analysis for the pesticide discharges in California. The EPA lists the minimum thresholds for DF for bifenthrin, permethrin, fipronil, and cypermethrin to meet the AB. SSO values were then matched with the WWTPs estimated DF to assess the buffering capacity of each stream.

$$HQ_{eff} = \frac{EEC}{AB} \quad (4)$$

$$DF_{req} = \frac{HQ_{eff}}{LOC} \quad (5)$$

3.3.5 ASSESSING THE INTERSECTION OF ENDANGERED INVERTEBRATE HABITATS AND PESTICIDE SAFETY EXCEEDANCE IN EFFLUENT-RECEIVING STREAMS

We identified watersheds at a higher risk of pesticide levels from WWTP effluent, intersecting with the presence of endangered species, particularly invertebrates. In doing so, we first estimated the number of WWTP discharge sites that do not meet the required dilution factor respective to the safety threshold for EPA aquatic life benchmarks for chronic exposure to sensitive aquatic invertebrates within each HUC8 watershed (see Table 1). We divided the number of these non-compliant discharge sites by the total number of WWTPs per watershed for normalization. In addition, we obtained spatial data on endangered species from the California Natural Diversity Database [63], which included the areas (in square kilometers) inhabited by endangered invertebrates. We calculated the total area of endangered invertebrate habitats per HUC8 watershed using the Summarize Within Tool in ArcGIS Pro V2.9.5. We then divided the total area of endangered invertebrate habitats by the area of each respective watershed to estimate the density of these habitats. We overlayed the density of endangered species with the percent of pesticide exceedance using bivariate mapping, to identify the regions where the habitats of endangered species intersect with areas of pesticide safety exceedance from WWTP effluent.

3.4 RESULTS

3.4.1 BENCHMARK EXCEEDANCE ACROSS REGIONS AND STRAHLER STREAM ORDER

Five pesticides (bifenthrin, cypermethrin, imidacloprid, permethrin, and fipronil) were investigated at levels in secondary WWTP effluent that require dilution to meet the chronic aquatic life benchmarks within receiving streams, with an applied safety factor of 10. The pesticides selected for this study are considered highly toxic to aquatic organisms at low concentrations based on their reporting limits for acute and chronic exposure [9, 64], as well as their prevalence in municipal discharge [9, 13]. From the previously sampled monitoring data, the median range of WWTP effluent pesticide concentrations was exceptionally low, with the maximum value capped at 0.021 µg/L for fipronil. Conversely, 90th percentile concentrations of the effluent ranged from 0.0021 µg/L for cypermethrin, with the largest proportion at 0.1741 µg/L for imidacloprid. After quantifying the required DF to meet the aquatic benchmarks, bifenthrin had the highest estimated DF of 440.0 due to its relatively low value (0.00005 µg/L). On the opposite scale, fipronil had the lowest DF of 45.5. After quantifying the required DF, we did a spatial joining of the CWNS data to the closest effluent receiving stream on NHDPlus V2. The WWTP sites were then color-coded based on the DF of each receiving stream under various conditions (see Figure 3). At least one site was located in each of the nine California Water Board Regions, ensuring a homogenous analysis. Based on the resulting calculated discharge DF, we identified March and October to serve as the maximum and minimum monthly streamflow conditions for the 165 WWTP sites, respectively. March represents the wettest month for much of California and historically has the highest monthly streamflow average, while October represents the drought season for lower streamflow volumes [44, 65].

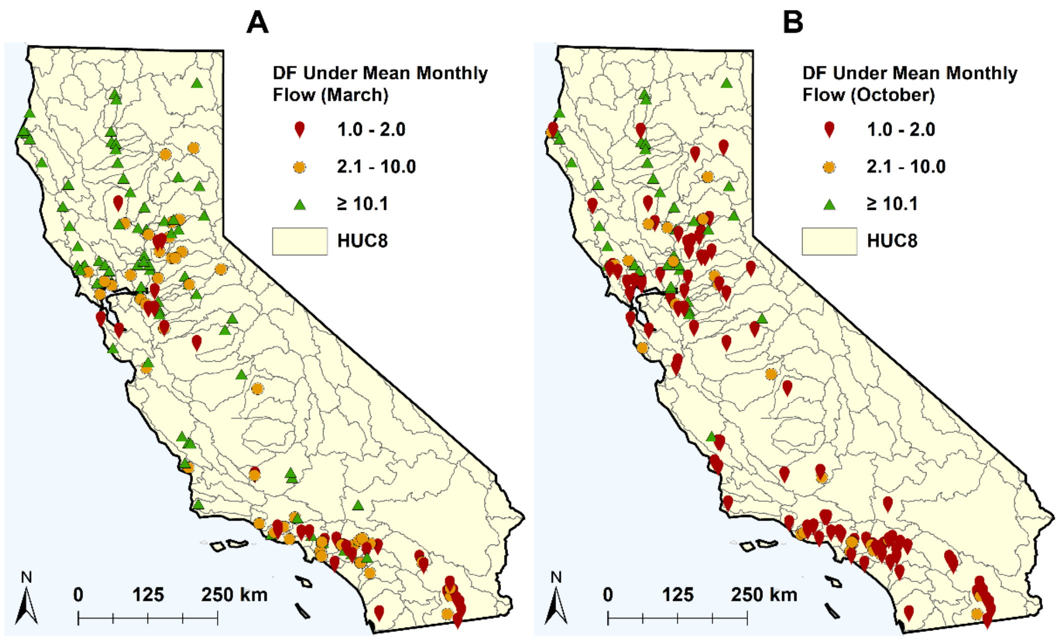

Figure 3: Color-coded Maps of Dilution Factors for Receiving Streams at WWTPs' Discharge Sites under Mean Monthly Flow Conditions in (a) March (highest monthly streamflow average) and (b) October (lowest monthly streamflow average)

In addition to streamflow conditions, the Strahler Stream Order (SSO) of each receiving stream greatly impacts its natural ability to buffer treated wastewater contributions[58]. In response to this phenomenon, receiving streams were classified by SSO and by DF per region. Our results indicate that roughly 40% of the discharge sites were into streams of an SSO equal to or less than three which are relatively more sensitive to climate-related variations as compared to higher SSOs. Due to the dilution effect from increasing stream order, it was expected that the EECs would steadily decrease across regions to exceed minimum aquatic benchmarks. However, this assumption proved false, with up to 84% of the streams consistently falling below the benchmarks under mean annual conditions for bifenthrin and cypermethrin. Marginal improvement was seen in March, where 80% of sites exceeded benchmarks for bifenthrin and cypermethrin. This value worsened under low flow conditions, with 92% of sites being at risk during October. Similar trends for exceedance were observed for imidacloprid (74-87%), permethrin (66-81%), and fipronil (66-80%) under annual and mean monthly conditions. Differences in results between March and October illustrate the impact that seasonal streamflow variation, particularly seasonal drought can have on in-stream pollutant concentrations. Figure 4 shows the trends associated with each pesticide.

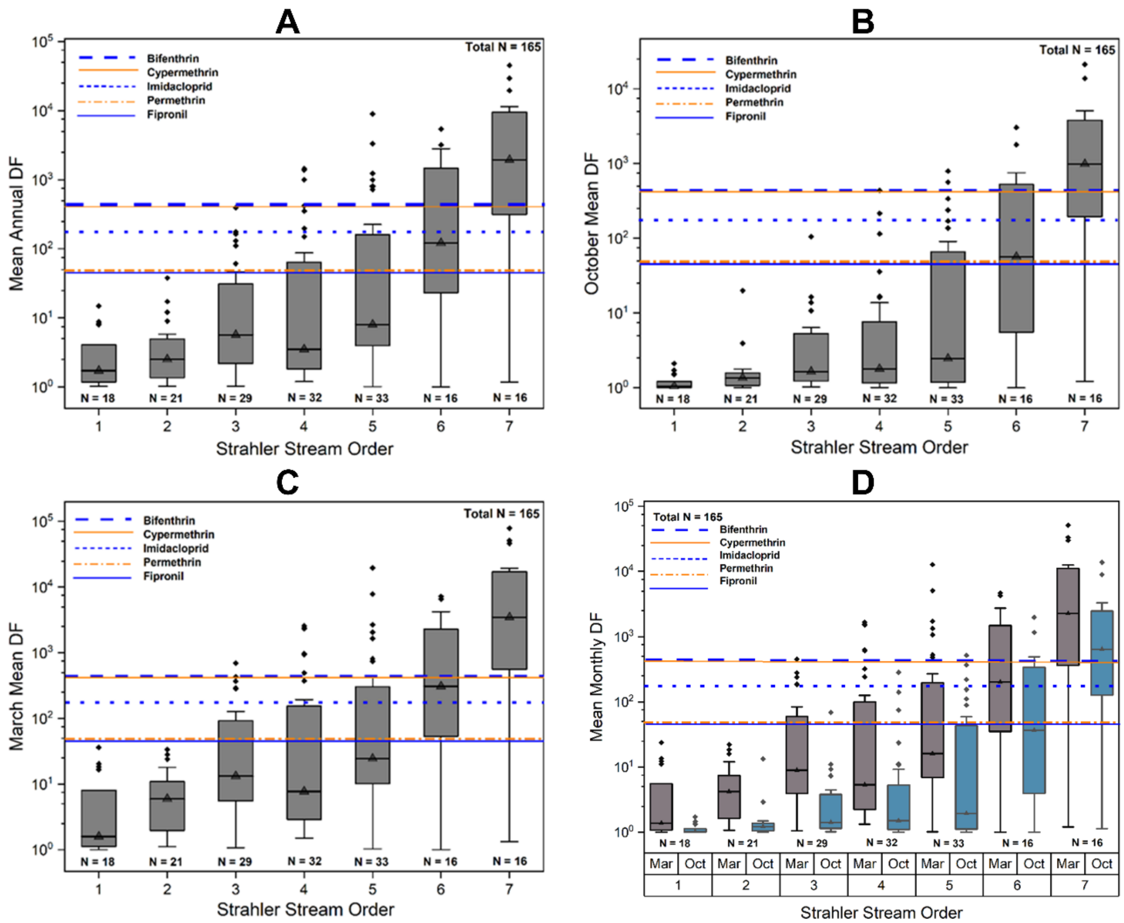

Figure 4: Boxplots showing the dilution factors (DF) of the surface WWTPs' receiving streams by Strahler Stream Order, and the required dilution factors to not exceed aquatic health benchmarks (cypermethrin, bifenthrin, fipronil, imidacloprid, and permethrin) under (a) mean annual conditions, (b) low monthly streamflow conditions, and (c) high monthly streamflow conditions. (d) shows the decline in EECs when monthly conditions are juxtaposed. Lines representing the required DF for each pesticide are presented in the same order as the key (upper left corner of figure), at risk sites are located below the line.

From the spatial joining of the WWTPs to the nearest receiving streams, discharge sites with higher EECs were considered more likely to be at risk of pesticide loads, and vice versa.

Central Valley Region 5 recorded the largest number of WWTP sites (n=75), with Lahontan Region 6 and San Diego Region 9 having 2 sites each. Under mean annual conditions, the median pesticide concentration across all sites was equal to 0.00023 µg/L for bifenthrin and cypermethrin, with 32% of the dataset reporting concentrations below 0.0001 µg/L and 62% of the dataset having concentrations below 0.0005 µg/L. For permethrin and imidacloprid, estimated median concentrations were 0.01932 µg/L and 0.80086 µg/L respectively. Fipronil recorded the highest median concentration values at 0.23 µg/L. When the safety factor of 10 was applied, the median concentrations increased as follows for bifenthrin and cypermethrin (0.0023 µg/L), fipronil (2.3 µg/L), imidacloprid (8.0086 µg/L), and permethrin (0.1932 µg/L). From this study, almost all sites across Regions 1(North Coast) to 9 (San Diego) were at risk for pesticide benchmark exceedances regardless of the mean monthly and annual conditions. Across the Figure 5 charts, Regions 1 and 5 had the most range in median EECs, while the other regions consistently failed to meet the lowest fipronil benchmark. Overall, roughly 20% of receiving streams had a dilution factor below 2, and half of discharge sites fell below a DF of 10. For Region 5, this meant that 73% of the sites failed to meet benchmarks for bifenthrin and cypermethrin, 58% failed for permethrin, 55% failed for fipronil, and 69% of sites exceeded for imidacloprid. In contrast, October had the lowest streamflow values for California, with the median dilution factor estimated to be 1.5. Approximately 58% of sites fell below a dilution factor of 2, and over 75% fell below 10. For Region 5, benchmark exceedances increased to 84% of sites for bifenthrin and permethrin, 68% of sites for permethrin, 66% of sites for fipronil, and 77% of sites for imidacloprid respectively.

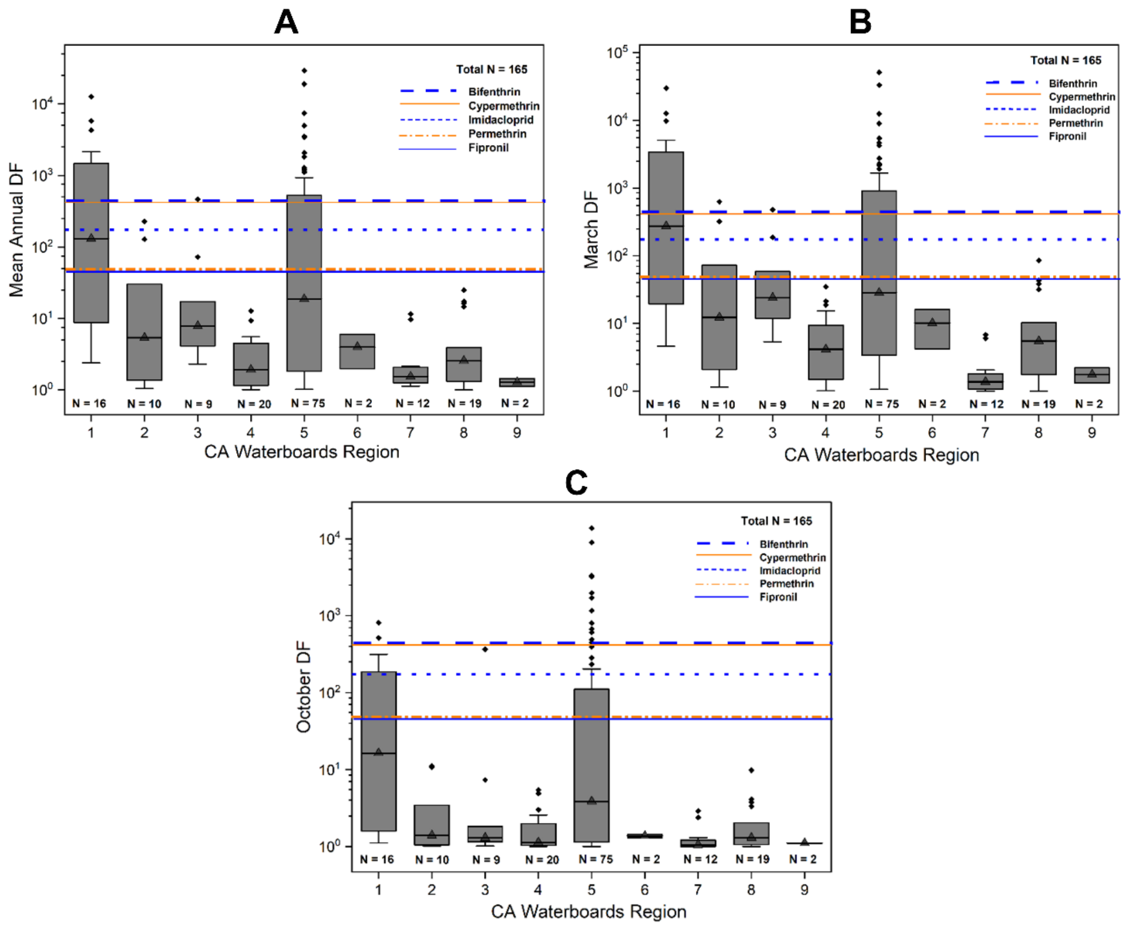

Figure 5: Boxplots showing the dilution factors (DF) of the surface WWTPs' receiving streams by regions and the required dilution factors to not exceed aquatic health benchmarks (cypermethrin, bifenthrin, fipronil, imidacloprid, and permethrin) under (a) mean annual conditions, (b) low monthly streamflow conditions, and (c) high monthly streamflow conditions. Lines representing the required DF for each pesticide are presented in the same order as the key (upper left corner of figure), at risk sites are located below the line.

3.4.2 RESULTS UNDER EXTREME LOW STREAMFLOW (7Q10) CONDITIONS

Under low-flow conditions (modeled as 7Q10), the median pesticide concentrations across the sites were estimated to be up to ten times below the benchmark for bifenthrin, cypermethrin, and imidacloprid at 0.000005 µg/L for the 107 sites with available streamflow estimates. This is primarily due to their high required DF, with 66 of the 107 sites across all the regions having a DF below 2.0 (see Figure 6). This represents more than two-thirds of all the WWTP sites being at risk for pesticide contamination during long periods of drought, excluding a few located in Region 5. This trend was also observed with SSO, where smaller ranked streams, i.e., SSO ≤5 fell below the stipulated benchmarks for all the pesticides in this study. Figure 6 provides a side-by-side visual representation of the change in DF under 7Q10 flow as compared to mean annual flow. The median dilution factor decreased by 78% under the low flow scenario, which highlights the dependence on streamflow conditions and warrants the inclusion of future streamflow predictions.

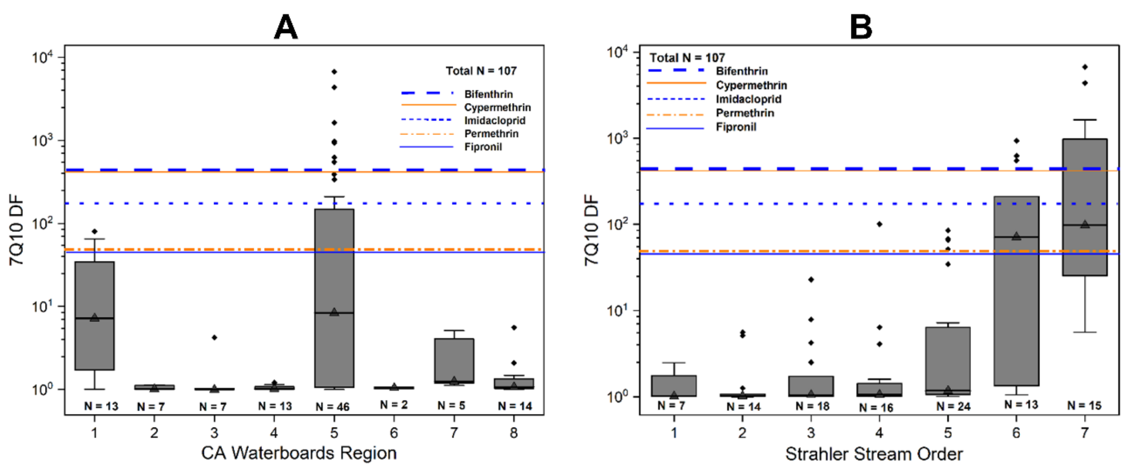

Figure 6: Boxplots showing the extreme low flow dilution factors (DF) of the surface WWTPs' receiving streams by (a) regions and by (b) SSO, and the required dilution factors to not exceed aquatic health benchmarks (cypermethrin, bifenthrin, fipronil, imidacloprid, and permethrin) Lines representing the required DF for each pesticide are presented in the same order as the key (upper left corner of figure), at risk sites are located below the line.

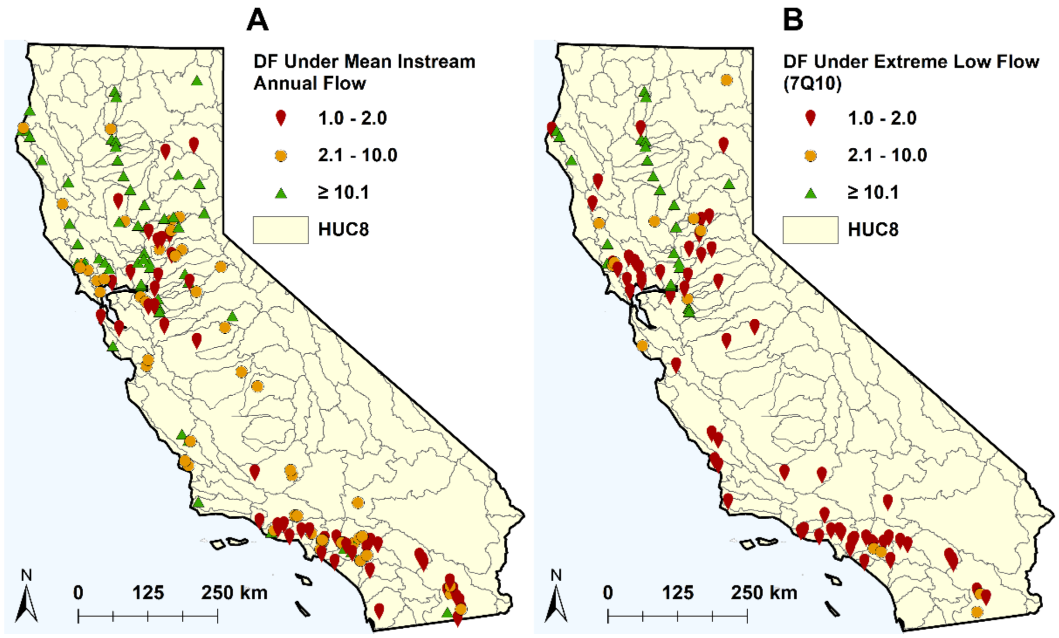

Figure 7: Color-coded Maps of Dilution Factors for Receiving Streams at WWTPs' Discharge Sites under a) mean annual flow and b) low flow (7Q10)

3.4.3 IDENTIFYING HIGH-RISK WATERSHEDS FOR DOWN-THE-DRAIN PESTICIDE EXPOSURE IN ENDANGERED INVERTEBRATE HABITATS

We identified watersheds where the habitats of endangered invertebrates intersect with the exceedance of pesticide safety thresholds in effluent-receiving streams. Figure 7a shows the percentage of WWTP discharge sites that do not meet the required dilution factor for the Bifenthrin safety threshold under mean annual stream flow conditions and median Bifenthrin concentrations in effluent. We selected Bifenthrin because it requires the highest dilution factor to meet the safety threshold due to its low aquatic benchmark (0.00005 µg/L). A total of 60 out of 146 HUC8 watersheds in California contain WWTPs with surface water discharge, and in 41 watersheds, the Bifenthrin safety threshold was exceeded in over 76% of discharge sites (See Figure 7a). Additionally, endangered invertebrates are found in 67 HUC8 watersheds (See Figure

7b). The hotspots of endangered invertebrates, which are watersheds with a high density of these species surrounded by neighboring watersheds with similarly high densities, are located in Region 5, Central Valley, specifically the Sacramento Valley (See Figure A2).

Figure 7c indicates the watersheds at higher risks of Bifenthrin from WWTP effluent intersecting with endangered inveterate habitats. Among 41 watersheds with endangered invertebrate habitats overlapping WWTP surface water discharges, 36 had at least one WWTP discharge site where Bifenthrin levels surpassed the safety limit. At-risk watersheds are located in San Diego (Region 9), Central Valley (Region 5; specifically, San Joaquin Basin and Sacramento Valley), and Central Coast (Region 3). In addition to Bifenthrin, which required the highest dilution factor to meet safety thresholds, we also identified Fipronil exceedances at WWTP discharge sites and their intersections with endangered invertebrate habitats. Our analysis included pesticides with both the highest (Bifenthrin) and lowest (Fipronil) required dilution factors in order to gain a comprehensive understanding of the potential risks associated with different pesticides pose to endangered invertebrates. Fipronil, despite requiring a lower dilution factor to meet safety thresholds due to its higher aquatic benchmark value, still presented exceedance in more than 76% of discharge sites within 41 watersheds out of 60 with surface water discharge from WWTPs. These observations are illustrated in Figure A3, where a similar pattern of Fipronil exceedance is observed, with the exception of fewer high-risk watersheds for exposure in endangered invertebrate habitats in the upper region of the Central Valley (Region 5), compared to the exceedance of Bifenthrin. The intersection of endangered invertebrate habitats with effluent-receiving streams, specifically those unable to provide sufficient dilution to meet pesticide safety thresholds, provides valuable information for conservation efforts, as it identifies the specific geographic areas where targeted actions can be taken to mitigate the risks posed by down-the-drain pesticide contamination to endangered invertebrate habitats.

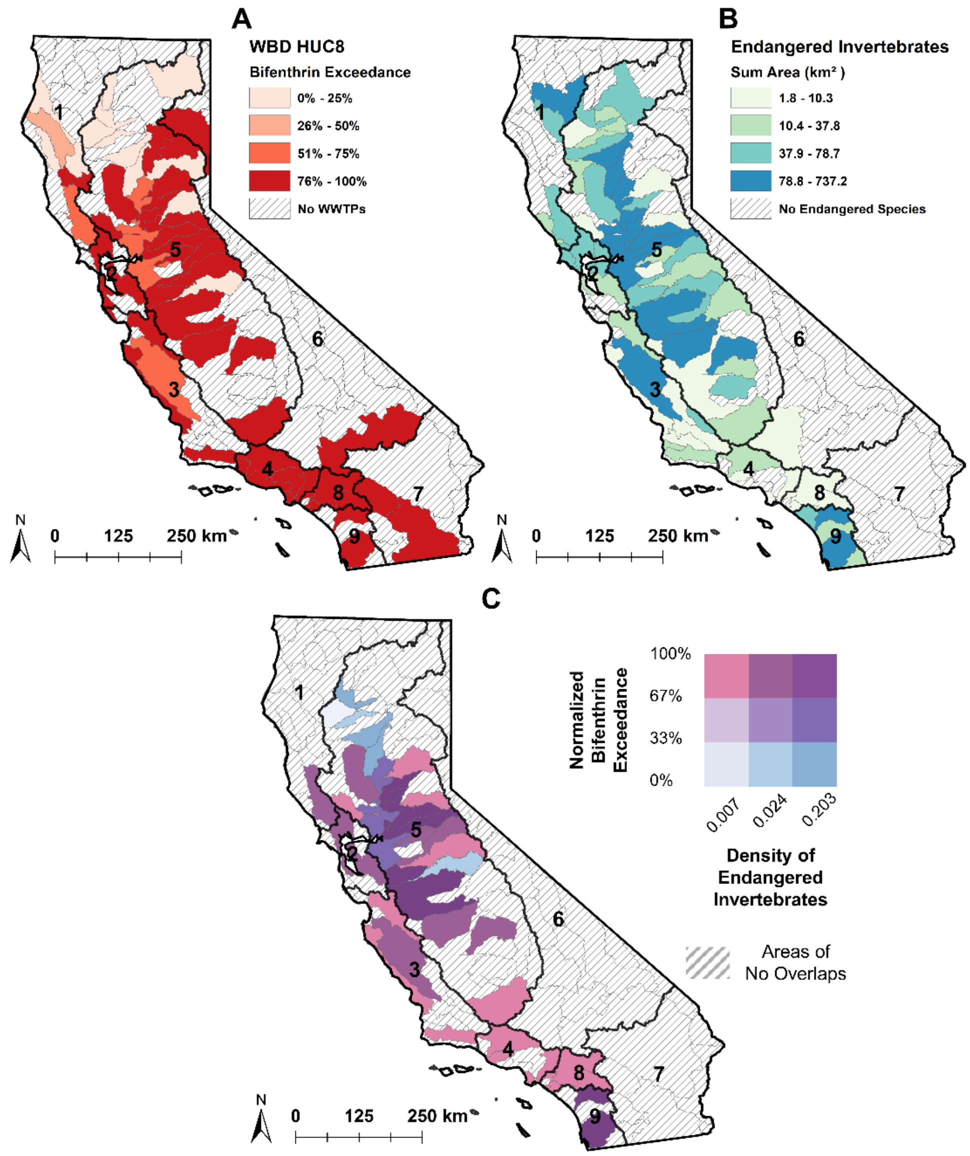

Figure 8: High-risk watersheds for down-the-drain Bifenthrin exposure in endangered invertebrate habitats in California. a) The percentage of WWTP discharge sites failing to meet the required dilution factor for Bifenthrin safety under mean annual stream flow conditions and median Bifenthrin concentrations in effluent. b) Endangered invertebrate habitats across CA,

grouped based on quantile quantification (i.e., equal numbers of watersheds per class). c) Intersection of endangered invertebrate habitats and effluent-receiving streams where the Bifenthrin safety threshold is exceeded.

3.5 DISCUSSION

This study provides a comprehensive analysis of the ecological threats associated with effluent-driven pesticide contamination in California's streams. Our findings indicate direct impacts of California’s seasonal streamflow conditions have a direct effect on the concentrations of selected pesticides that emerge from urban residential applications. This agrees with previous research that highlighted the impact of climate conditions such as droughts and floods on the hydrologic flow of the receiving streams[44, 66, 67]. Climatic events vary from year to year, and we aligned our study based on previous studies of California’s climate to acknowledge underlying bias corrections and simulated streamflow assumptions from estimated climate models for annual, monthly, and long-term projected predictions. Due to California’s long periods of drought, pesticide concentrations detected during dry weather conditions are more likely to represent chronic pesticides loading into urban streams. The climate-driven alteration of streamflow characteristics due to snowmelts and other seasonal extremes could affect the buffering capacities of each receiving stream against anthropogenic activities, subsequently impacting the pesticide concentrations in effluent-receiving streams[56]. Our results are consistent with previous research findings from Budd et al [21], where multiple household pesticides such as bifenthrin, cypermethrin, and permethrin were consistently detected in urban watersheds at thresholds above aquatic limits based on annual mass loadings. Previous studies[19, 21] also indicated that the predicted annual loads for fipronil during the dry period can be orders of magnitude higher than during the wet season in California regions with only short episodic rain events. These findings are consistent with our study, which observed an increase in median stream DF and a corresponding decrease in pesticide concentrations across all receiving surface waters during the wettest month (March) compared to the driest month (October). This trend can be attributed to the higher instream flow conditions in March. Overall, there is a consensus that non-storm-related events (such as down-the-drain discharge from urban residential homes) account for significant amounts of pesticide discharge into urban receiving streams[9, 13, 14, 34]. Numerous detected pesticides are widely used in household products and are carried to surface waters through the effluent discharged from WWTPs into surface streams[9, 13]. Continued periodic monitoring of these household pesticides in urban streams is therefore warranted to clearly understand both spatial and temporal trends in pesticide concentrations to allow for effective mitigation measures to be put in place from these sources.

Based on our analysis of predicted pesticide concentrations downstream of the WWTPs and comparison with the safety threshold, it is evident that WWTP technology is insufficient for pesticide residue removal before discharge into urban receiving streams. According to Hawkins [68], municipal WWTPs in California discharge a collective 1.144 billion gallons of treated effluent per day or 1.28 million acre-feet per year into coastal surface waters, with WWTPs in highly urbanized city centers (San Francisco and Los Angeles regions) accounting for more than 40% of the total flow volumes. This raises concerns as the wastewater infrastructure is overburdened and slow to catch up with the dynamics of high amounts of urban pesticide usage channeled from the surrounding populations. Recent sample surveys of California WWTP receiving streams[27] indicate the frequent detection of pyrethroids such as bifenthrin, cypermethrin, and permethrin in effluent concentrations across multiple treatment stages (i.e., primary, secondary, tertiary). Fiproles and imidacloprid exhibit similar results in Sadaria et al. 's [69] study of eight WWTPs located in northern California that treated indoor urban pesticide runoff. These studies are however limited to a few WWTPs based on their treatment capacity and geographic locations. For most California WWTP studies, receiving stream sizes as well as precipitation patterns were not considered for a full evaluation of seasonal influences on buffering abilities. We considered these seasonal influences in our study, where estimated pesticide concentrations for WWTP effluent showed clear differences across sites for our exceedance analysis. As municipal WWTP effluent flows usually fall below full facility design capacity, this reduces potential overreporting errors in the CWNS data that we used. We did note that there was not a very large difference in the calculated DF changes when we compared both flow values. However, considering other geomorphological factors, the differences between reported WWTP influent and effluent flow could be better understood and analyzed to fully differentiate between storm and non-storm pesticide transport channels. Finally, although evidence suggests that pesticide residue decreases with further treatment [70], more work needs to be done to establish the most cost-effective treatment methods for pesticide residue removal[71].

Our exceedance analysis of pesticide concentrations in the georeferenced WWTP effluents with established toxicity values indicates potential harm to aquatic species, warranting further investigation. We have identified watersheds where the habitats of endangered invertebrates overlayed with WWTP discharge sites that do not meet the safety pesticide thresholds. Out of 60 watersheds with WWTPs discharging into surface water, 41 overlapped with habitats of endangered invertebrates, and 36 watersheds have at least 1 WWTP that did not meet a pesticide safety threshold. In this case, Cassady et al. (2023) revealed a positive correlation between the presence of threatened and endangered species and the existence of treatment plants in California's watersheds, where a quarter of these species were found exclusively in watersheds where at least one treatment plant exists [47]. The findings of our study and that of Cassady et al. underscore the urgent need for enhanced environmental management and conservation efforts to protect these vulnerable species and their habitats from WWTP effluent. We predict that as trends in urban synthetic pesticide usage increase over time, the EPA may adjust its acute and chronic benchmarks to meet those demands. Even though the current aquatic benchmark exceedances provide a snapshot of the potential harm that effluent poses on aquatic environments, the effects are assumed to occur only at the immediate WWTP discharge points[6, 59]. These effects could be highlighted by observing impacted aquatic creatures such as invertebrates, fish, or amphibians that inhabit these receiving streams at short and long-term intervals.

Our findings indicate that more than a third of California WWTP receiving streams have an SSO of less than 2, suggesting lower buffering capacities at each WWTP discharge point. Moreover, these effluent-receiving streams with lower SSO are not only impacted more by contaminant concentrations from effluent due to their low buffering capacity but also rely on the effluent to maintain their ecosystems. This underscores the need for advanced treatment levels and monitoring programs to be implemented and prioritized in these streams. In addition, our study did not consider pesticide persistence (e.g., fipronil) that might not decay and be transported downstream to the ocean. Our study approach can be enhanced by incorporating sample field data at strategic locations along the more vulnerable streams where wastewater effluent proportions would be most significant, or where multiple WWTP receiving streams may converge. In addition, Future research should focus on improving wastewater treatment methods for effective pesticide removal, investigating the impact of pesticide contamination on aquatic species, and differentiating between storm and non-storm pesticide transport pathways. This information could guide regional or state studies to monitor or assess the contributions of WWTPs to pesticide levels in surface water.

3.6 CONCLUSIONS

This study assessed the impact of georeferenced treated wastewater effluent and their effect on the buffering capacity of WWTP receiving streams in California. This analysis was conducted using available hydrological data in conjunction with each receiving stream's attributes (dilution factor and Strahler stream order) to target the most affected streams. Our results show that low flow conditions and seasonal changes in climate impact the buffering capacity of receiving streams. Lower SSO further exacerbates this, and it emerged that cypermethrin recorded the highest dilution factor required to meet aquatic standards in treated effluent discharging into streams across California. In addition, we identified watersheds where the habitats of endangered invertebrates intersect with the exceedance of pesticide safety thresholds in effluent-receiving streams, with at-risk watersheds located in the San Diego basin, Central Valley, and Central Coast. This study could not determine the effect of the effluent benchmarks on aquatic creatures and the environment. It also assumed that there would be a mixture of several pesticides in the treated effluent regardless of the location (urban/agricultural) without indicating the exact proportions. Also, the effluent discharge for each WWTP was assumed to be constant to ensure uniformity, but the data from CWNS is dated (greater than a decade old). The resulting DF and estimated concentrations, therefore, do not paint a full picture of the effluent discharge, as they fail to account for more recent technological upgrades or changes to facility capacities. Future work will need to integrate a more robust method to differentiate between point and non-point sources of pesticides and to determine which WWTP is most suited for specific pesticide residue reduction or elimination based on populations served. This will then provide a more in-depth justification for targeting streams altered by residential pesticide sources and observing their risk to both aquatic creatures and humans.

This study adds to the previous exceedance analyses of California WWTPs that treat influent from point and non-point pesticide discharges. These municipal WWTP flows are particularly important in the context of water resources management because the effluent disposals could be redirected for reuse in irrigation or other recycling purposes, thereby lessening their ecological impacts. The potential for recycled water usage in California must be further investigated in future studies in order to establish its effectiveness. Newer studies should incorporate residential data to better approximate urban pesticide inflow into wastewater systems with the end goal of quantifying sites most suited for recycling. Alternatively, the effective reduction of pesticide residue in effluents via advanced treatment processes such as ozonation and oxidation should be probed and refined to draw the attention of the regional stakeholders. Future work will need to develop innovative solutions to existing barriers (e.g., high upfront costs) towards the implementation of the said advanced wastewater projects before the state will be able to meet its water quality potential. Since municipal WWTP effluent has been established in this study as an environmental hazard, this information could serve as a foundational framework for developing best management practices as well as strategic financial planning geared towards upgrading California’s WWTP technology.

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3.8 APPENDIX

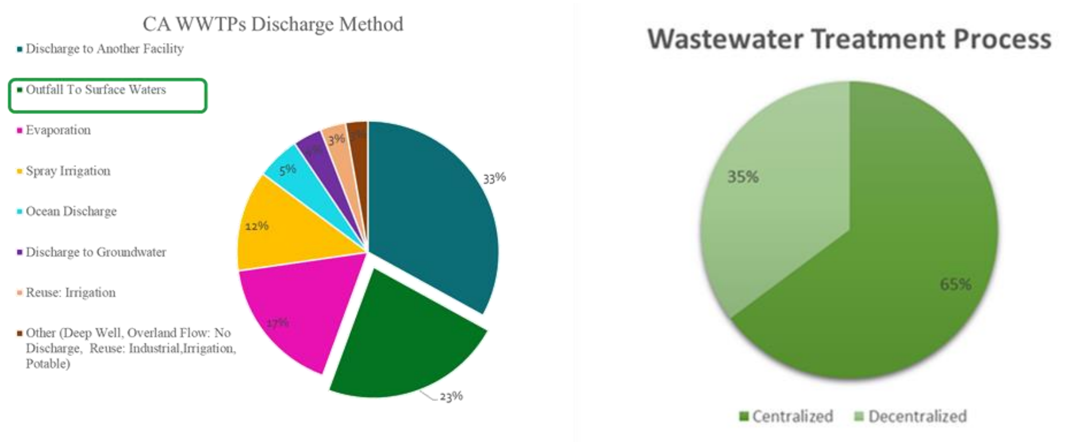

Figure A 1: Chart showing the total number of WWTPs with discharge to Surface Waters in California (165), with designation to centralized and decentralized treatment.

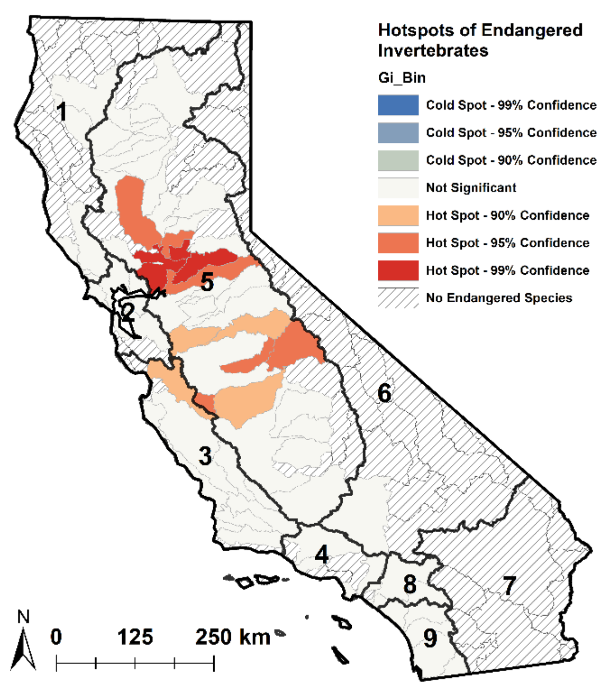

Figure A 2: Hotspots indicating high density of endangered invertebrates. The analysis is conducted using the Getis-Ord Gi* method on ArcGIS Pro V.2.9.5, measuring the variation in density values at specific spatial locations compared to their neighboring areas.

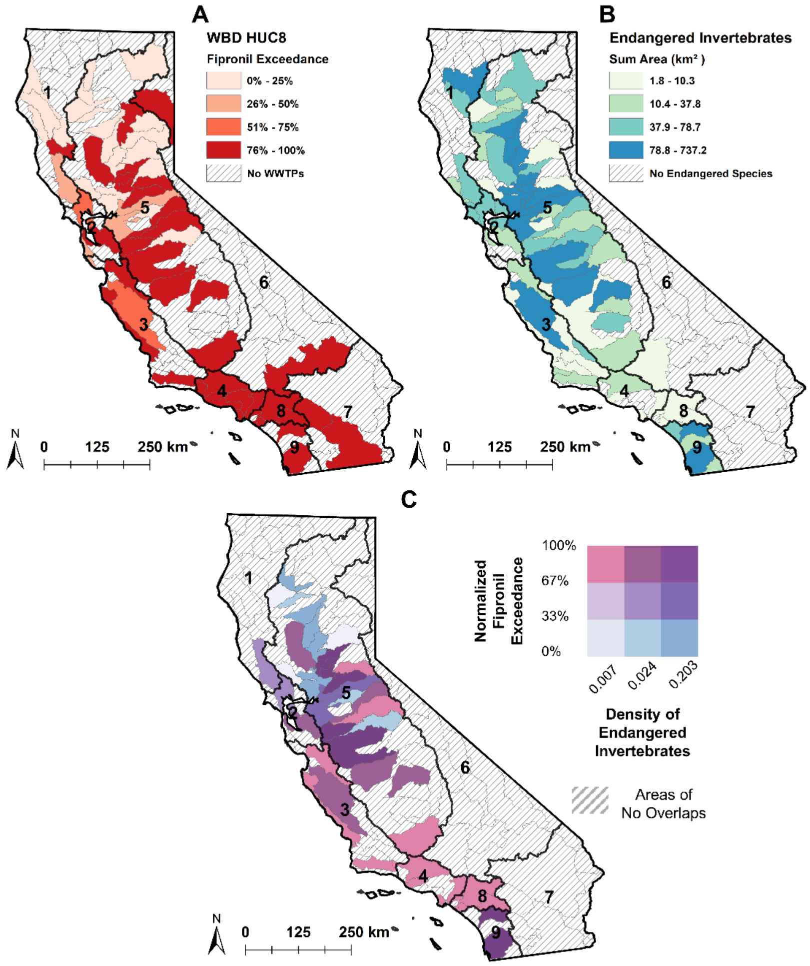

Figure A 3: High-risk watersheds for Fipronil exposure in endangered invertebrate habitats in California. a) The percentage of WWTP discharge sites failing to meet the required dilution factor for Fipronil safety under mean annual stream flow conditions and median Bifenthrin concentrations in effluent. b) Endangered invertebrate habitats across CA, grouped based on quantile quantification (i.e., equal numbers of watersheds per class). c) Intersection of endangered invertebrate habitats and effluent-receiving streams where the Fipronil safety threshold is exceeded.

CHAPTER 4: AN INDEX-BASED APPROACH FOR IDENTIFYING WATERSHED PESTICIDE VULNERABILITY IN CALIFORNIA

*This chapter is in preparation for submission to *SETAC Integrated Modeling and Assessment Journal*

4.1 ABSTRACT

California is one of the leading users of pesticides in the country, which is compounded by high population densities and agricultural activities. The discharge of pesticides into the environment is demonstrated by urban and agricultural runoff that feeds into the watershed, which then affects the aquatic environment. Monitoring how point and non-point sources of pesticides affect surface water quality and watershed conditions is an important factor for tracking and regulating aquatic creatures' exposure to pesticide loads. A multi-metric Pesticide Vulnerability Index (PVI) was developed in this study to assess the vulnerability of California watersheds to pesticide contamination. The PVI was based on hydrological, climatic data and point and non-point pesticide sources on a watershed scale. Across California, urban watersheds most susceptible to pesticide pollution included the Lower Sacramento, San Joaquin, and Los Angeles watersheds. Watersheds in urban areas were susceptible to pesticide loads due to their high population and corresponding usage levels. Climate change is predicted to intensify the watershed pesticide vulnerability within the urban and Central Valley regions due to increased precipitation, temperature and runoff. A hotspot comparison of both the PVI and endangered species found similarities associated in the Central Valley and San Diego regions, highlighting the adverse effects of pesticide discharge within those component watersheds. Results of this study can be utilized to prioritize problem areas for watershed management and restoration.

4.2 INTRODUCTION

Pesticides pose a significant threat to aquatic life based on their increased detection in the environment [1-3]. The effects of these pesticides has not been fully examined due to challenges in acquiring sufficient monitoring data [4]. The EPA and other agencies have raised concerns about the impacts of pesticides to aquatic and human health by establishing health benchmarks[5, 6] to regulate the discharge of pesticides within surface waters [7-9]. Regional trends however indicate that more than 50% of streams in the conterminous US exceed chronic aquatic health benchmarks [4, 10]. Within California, water samples have tested above the recommended aquatic benchmarks for bifenthrin [10, 11], chlorpyrifos [12, 13], fipronil and permethrin [7, 14-16] respectively. The risks associated with acute and chronic pesticide exposure include mutations of aquatic species [17-19] and disruption of environmental ecosystems [17, 20]. Animals higher up on the trophic food chain are also exposed to these pesticides at toxic levels through consumption of the fishes and other aquatic creatures [21].

The identification and categorization of point and nonpoint pesticide sources is critical for monitoring and mitigation purposes. Pesticides are commonly used in products that lead to point and nonpoint pollution. Pesticide use is generally detected in regions of high population density, where the demand for food and supplies significantly impacts usage rates [21, 22] [23]. Pesticides have been detected in surface waters downstream of various nonpoint sources, including land applications for agricultural practices, residential and commercial landscapes, and rights-of-way (RoW) [14, 24], as well as for structural use on buildings. However, pesticide use is not fully regulated in residential, industrial, and other areas [25]. Municipal wastewater treatment plants (WWTPs)[3, 26] are a significant point source of pesticides through the down-the-drain pathway of residential pesticide applications [27, 28]. Conventional wastewater treatment methods are generally inefficient at pesticide removal, furthering the aquatic pesticide exposure risk in receiving streams.

Modeling pesticide vulnerability involves investigating the susceptibility of freshwater streams within each watershed to pesticide load contaminations from anthropogenic activities [29, 30]. Additionally, based on receiving streamflow conditions, hydrological characteristics directly impact the degree of pesticide vulnerability [31-33]. The EPA conducted an integrated index-based assessment of watershed health at state and regional levels in a report titled the California Integrated Assessment of Watershed Health (CIAWH) [34]. This report incorporated several metrics including hydrologic data, water quality, habitat characteristics, and biological data for a holistic relative assessment of healthy watersheds across the state.

We adapted the CIAWH methodology to assess each California watershed's level of vulnerability toward pesticide exposure through a spatial multi-metric index. For this approach, we created a geospatial model that integrated point and nonpoint pesticide sources. The resulting model was then used to develop a Pesticide Vulnerability Index (PVI) within the context of climate change. Next, we identified areas of priority concern for pesticide exposure through a hotspot analysis. After generating the hotspots, we then geospatially investigated the intersection of priority concern areas with endangered species habitats. Finally, we conducted a Spearman rank statistical correlation of the PVI values against recent field pesticide surveillance. This index-based approach can be updated for a range of pesticides depending on available information and is readily testable against further surface water observations.

4.3 METHODS AND MATERIALS

4.3.1 CASE-STUDY SITE

California accounts for nearly 20% of the country's total pesticide use, with approximately 209 million pounds of pesticides reported for agricultural use in 2018 [35]. Urban development has also seen an annual increase of 40-50,000 acres in relation to population growth, which translates into increased urban pesticide usage[24]. Accurate records of residential pesticide use are challenging to obtain due to privacy concerns [36], however commercial, structural and agricultural usage records have been differentiated by the California Department of Pesticide Regulation (CDPR) from annual Pesticide Use Reports (PUR) [26]. California has consistently been at the forefront of environmental regulation, exemplified by its pioneering pesticide laws that surpass federal mandates. Notably, California introduced the California Environmental Quality Act (CEQA) in 1970, which required the state to assess the environmental impact of pesticide use [37]. Moreover, the state was the first to ban the use of the highly toxic pesticide DDT in 1969, nearly a decade before the federal government followed suit [38]. In addition, the California Department of Pesticide Regulation (DPR) established stringent regulations to protect farmworkers from exposure to harmful pesticides, emphasizing both the safety of workers and the environment [25, 38]. These proactive measures in California's pesticide regulation have set a precedent for other states and demonstrated the state's commitment to environmental and public health concerns beyond federal requirements.

4.3.2 PESTICIDE VULNERABILITY INDEX

For this study, we developed a multimetric Pesticide Vulnerability Index (PVI) to identify California watersheds relatively more vulnerable to combined point and non-point pesticide pollution. Hydrologic conditions for each watershed were characterized by modeling runoff and precipitation impacts on streamflow. Geospatial correlations between the modeled most vulnerable watersheds and endangered species habitats were investigated to elucidate areas for future priority mitigation consideration. Using ArcGIS Pro 3.1, the PVI was developed across 140 California hydrologic watersheds at an 8-digit hydrologic unit code scale (HUC8). Ten metric indicators generated for the PVI included pesticide pollution sources (point and non-point), climatic (future precipitation, runoff and temperature) and hydrological (current precipitation and runoff) conditions. Figure 9 provides an overview of the metrics used in this study, which incorporates data from the PUR, National Climate Change Viewer (NCCV), Center for Watershed Needs Survey (CWNS), and web scraping [39-41]. Further details on the metrics and calculations can be found in Table A1 of the Appendix.

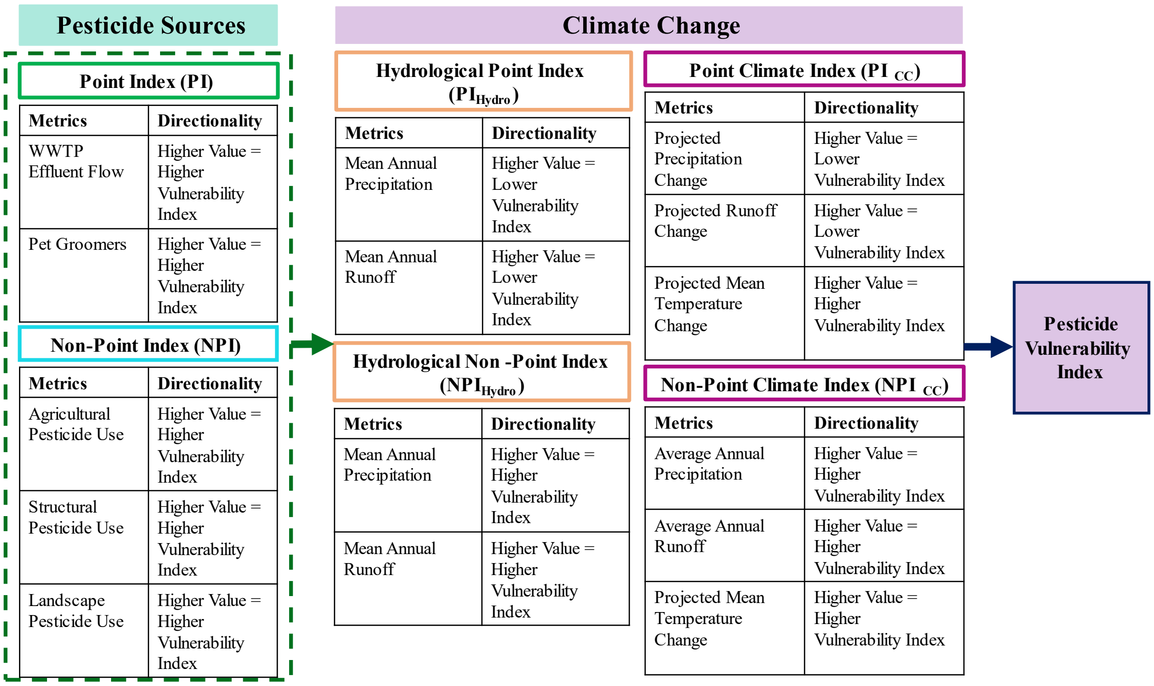

Figure 9: Index categories, metrics and directionality adopted for the CA Pesticide Vulnerability Index (PVI) under a) current conditions and b) future conditions to identify HUC8 watersheds relatively more vulnerable to pesticide pollution

4.3.3 PESTICIDE POLLUTION AND AQUATIC SPECIES DATA

Point pollution sources for California were obtained from Clean Watershed Needs Survey (CWNS) 2012 reports for 165 surface water discharge WWTPs [41]. Pesticides were selected based on their reported relative usage within California and assumed to have similar mobilities within the environment [42]. Aquatic species' habitats were incorporated from the California National Database (CNDBB) into this study to model the ecological impacts of pesticide load exposure to aquatic ecosystems[43]. These data were aggregated on a watershed scale and normalized per watershed area to ensure uniform weighting and equal directional scaling. To account for other sources of urban pesticide use, we gathered data from 976 pet grooming locations across the state via web scraping with Apify [44]. A subset of the locations was visually verified through Google Earth. For the non-point source metric, pesticide use reports (PUR) were generated for selected pesticides (bifenthrin, cypermethrin, permethrin, fipronil, imidacloprid) from the California Department of Pesticide Regulation (CDPR) PUR database [42]. These pesticides were selected based on their large amounts of reported annual use within each county. They were categorized based on the following use patterns per county: agricultural, structural, landscape, and right of way across multiple years (2016-2018). Right-of-way data were removed from the analysis due to limitations in data availability (less than 50% complete).

4.3.4 HYDROLOGIC AND CLIMATIC DATA

Hydrologic watershed data were obtained from the National Hydrology Dataset Plus Version 2 (NHDPlus V2) [45]. For our analysis, NHDPlus V2 data was extracted and downscaled at an 8-digit hydrologic unit (HUC8), which represents each of California's 140 subbasins. Additionally, we obtained both annual and projected precipitation and runoff data from the National Climate Change Viewer (NCCV) at the HUC8 level to model watershed conditions [40]. Precipitation and runoff data were derived from 2012 to 2019 to estimate current hydrologic conditions, while changes between the historical period (1981-2010) and future projections (2025-2049) were estimated for climatic metrics. We selected the 2025 to 2049 time period as our future projections to assess the near-term impacts of climate change on pesticide loads across watersheds. This approach allows for understanding the imminent consequences and potential risks, thereby informing timely policy interventions.

4.3.5 INDEX CALCULATIONS TO MODEL PESTICIDE VULNERABILITY

Using ArcGIS Pro 3.1, pesticide usage and discharge data were spatially aggregated on the HUC8 watershed scale and normalized per watershed area to ensure uniform weighting and equal directional scaling for analysis [46]. Further details of the geospatial model development are in the Appendix. Normalization ensured that multiple metrics were converted into uniform, unitless scores for even scaling. Sub-index scores were calculated for each pesticide sub-index (i.e., point source, non-point source) using equation 3. Scores of the precipitation, temperature and runoff data were then averaged to form a single score, then combined with the point and nonpoint pollution sub-indices to assess their seasonal impacts. Opposite directionality was assumed for both precipitation and runoff data when combined with the point source sub-index, i.e., a higher score indicated lower pesticide vulnerability and vice-versa.

Metric scores were then equally weighted to calculate the new pesticide pollution sub-indices. Finally, the Pesticide Vulnerability Index (PVI) was calculated as the average of the hydrologic or climatic sub-index scores of the point and non-point pesticide pollution sources. The overall PVI scores range from 0 to 100, with lower scores indicating a lower estimated vulnerability to pesticide concentrations and vice versa. Equations 1-11 show the approach used for the PVI estimations under hydrologic and climate change:

(1) $$\text{Metric Normalization} = \left(\frac{\text{Observed metric value per watershed}}{\text{Watershed area (acres)}}\right)$$

(2) $$\text{Metric Score} = \left(1 - \frac{\text{Normalized metric value per watershed}}{\text{Max. normalized metric value}}\right) * 100$$

(3) $$\text{Sub} - \text{index score} = \frac{\sum_{i=1}^{n} \text{MetricScore}_i}{n}$$

(4) $$\text{Hydrologic Metric Score (nonpoint)} = \frac{x_i - x_{i,min}}{x_{i,max} - x_{i,min}}$$

(5) $$\text{Hydrologic Metric Score (point)} = \frac{x_{i,max} - x_i}{x_{i,max} - x_{i,min}}$$

(6) $$NPI_{hydro} = \frac{NPI + \text{Hydrologic MS}}{2}$$

(7) $$PI_{hydro} = \frac{PI + \text{Hydrologic MS}}{2}$$

(8) $$PVI_{hydro} = \frac{PI_{hydro} + NPI_{hydro}}{2}$$

(9) $$PI_{cc} = \frac{PI + \text{Climatic MS}}{3}$$

(10) $$NPI_{cc} = \frac{PI + \text{ClimaticMS}}{3}$$

(11) $$PVI_{cc} = \frac{PI_{cc} + NPI_{cc}}{2}$$

The NPI (nonpoint index) incorporates aggregated agricultural, structural and landscape use per watershed, PI (point index) incorporates aggregated WWTP effluent flow and number of pet groomers per watershed; climatic metric scores incorporate average and projected change in mean temperature, runoff and precipitation. From the above equations, NPI_{hydro} , PI_{hydro}, and PVI_{hydro} represent the hydrologic nonpoint vulnerability index, point vulnerability index and PVI respectively; NPI_{cc} , PI_{cc}, and PVI_{cc} represent the nonpoint vulnerability index, point vulnerability index and PVI under climate conditions respectively.

4.3.6 GEOSPATIAL ASSESSMENT OF PVI AND ENDANGERED AQUATIC SPECIES

We spatially identified watersheds at a higher risk of pesticide levels from multiple sources and their intersection with the presence of endangered species. Table A2 in the Appendix provides a list and classifications of the endangered species obtained from CNDDB for this study. Spatial correlations between the PVI hotspots and endangered aquatic species (i.e., invertebrates, fishes, and amphibians) were then examined. We calculated the total area of endangered invertebrate habitats per HUC8 watershed using the Summarize Within Tool in ArcGIS Pro 3.1. We then divided the total area of endangered species habitats by the area of each respective watershed to estimate the density of these habitats. A ratio of the aggregated species' spatial locations (in acres) was calculated within each HUC8 watershed area using the sum rule in ArcGIS Pro 3.1 prior to generating the hotspots. After generating each species' spatial densities, their cumulative hotspot was generated using the Getis-Ord Gi* hotspot tool. We then used the hotspot analysis comparison tool to examine the endangered species' spatial similarities and differences against the PVI hotspot. Statistically significant level categories (99% hot, 95% hot, 90% hot, not significant, 90% cold, 95% cold, and 99% cold) between the corresponding hotspot layers were observed. Similarity values measured how closely the hot spots, cold spots, and insignificant areas of both hot spot results spatially aligned.

4.3.7 STATISTICAL ANALYSIS OF PVI

To assess the effectiveness of the PVI in identifying watersheds with higher pesticide loads, we compared the PVI scores to field concentrations using monitoring data obtained from EPA's Surface Water database (SURF) with Spearman's rank correlation [47]. Selected field pesticides (bifenthrin, cypermethrin, permethrin, fipronil, and imidacloprid) detection values were extracted from SURF, with detection values of zero being replaced with half-point values of the required detection limits. The datasets ranged from 2016 to 2021 for the following pesticides: bifenthrin (n=5006), cypermethrin (n=4202), fipronil (n=2511), permethrin (n=6543), and imidacloprid (n=2380). After a spatial join of the selected field pesticide values to each

HUC8 watershed, grouped tests were conducted with IBM SPSS Statistics 29 software to evaluate the correlation between highly vulnerable and less vulnerable watersheds.

4.4 RESULTS

4.4.1 SPATIAL DISTRIBUTION OF PESTICIDE VULNERABILITY

To assess the impacts of pesticide loadings on California's surface water, we generated a geospatial pesticide vulnerability index at the watershed level to model the likelihood of pesticide occurrence in surface water. Figure 10 shows that the Lower Sacramento, San Gabriel and Los Angeles regions ranked as the top three most impacted watersheds from both point and nonpoint pesticide loading. Overall, watersheds located in urban areas were more likely to be susceptible to pesticide loads due to their high population and corresponding usage levels. For example, the urban city of Los Angeles is the largest city, with a population of 3.8 million as of 2022 [48]. High population densities directly translate into increased pesticide usage that impacts urban streams [26]. The top three watersheds with the highest point pesticide vulnerability include San Gabriel, San Francisco Bay, Los Angeles, Lower Sacramento, and Santa Monica Bay. The Sacramento watershed is a 23,300km^2 region with about 15% agricultural land use and 2% limited urban land centralized around the San Francisco-Sacramento Bay [49]. Most farming activities occur within the Sacramento Valley, which contains the largest river in the state [50, 51]. Watersheds most likely impacted by nonpoint pesticide loading include Coyote, San Joaquin Delta, San Gabriel, and Lower Sacramento.

Regional variations for specific point and nonpoint pesticide sources were identified. Figure A4 in the Appendix displays the spatial distribution of pet groomers and municipal WWTPs in California. Pet groomers were most concentrated in the urban areas such as the San

Francisco/San Jose and Los Angeles regions. Wastewater treatment plants (WWTPs) were found to be more densely concentrated in the Central Valley and Los Angeles regions in terms of numerical distribution. For non-point pesticide loads, each selected pesticide was categorized by their reported uses based on agricultural, structural, and landscape services. From the data provided, the most prolific use of each pesticide was found to be through agricultural use, with over 95,000 lbs of annual pesticide use reported for a Central Valley region watershed. Structural pesticide use ranked second in total pounds of reported applications, with a maximum of 15,000 lbs of annual reported use in the Santa Ana watershed.

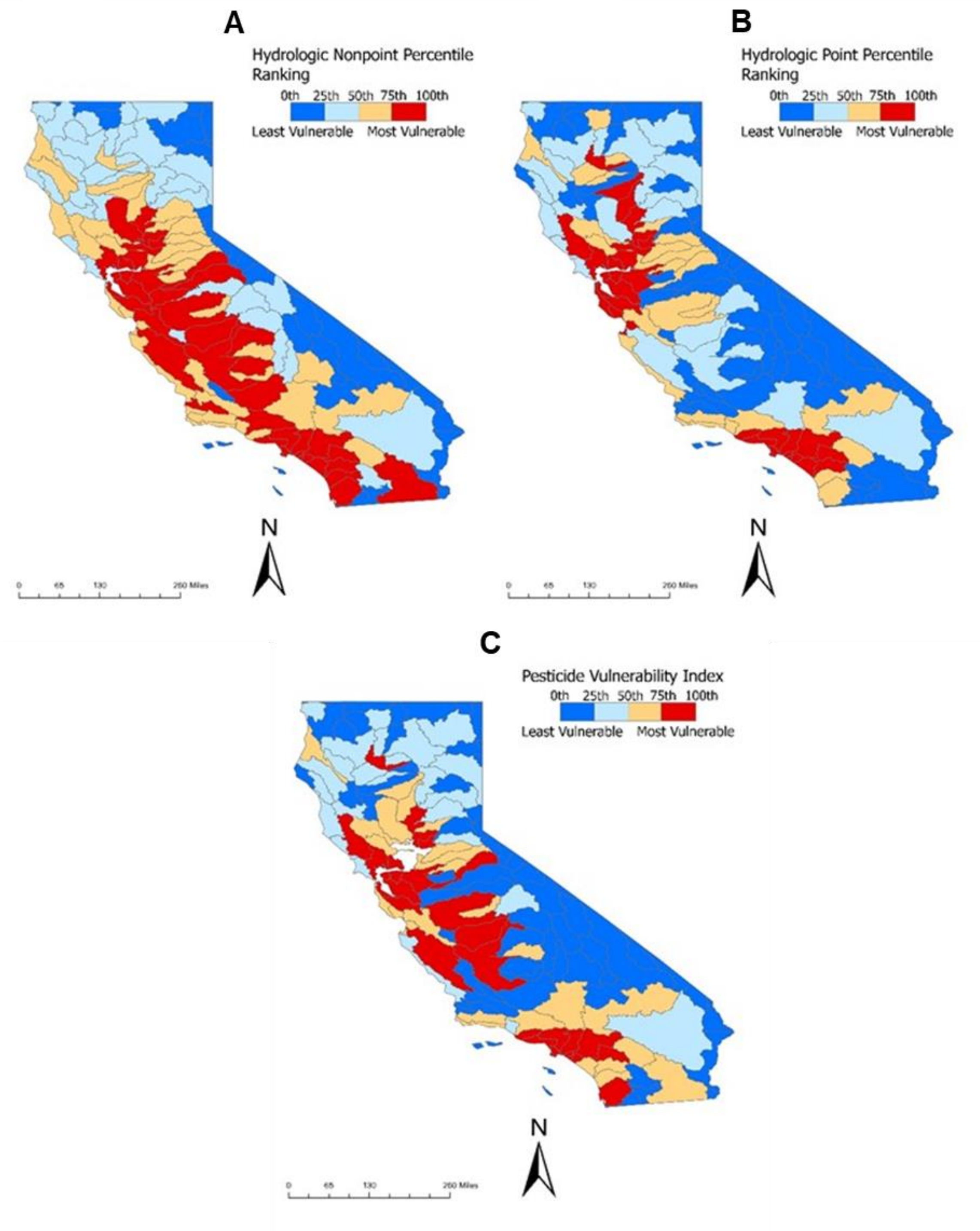

Figure 10: Color-coded map showing percentile distribution of a) nonpoint pesticide sources, b) point sources of pesticides, and c) combined pesticide vulnerability across the state of California.

4.4.2 PVI UNDER PROJECTED CLIMATE CHANGE CONDITIONS

To estimate watershed vulnerability to pesticide pollution under future climate scenarios, we developed climate change indices that incorporated changes in mean temperature, runoff, and precipitation. We assessed their varying impacts on point and nonpoint pollution sources, i.e., higher point dilution rates with increased temperature and precipitation and higher nonpoint pesticide loading volumes with increased precipitation and runoff. Due to the projected increases in precipitation, temperature and runoff across the state, Central Valley watersheds are predicted to be more vulnerable to nonpoint pollution. Predicted vulnerable watersheds to the point source loads are observed in the urbanized San Francisco and Los Angeles regions. In the future, it is anticipated that urban and agriculturally intensive watersheds will exhibit a heightened vulnerability to pesticide contamination.

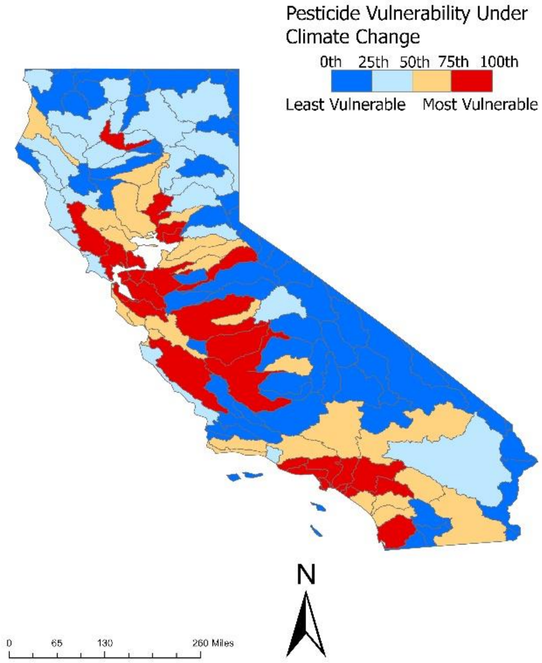

Figure 11: Color-coded map showing percentile ranking of pesticide vulnerability under climate change across the state of California

4.4.3 GEOSPATIAL COMPARISON OF PVI AND ENDANGERED SPECIES HOTSPOTS

A hotspot comparison was conducted to investigate the potential intersection of increased pesticide pollution and endangered species habitats. Endangered species hotspots were concentrated in the northern California watersheds, while the PVI hotspots were concentrated at the southern California watersheds (see Figure 12). Northern California was the primary region for high species clusters (hotspots with >90% confidence) while southern California displayed lower species clusters (cold spots with >90% confidence). For the amphibians, hotspots for species clusters were observed along the upper Californian coastlines including San Francisco Bay, Suisun Bay, and San Pablo Bay (see Figure A4 in the Appendix). Figure 12b indicates that species located within highly urban and Central Valley watersheds are more likely to be impacted by pesticide loads from point and nonpoint sources.

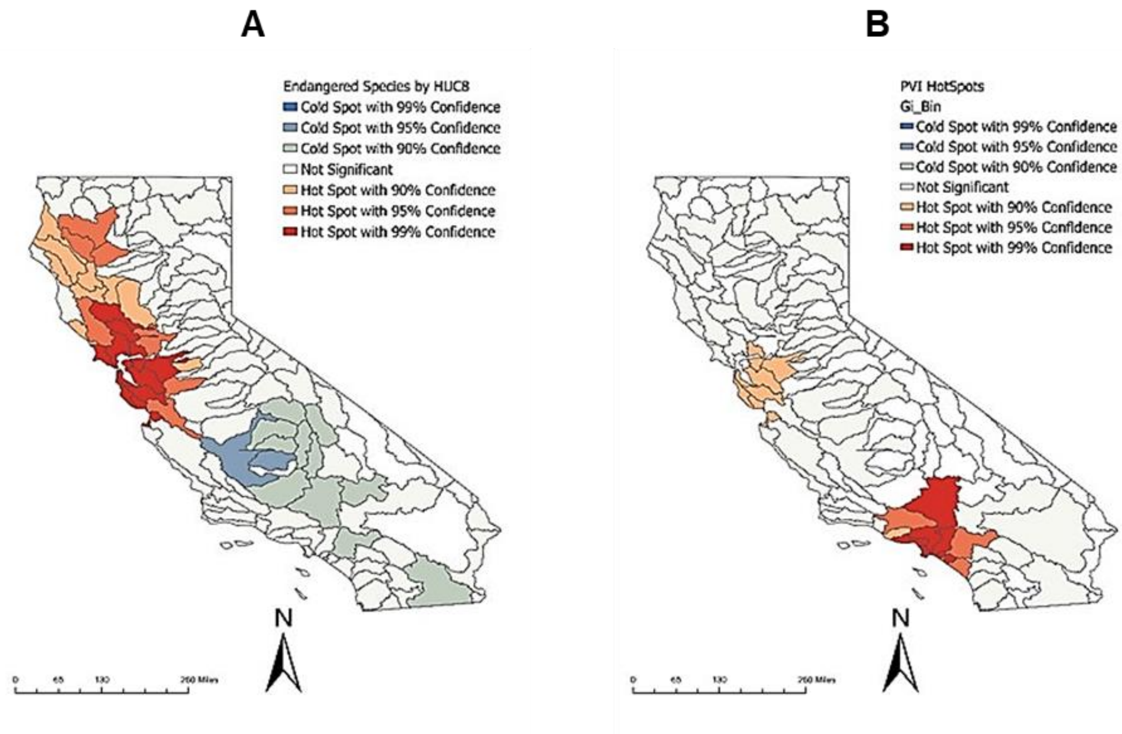

Figure 12: Color-coded map showing hotspots and cold spots for a) aggregated endangered species and b) PVI across the state of California

Modeled PVI hotspots were geospatially compared against endemic endangered species habitats across California watersheds. Output significance levels for the comparison between 0(not similar) and 1(highly similar) indicated degrees of partial similarity for the hotspot layers. Overall, six (6) watersheds emerged as statistically significant from the comparison. These watersheds include the Suisun Bay, San Francisco Bay, Coyote, and Monterey Bay. From Figure 13, we observed high similarity from the upper California watersheds through the Central Valley and down to the southern California watersheds. Mid- to low-level similarities were observed for the highly urbanized watersheds. For the significance level pairs, for the watersheds that were 90% hot spots in the PVI, 85.71 percent of the endangered species hotspots remained as 99% hot spots, while 33.3 percent changed to 90% cold spots.

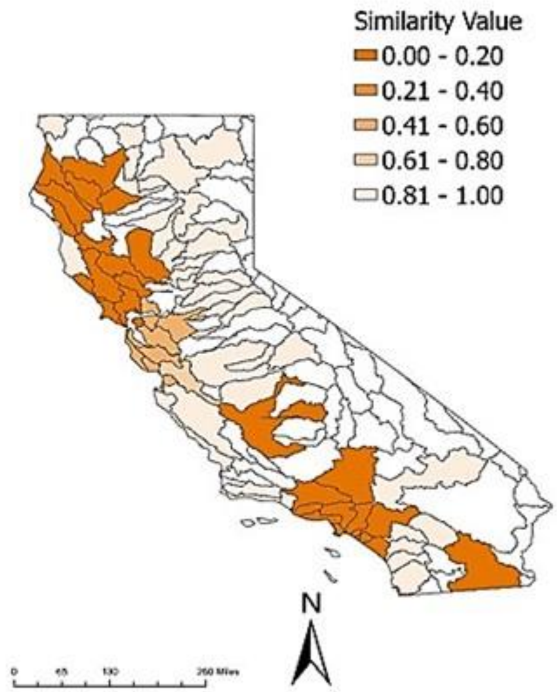

Figure 13: Color-coded map showing the similarity values of the hotspot comparison for both PVI and the aggregated endangered species across California

4.4.2 STATISTICAL CORRELATIONS BETWEEN PVI AND RECENT PESTICIDE SURVEILLANCE

Spearman's rank correlation analysis was conducted to determine the correlation between sampled field data and the corresponding simulated index values. From the correlation results, the Spearman’s rank generated no significant relation between the pesticide field concentrations and PVI scores. This is likely due to comparing the values at the HUC-8 watershed scale. The most significant correlations were found in the point index scores for predicting bifenthrin concentrations (rho = -0.44, $p = .003$) and cypermethrin concentrations (rho = -0.087, $p < .001$). The two pesticides exhibited the highest frequency of measurement within the datasets.

4.5 DISCUSSION

For this study, we developed a multimetric pesticide vulnerability index (PVI) for identifying watersheds that are relatively more impacted by pesticide loadings. The PVI combined data for receiving stream hydrology with point and nonpoint sources that are expected to result in identifying at-risk watersheds. The PVI was generated to assess the aggregated effect of pesticide loading and fate within watersheds on a geospatial framework. Differentiating between point and nonpoint pesticide sources enabled us to classify their significant anthropogenic contributions across each watershed. Based on the PVI, watersheds located in the San Francisco and Central Valley regions are more likely to indicate a high occurrence of pesticide loads from both point and nonpoint sources. These trends may be driven by the population sizes associated with the areas, as well as the type of pesticide applications that are carried out in these municipalities [27]. From 2011 to 2015, previous studies indicate that approximately 85,185 pounds of fipronil, 98,233 pounds of imidacloprid, and 530,235 pounds of pyrethroids were annually utilized in California with the potential for down-the-drain transport [26]. These significant quantities of pesticides have adverse implications for urban watersheds. They can contaminate surface water bodies, affecting aquatic ecosystems and potentially causing harm to non-target organisms, including fish, amphibians, and invertebrates [52]. Pesticide runoff from urban areas into watersheds can disrupt the balance of these ecosystems and pose risks to human health, further underscoring the need for effective pesticide management and pollution control measures in urban environments [7, 15].

Outcomes from this PVI were compared from current and future climatic projections, highlighting their impacts on highly urbanized and agricultural watersheds. The results of this study reveal significant implications for various watersheds across California under future climate scenarios. The development of climate change indices incorporating changes in temperature, runoff, and precipitation further highlights the vulnerability of these watersheds to pesticide pollution. Specifically, Central Valley watersheds are anticipated to become more susceptible to nonpoint pollution due to projected increases in precipitation, temperature, and runoff. Notably, urbanized regions such as San Francisco and Los Angeles are expected to face heightened vulnerability to point source pollution loads. This suggests that in the future, watersheds characterized by urbanization and intensive agriculture will be at an increased risk of pesticide contamination [53-55]. These findings underscore the need for targeted management and mitigation strategies in these regions to safeguard water quality and environmental health.

We also evaluated the spatial similarities and differences associated with the PVI and the occurrence of endangered species within each watershed. Spatial similarities were observed between the PVI and endangered species located in the Central Valley and northern California regions. This suggests that species situated in those areas are more likely to be negatively impacted by pesticide loads that occur in those areas [52]. Previous research has demonstrated that aquatic species' long-term exposure to pesticides can lead to mutations, population declines and physiological defects [56-58]. These effects are even more pronounced in invertebrates due to their relatively low masses which are directly correlated to their dosage exposure levels [21].

The watersheds with statistically significant hotspots from the comparison included the Suisun Bay, San Francisco Bay, and Coyote. These watersheds are located in the highly urbanized San Francisco area, with the Bay serving as a highly diverse ecosystem habitat for aquatic species such as the chinook salmon [1, 57]. Thus, the hotspot comparison provides a snapshot of the predicted risk associated with aquatic creatures' exposure to pesticides.

The Spearman's rank correlation analysis conducted in this study aimed to explore the potential relationships between sampled field data and simulated index values, specifically on pesticide concentrations and the Pesticide Vulnerability Index (PVI) scores. The results revealed no statistically significant correlation between pesticide field concentrations and PVI scores. This lack of significance can be attributed to the challenges associated with comparing data at the HUC-8 watershed scale, which may not capture more minor variations and localized effects. Our findings suggest that the PVI was more effective in predicting pesticide concentrations for the pyrethroids (i.e., bifenthrin and cypermethrin), which were the most frequently measured pesticides in the dataset. This underscores the importance of considering the specific pesticide type and its prevalence when assessing the effectiveness of the PVI in predicting pesticide exposure within the studied watershed. Further research may explore these particular correlations and their implications for pesticide management and environmental protection strategies.

4.6 CONCLUSION

For this study, we assessed pesticide susceptibility at watershed level in California using a multi-metric index. Our PVI results show that the most impacted watersheds are primarily located in the Central Valley and urban areas such as Los Angeles and San Francisco. These results are consistent with the reported uses of pesticides within these regions, where high indoor and outdoor pesticide applications are frequently recorded [26]. Additionally, our predicted assessment of the impact of climate change on highly urbanized and agricultural watersheds in California underscores their heightened vulnerability to pesticide pollution. The findings emphasize the urgency of implementing region-specific management and mitigation measures to protect water quality and environmental health in these areas, particularly in Central Valley watersheds facing increased nonpoint pollution risks and urbanized regions like San Francisco and Los Angeles confronting elevated point source pollution. Hotspot comparisons for the PVI and endangered species locations showed similarities in the Central Valley and San Diego regions, indicating a high level of endangered species exposure to pesticide loads in those areas. Spearman's rank correlation analysis revealed no significant relationship between pesticide field concentrations and PVI scores when assessed at the HUC-8 watershed scale. However, notable negative correlations were observed for point index scores, indicating a more meaningful association in predicting bifenthrin and cypermethrin concentrations, likely influenced by the higher frequency of measurements for these two pesticides in the datasets.

This study had limitations due to incomplete data on both point and non-point pesticide sources. Future research should update pesticide use values as more data becomes available. Generalizations were also made at the HUC8 watershed level to ensure consistency in our analysis. The PVI model can be adapted to various geographical scales and include additional metrics for more detailed analysis. To comprehensively assess pesticide sources and their proximity to human and aquatic ecosystems, residential and industrial usage data should be incorporated. This approach offers a more detailed understanding of pesticide origins and their environmental impacts. The study's findings support the targeting of monitoring efforts in watersheds more susceptible to pesticide occurrence.

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401768082175&hsa_kw=apify&hsa_mt=e&hsa_net=adwords&hsa_ver=3&gad_source=1&gclid=Cj0KCQjw-pyqBhDmARIsAKd9XINQ6ZIxm7mvWRoSfAZoOk9InDKiBLXoP64rAWFlZa6Pd4t1cblPVh0aAuJyEALw_wcB.

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4.8 APPENDIX

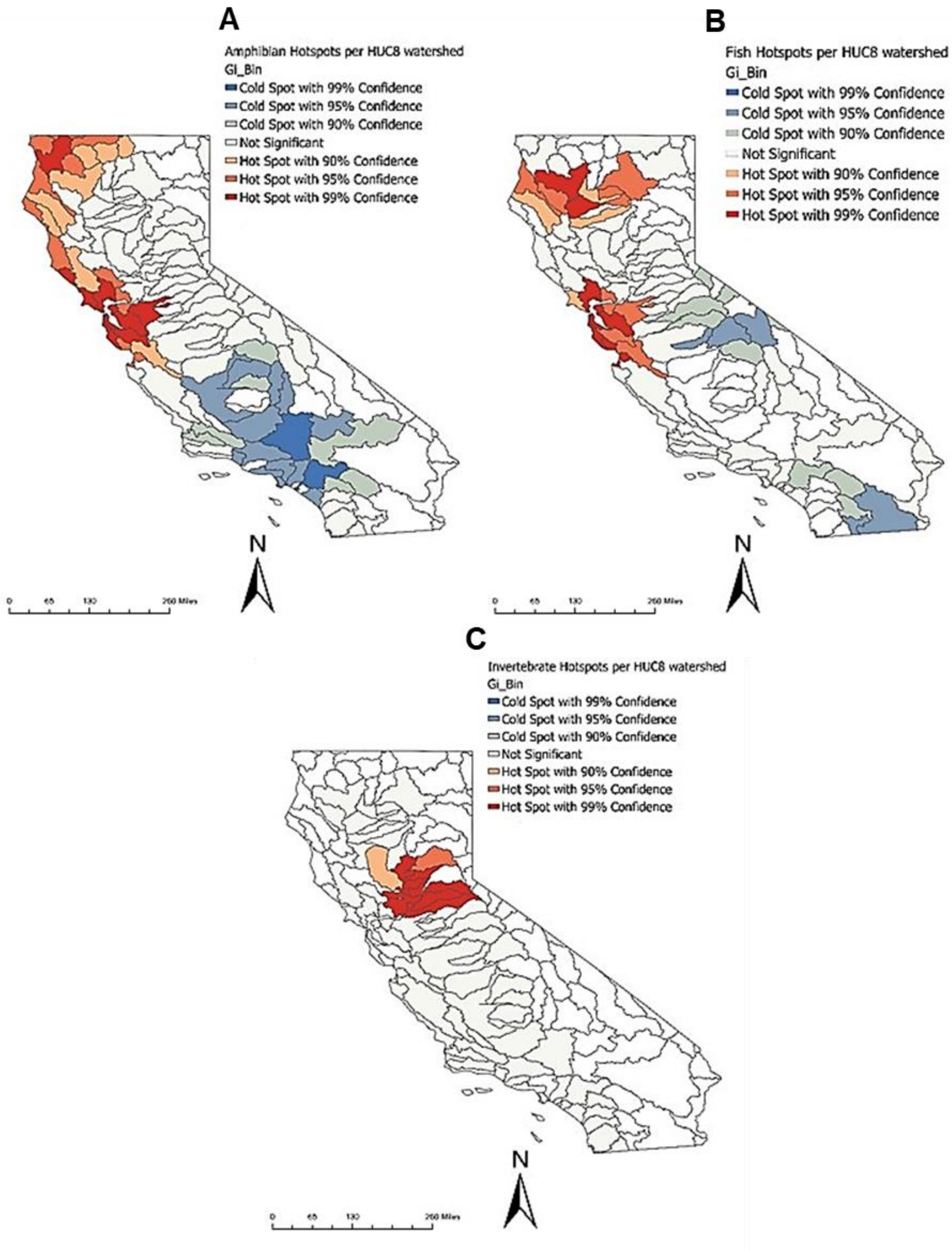


Figure A 4: Color-coded map showing hotspots and cold spots for a) amphibians, b) fishes, and c) invertebrates across the state of California

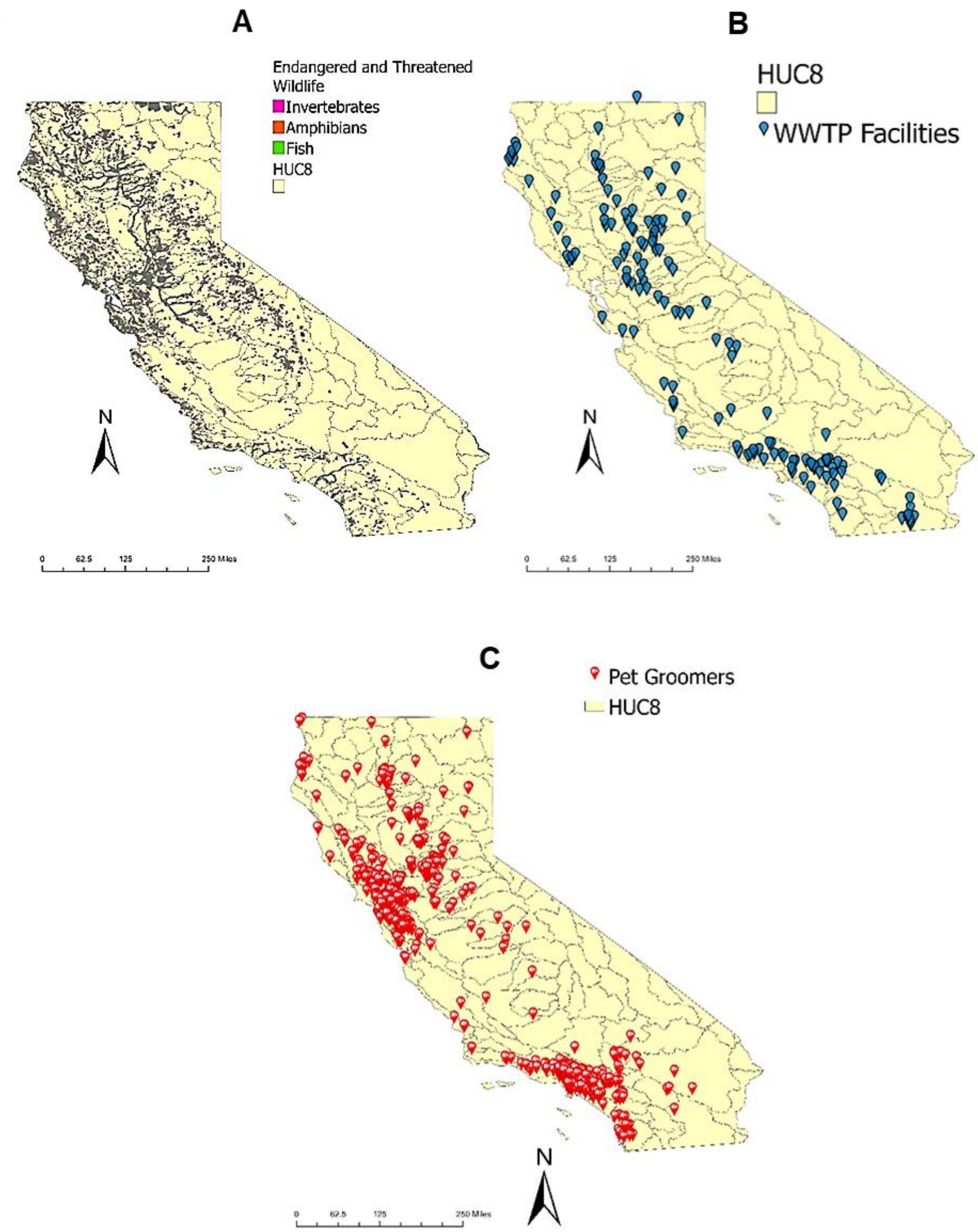


Figure A 5: Color-coded map showing the spatial distribution of a) endangered species b) WWTP facilities, and c) pet groomer locations across the state of California

Table A 1: Table showing the sub-indexes for the PVI and the metrics that were used for their calculations. Pesticide sub-indices were aggregated from HUC12 to HUC8 watersheds in ArcGIS and normalized by watershed area to show the spatial distribution.

Index	Sub-Index	Data Sources	Metric
Pesticide Pollution Sources	Point sources of pesticides (PI) (WWTP effluent flow, pet groomers)	• CWNS 2012 • NHDPlus V2 • Webscraping	• Aggregated WWTP Effluent Flow (Existing Flow) normalized by HUC8 watershed area • Estimated Number of Pet Groomers per watershed
	Non-Point sources of pesticides (NPI) (Landscaping, Agricultural, Structural)	• Pesticide Use Reports (PUR)	• Agricultural Use per watershed • Structural Use per watershed • Landscape Use per watershed
Hydrologic Conditions	Watershed conditions (Precipitation, Runoff, Temperature)	• USGS National Climate Change Viewer	• Average precipitation per watershed • Average runoff per watershed
Climate Change	Projected change (Precipitation, Runoff, Temperature)	• USGS National Climate Change Viewer	• Projected Precipitation Change • Projected Runoff Change • Projected Mean Temperature Change

Table A 2: Table showing the selected state and federally endangered and threatened species of wildlife selected for the PVI. The selected wildlife were spatially mapped to demonstrate their proximity to surface waters across the state.

Amphibians	**Fish**	**Invertebrates**
Salamanders: Santa Cruz long toed Calif. Tiger Desert slender Kern Canyon slender Tehachapi slender Limestone Shasta Siskiyou Mtns. Scott Bar Toads: Yosemite toad Black Arroyo Frogs: Calif red-legged Foothill yellow-legged Cascades Oregon spotted Southern mountain yellow-legged Sierra Nevada yellow-legged	Coho Chinook Steelhead Mohave tui chub Owen's tui chub Bonytail Colorado pikeminnow Short nose sucker Razorback sucker Lost river sucker Desert pupfish Owen's pupfish Unarmored three spine stickleback Tidewater goby Green sturgeon Lahontan cutthroat trout Little Kern golden trout Paiute cutthroat trout Delta smelt Eulachon Santa ana sucker Modoc sucker Rough sculpin Longfin smelt Clear lake hitch	Fairy shrimp: Conservancy Longhorn San Diego Riverside Vernal pool Vernal pool tadpole shrimp Calif. freshwater shrimp Shasta crayfish Trinity bristle snail

CHAPTER 5: QUANTIFYING THE ESTIMATED ANNUAL COSTS AND ENVIRONMENTAL BENEFITS ASSOCIATED WITH ADVANCED WWTP PESTICIDE REMOVAL

*In preparation for submission to *Environments*.

5.1 ABSTRACT

This study presents an overview for quantifying the estimated annual costs and environmental benefits of advanced wastewater treatment plant (WWTP) pesticide removal. This research assesses the economic feasibility and environmental impact of implementing advanced pesticide removal technologies in WWTPs. The study begins by analyzing current pesticide contamination levels and the potential risks associated with untreated effluents entering receiving water bodies. Next, different advanced treatment options are evaluated, including activated carbon adsorption, membrane filtration, and advanced oxidation processes. To quantify the estimated annual costs, we consider the capital investment required for implementing these treatment technologies and the operational and maintenance expenses. The prices are compared with the potential benefits, such as reduced pesticides in the effluent and the subsequent positive impacts on aquatic ecosystems, drinking water sources, and human health. Furthermore, the environmental benefits are assessed by estimating the avoided cost of reducing pesticide concentrations discharged into receiving water bodies and the potential improvements in water quality. We also consider the potential long-term benefits, such as the restoration of aquatic habitats and the preservation of biodiversity. The results of this study provide valuable insights into the economic viability and environmental sustainability of advanced WWTP pesticide removal. The findings can be used by policymakers, water management authorities, and WWTP

operators to make informed decisions regarding implementing advanced treatment technologies to mitigate pesticide contamination in wastewater and protect the environment.

5.2 INTRODUCTION

Treated municipal wastewater effluent has been identified as a relevant source of pesticide residue channeled via sewer sheds into urban streams in California [1]. Identified pesticide pathways include mixed indoor and outdoor residential usage and pet treatment products before they are transported down the drain into municipal sewer systems [2]. According to a survey by Budd et al. [3], approximately one-third of residents in California utilize pesticides in and around their homes, further contributing to pesticide mass loading to surface waters. Pesticides commonly used in urban households for pet treatment, pest control, and other domestic tasks are also not readily biodegradable in the aquatic environment, leading to the depletion of non-targeted organisms from long-term exposure [4, 5]. Pyrethroids (e.g., bifenthrin), fipronil, and imidacloprid are highly toxic pesticides associated with general indoor pest control, with chronic aquatic toxicity benchmarks being as low as 0.1µg/L [6-8]. Due to their inherent toxicity to aquatic ecosystems, pesticides such as chlorpyrifos, imidacloprid, and fipronil have been assigned eco-toxicity scores ranging from 1(least toxic) to 8 (highly toxic) by the California Department of Pesticide Regulation (CDPR) [2]. Depending on the WWTP effluent composition and properties, pesticide chemical concentrations can reach several micrograms per liter, leading to potential long-term stream contamination and adverse ecological impacts [8-10]. Recently, public advisories have been issued on the consumption of harvestable fish, such as the chinook salmon and striped bass that inhabit the Sacramento River and Northern Delta, highlighting the possible side effects of pollutant exposure [11]. At low-flow conditions, the mass loading of pesticides into streams may increase the exceedance of aquatic toxicity thresholds and potentially harm aquatic ecosystems [12, 13].

Reducing pesticide residue in municipal WWTP effluent can play a vital role in mitigating their chronic ecological impacts on aquatic life by improving water quality in receiving streams. Conventional wastewater treatment is mostly inefficient at pesticide residue removal, as documented by several pilot studies [14, 15]. This is due to the disconnect associated with WWTP regulations and stated aquatic health benchmarks. The Clean Watershed Needs Survey (CWNS) is an essential tool for identifying and quantifying water quality and infrastructure needs in various watersheds at a broader regional and national scale [16]. Unfortunately, the CWNS may not always capture varying facility-specific needs and challenges. WWTPs often have their own monitoring and data collection systems, which may not be fully integrated into the CWNS database. Ozone-based advanced oxidation processes, generally employed for large-scale water treatment, have proven their potential to eliminate pesticides from secondary effluents even at low concentrations [17-19]. Pilot studies of ozonation report up to 97% removal efficiency for selected pesticide residue, highlighting its chemical efficiency [18, 19]. However, there is a lack of research on quantifying its associated implementation costs [20-22]. This gap is well-noted in the economic valuation of the environmental benefits of avoiding contaminated effluent discharge into receiving streams [23-25]. Another drawback is that ozonation processes require specific critical parameters to facilitate pesticide removal efficiency for future feasibility studies. Ozonation implementation is generally energy-intensive and more costly when compared to other less complex treatment methods [20]. Additionally, ozonation residuals have the potential to be carcinogenic and require the addition of reducing agents to accelerate ozone breakdown.

Quantifying and incorporating the economic and environmental benefits into current cost-benefit analyses for proposed wastewater treatment upgrades is imperative for achieving a comprehensive understanding of the true value of such investments [24, 25]. Wastewater treatment infrastructure is pivotal in safeguarding public health, environmental sustainability, and economic development [26]. However, traditional cost-benefit analyses tend to focus on the immediate capital and operational expenditures associated with upgrades while overlooking the broader long-term advantages [24, 27]. By expanding the analytical framework to encompass the economic and environmental benefits, decision-makers can gain insights into long-term cost savings, increased property values, job creation, and reduced healthcare expenses that may result from improved water quality. Additionally, a more comprehensive assessment can highlight the environmental benefits (i.e., enhanced water quality, biodiversity preservation, etc.) that have inherent economic value but are frequently not considered in such studies [28]. To ensure the efficient consideration of benefits from wastewater treatment upgrades, a holistic cost-benefit analysis, which integrates both the immediate costs and the multifaceted long-term advantages, is essential.

Shadow prices have been used to quantify contaminant removals in wastewater treatment plants (WWTPs) in recent years [25, 29]. This pioneering approach presents an innovation to previous economic cost functions by connecting the associated environmental and economic benefits in wastewater treatment [24, 30]. By assigning economic values to the removal of specific effluent contaminants, shadow prices help quantify both immediate direct costs and intangible societal and environmental benefits. This methodology was first developed by Färe et al. [31] and adapted in subsequent wastewater treatment contexts by other researchers [25, 28]. The shadow price approach enables policymakers and stakeholders to make more informed decisions regarding WWTP upgrades and operational strategies, as it encompasses the long-term economic consequences of enhanced water quality and the preservation of ecosystems and ecosystem services [29, 32, 33]. The utilization of shadow prices in quantifying WWTP contaminant removals is a valuable contribution to cost-benefit analyses, thereby producing a more holistic understanding of the multifaceted value of wastewater treatment and its role in sustainable development and environmental protection.

In this study, we investigated the shadow prices associated with potentially upgrading the Sacramento Regional WWTP (hereby referred to as Sac WWTP) with ozonation as an additional treatment step toward targeted pesticide removals. Utilizing ozonation for pesticide removal is associated with potential savings, improved water quality, etc. [18]. Throughout this study, ozonation was termed as the 'cost of taking action' to meet the aquatic benchmark concentration downstream of the WWTP. We approached the shadow price estimation by modifying the Cobb-Douglas production function into the output distance function to model anticipated wastewater effluent output [24, 29]. Shadow prices were derived using the trans-log output distance function, incorporating market price data and unit costs of treatment, with a focus on the desired output levels. The estimation of these shadow prices, representing the environmental benefits of projected pesticide removals, was conducted using the SciPy library in Python 3.8[25]. To simplify the calculations, the resulting shadow prices for the environmental benefits are to remain relatively stable over the analysis period. This method improves traditional cost-benefit analyses that do not consider social equity or environmental factors [24].

Additionally, a comparative assessment was conducted to evaluate the upgraded Sac WWTP potential to meet specified aquatic benchmarks. The assessment was conducted under two scenarios where the receiving stream was assumed to receive effluent from a) point source (i.e., WWTP) only and b) point and nonpoint (i.e., WWTP + other pathways) sources. Under the second scenario, the variability of the WWTP effluent downstream of the discharge was addressed via a Monte Carlo simulation using 1000 iterations. The most relevant parameters pertaining to the Cobb-Douglas function were identified for future feasibility studies.

5.3 METHODS AND MATERIALS

5.3.1 CASE-STUDY SITE SELECTION

The Sac WWTP is a large-scale secondary WWTP located in Elk Grove, California. The WWTP is situated in the highly urbanized Sacramento watershed, which, from our previous study, has significant municipal WWTP pesticide loading to a receiving stream. It serves a population of about 1.61 million within the Central Valley Region of the California Regional Water Quality Control Board. It is an activated sludge facility with a design capacity of 181 million gallons per day (MGD)[34]. The facility is staffed and operated 24 hours per day and the liquid treatment process consists of influent pumps, a septage receiving station, mechanical bar screening, aerated grit handling, grit classifiers that wash and dewater grit, covered primary sedimentation tanks, pure oxygen biological treatment by activated sludge, secondary sedimentation, nitrifying side stream treatment for ammonia removal, disinfection with sodium hypochlorite, and dichlorination with sodium bisulfite [34]. It also has a partially constructed and partially operating Primary Effluent Pump Station (PEPS) and biological nutrient removal facilities [34]. Effluent can be diverted to lined emergency storage basins (ESBs), as needed, to meet effluent dilution, thermal, and disinfection requirements or divert excess flows. Odors are controlled through stripping towers and carbon treatment. Treated wastewater effluent is discharged into the Sacramento River, which is a critical habitat for endangered species such as the chinook and steelhead salmon [11]. Relevant facility data were extracted from the National Pollutant Discharge Elimination System (NPDES) report (R5-2021-0019) [34].

Figure 14: Google image showing visually verified Sacramento Regional WWTP and discharge locations [34].

Table 2: Supporting details for the Sacramento Regional WWTP, information obtained from NPDES report [16, 34].

Property	Description
WWTP	Sacramento Regional WWTP
Facility coordinates	38.44807 -121.46238

Population served	1.61 million
Wastewater and stormwater runoff capacity	60 MGD
Existing flow	165 MGD
Design flow	181 MGD
Treated wastewater	624592947 L/day × 365 days = 2.2797×10^{11} L/year
Receiving stream flow	1300 CFS (840 MGD)
Treatment type	Secondary (Activated sludge)
Dilution factor (river to effluent)	(14:1) 95.47

5.3.2 ESTIMATION OF POLLUTANT LOADS

Three pesticides (i.e., fipronil, imidacloprid, permethrin) were targeted for this study according to their different physicochemical properties and represent the range of pesticides typically detected in municipal wastewater effluent [2]. The pesticides analyzed in this study are only on the parent compounds and do not assess their degradants or metabolites. Mean annual point pesticide concentrations were estimated using dilution factors from our previous study, and pesticide loads were calculated for the Sac WWTP effluent using equation 1. Historic nonpoint data were drawn and summed up from the California Department of Pesticide Regulation Pesticide Use Reporting (PUR) database using equation 2 [35]. By estimating the loads on an annual basis, seasonal patterns of residential down-the-drain runoff were considered for the estimation. All the pesticide loads were converted to milligrams per liter to ensure even shadow price estimations.

$$(1)\ \text{WWTP pesticide load}\left(\frac{\text{mg}}{\text{L}}\right) = \frac{\left[\text{WWTP existing flow (mgd)} \times \text{pesticide concentration}\left(\frac{\text{mg}}{\text{L}}\right)\right]}{133{,}171.2\text{kg/day}} \times 1000\text{mg}$$

$$(2)\ \text{Nonpoint pesticide load}\left(\frac{\text{mg}}{\text{L}}\right) = \frac{\left[\text{nonpoint pesticide load}\left(\frac{\text{lbs}}{\text{gal}}\right) \times 453{,}592.37(\text{mg})\right]}{3785.41\text{mL}}$$

5.3.3 QUANTIFYING THE TOTAL COSTS OF PESTICIDE REMOVAL

‘Taking action’ refers to upgrading the current Sac WWTP with advanced wastewater treatment (ozonation) for additional pesticide residual removal, which has an assumed environmental merit. Literary cost estimates for ozonation primarily focus on energy consumption while staff, maintenance, and other costs are omitted [20, 22]. Additionally, the applicability of these cost functions to the United States is constrained by divergent markets and other external factors [36]. Here, we used the Sac WWTP 2023/24 annual comprehensive financial report to estimate the differences in capital, operational, and investment costs from upgrading the existing system to include ozonation [37]. The value differences were then used as proxy inputs for the shadow price estimations. To simplify the calculations, ozonation functional costs were categorized based on available EPA guidelines: energy consumes 45% of total WWTP costs, labor and staff cost is 30%, maintenance cost is 20%, and other cost is 5% [28, 38]. From these estimations, the total cost per volume of taking action (i.e., upgrading WWTP technology) was calculated using the following equation:

(3) Treatment cost per volume of effluent = $[C_{costs}(\$) + M_{costs}(\$) + I_{costs}(\$)] / V(L)$

Where C_{costs} is the total capital cost from equipment, labor, and associated construction costs in dollars, M_{costs} is the total annual cost associated with operation, maintenance, energy, and material costs for Sac WWTP upgrades in dollars, I_{costs} is the total indirect costs such as land, legal fees, overhead and debt interest rates in dollars, and V represents the reported annual effluent flow volume of Sac WWTP in liters. These values are amortized over the estimated lifespan of the WWTP project, which is given as 30 years [37]. The functional unit costs per liter were calculated by dividing the estimated cost of the upgraded Sac WWTP by its reported annual discharge. Table A3 in the Appendix provides the detailed financial cost breakdown for the shadow price estimations.

Table 3: Budgeted cost breakdown for Sac WWTP upgrade (ozonation)

Cost Classifications	**Units ($)**
Energy (45%)	57,063,623
Labor and Staff (30%)	38,042,416
Maintenance (20%)	25,361,610
Others (5%)	6,340,403
Total (100%)	126,808,052

5.3.4 QUANTIFYING OTHER INDIRECT COSTS FROM PESTICIDE DISCHARGES

Considering the current secondary wastewater treatment as the 'status quo,' long-term impacts of aquatic ecosystem exposure to WWTP pesticide residue are difficult to quantify due to a lack of available data. Based on public consumption advisories, revenue losses due to aquatic population decline from chronic pesticide exposure were inferred from previously estimated annual fishery losses from pesticide usage [39]. However, these losses cannot be updated and quantified within the Sacramento context due to limited aquatic population data. Even though the United States' harvestable fish populations provide $4.8 billion to the country's economy, the long-term losses from pesticide exposure are not accounted for [40]. Due to this lack of data, the long-term losses were factored into the projected 'investment costs' for the Sac WWTP. This indirect cost provides a rough estimate of the indirect costs associated with pesticide residue exposure.

5.3.5 SHADOW PRICE ESTIMATION

After estimating the costs for the Sac WWTP, shadow prices of pesticide residue removal using ozonation were estimated using the output distance function (equation 6)[31]. This function is modified from the Cobb-Douglas function (equation 5) that calculates the production output from a system using elasticity coefficients [41]. Compared to the Cobb-Douglas function, the output distance function models the joint production of multiple outputs (treated water, nutrients, pesticides) based on multiple inputs (energy, staff, etc.), which makes it a more effective method of estimating the environmental benefits of WWTPs [25, 28]. It is also not dependent on behavioral factors and does not require a minimum or maximum base cost for analysis[28].

(4) $$Q = AK^{\alpha}L^{\beta}$$

Where Q is the output in milligrams per liter (mg/L), A is the total productivity factor (dimensionless), K is the capital input in dollars, L is the labor input in hours or days, and α and β are the output elasticities for capital and labor (dimensionless) respectively. The output elasticities represent the percentage change in output for a 1% change in the respective input. The Q, which represents an ideal objective output, is optimized in equation 5 below:

(5) $$D_0\ (x, u) = \text{Min}\ \{\theta{:}\left(\frac{u}{\theta}\right) \in P(x)\}$$

Following the Cobb-Douglas production function framework, $D_0\,(x, u)$ is the minimal optimization value associated with the WWTP treatment input, *x*, to produce a desired output, *u*. For the output distance function (D_0), let *x* and *u* denote the vectors of input and output quantities, respectively. P(*x*) denotes all the input vectors that are technically feasible for treatment processes and notes that $u \in P(x)$ if and only if $D_0(x, u) <= 1$. Therefore, we assume that advanced treatment technology produces both desired output (clean, treated water) and undesired outputs (TSS, BOD, N, pesticides). Using linear parameterization, we estimated the minimum cost required to obtain the maximum environmental benefit, i.e., avoided cost from WWTP pesticide removal. The trans-log form of the output distance function was utilized to ensure production homogeneity. This functional form generated the objective function, which was resolved using Python 3.8:

$$(6)\ \ \ln D_0\ (x,u)\ = \alpha_0 + \Sigma_{m=1}^{M} \alpha_m \ln u_m + \Sigma_{n=1}^{N} \beta_n \ln x_n + \frac{1}{2} \Sigma_{n=1}^{N} \Sigma_{m=1}^{M} \gamma_{nm}\ (\ln x_n)(\ln u_m) + \frac{1}{2}\ \Sigma_{n=1}^{N} \Sigma_{n'=1}^{N} \beta_{nn'}\ (\ln x_n)(\ln x_{n'}) + \frac{1}{2}\ \Sigma_{m=1}^{M} \Sigma_{m'=1}^{M} \alpha_{mm'}\ (\ln u_m)(\ln u_{m'})$$

Where α_0 is the constant or intercept, N refers to the number of cost inputs: energy in dollars per liter (x_1), labor and staff in dollars per liter (x_2), operation and maintenance in dollars per liter (x_3), other costs in dollars per liter (x_4); M equals the number of outputs: desirable is treated water in liters per year (u_1); undesirables are TSS in milligrams per liter (u_2), N milligrams per liter (u_3), BOD in milligrams per liter (u_4), selected pesticides in milligrams per liter (u_5-u_7); parameters to be estimated are α, β, γ, which are coefficients of elasticity for the input, desired and undesired outputs. The parameterized values represent the avoided costs generated from the removal of total suspended solids (TSS), biological oxygen demand (BOD), nitrogen (N), and pesticides from the advanced WWTP process. Using a heuristic approach, the bounds for the minimized objective function ranged from -1 to 1 due to the inherent nonlinearity [31]. Since the objective function was inherently nonlinear, we used the SciPy library to minimize the trans-log of the output distance function. The estimated parameters were then factored into the Cobb-Douglas function to generate the avoided cost per volume of treated wastewater. The constraints for this equation were such that:

(i) $\ln D_0\ (x, u)\ \geq 0$

(ii) $\Sigma_{n=1}^{N} \alpha = 1;\ \Sigma_{n=1}^{N} \beta_n \Sigma_{n1}^{N} = \Sigma_{m=1}^{M} \gamma_{nm} = 0$

(iii) $\frac{\partial \ln D_0\ (x,u)}{\partial \ln x} \geq 0$

(iv) $\frac{\partial \ln D_0\ (x,u)}{\partial \ln u_{m'}} \geq 0, m' = 2, 3,4 \ldots$

The shadow prices are estimated by assigning a reference price (r_m) for the treatment of the wastewater. We utilized a revenue function *R(x, u)* and assumed a relationship duality between that and the output distance function $D_0\ (x, u)$ to calculate the shadow prices of the outputs [24]. The calculation of absolute shadow prices for the undesirable outputs (m') means that the shadow price of the absolute desirable output coincides with the market price (r_m^0) [24, 25]. In this way, each shadow price for the undesirable outputs is estimated using the following equation:

$$r_{m\prime} = r_m^0 \frac{\partial D_0(x,u)/\partial u_{m\prime}}{\partial D_0(x,u)/\partial u_m} \geq 0 \tag{7}$$

Based on the targeted shadow price estimations, we analyzed the results to understand the cost savings associated with the treatment upgrade of the Sac WWTP.

Table 4: Input cost data for the shadow price estimations

Inputs	**($/L)**
Energy	0.00055
Labor and staff	0.00036
Operations and maintenance	0.00024
Others	6.057×10^{-5}
Total cost	0.0012

Table 5: Output data for the shadow price estimations

Undesirable output	(mg/L)
Fipronil	Reporting Limit = 4×10^{-7} to 2×10^{-5} Discharge Concentration = 1×10^{-4} WWTP Annual load = 1×10^{-4}
Imidacloprid	Reporting Limit = 9.9×10^{-6} to 2.89×10^{-4} Discharge Concentration = 9.5×10^{-5} WWTP Annual load = 0.118
Permethrin	Reporting Limit = 1×10^{-4} to 0.001 Discharge Concentration = 0.043 WWTP Annual load = 0.053
BOD_5	120
TSS	120
Nitrogen	27

5.3.6 SCENARIO ANALYSIS FOR POINT AND NONPOINT DISCHARGES

To conduct the scenario analysis, monitoring downstream of the effluent discharge is necessary to characterize the extent of actual dilution. Targeted pesticide residue was evaluated at a point downstream of the effluent discharge, assuming a) 100% WWTP effluent and b) WWTP effluent + nonpoint runoff components. Assuming a steady flow state, aquatic benchmark comparisons were conducted using the mass-balance approach to determine the expected downstream receiving water concentrations [42]. Each downstream receiving water concentration was then compared to applicable aquatic benchmarks to determine if the ozonized effluent discharge had reasonable exceedance potential. If the resulting downstream concentration was greater than the reporting limit, aquatic exceedance was apparent. This approach allowed for dilution to be factored into the analysis. For the point source, we assumed a 50% to 95% reduction in WWTP effluent pesticide concentration to meet said benchmarks. The downstream receiving water concentration from point source discharge was then calculated using the following equation:

$$C_r = (Q_s C_s + Q_d C_d) / (Q_s + Q_d) \tag{8}$$

Where Q_s is the receiving stream flow in L/day, Q_d is the design effluent flow from the discharge point (maximum permitted discharge) in L/day, C_s is the stream pesticide concentration in ug/L, C_d is the reduced effluent pesticide concentration in µg/L, C_r is the downstream receiving water pesticide concentration in µg/L. According to the NPDES report, the receiving stream flow (Q_s) is 1300 cfs (840 MGD) [34]. The design effluent flow (Q_d) is 280 cfs (181 MGD), the maximum permitted effluent flow allowed for Sac WWTP. The SURF database was used to extract real-world in-stream concentrations for the pesticides (fipronil, permethrin, imidacloprid) and converted from parts per billion (ppb) to µg/L [43].

We followed a similar approach for the second scenario, where both point and non-point pesticide concentrations were factored into the steady-state model:

$$C_r = (Q_s C_s + Q_d\,(p_d C_d + p_n C_n) / (Q_s + Q_d) \tag{9}$$

Where Q_s is the receiving stream flow in L/day, Q_d is the design effluent flow from the discharge point (maximum permitted discharge) in L/day, C_s is the stream pesticide concentration in µg/L, C_d is the reduced effluent pesticide concentration in µg/L, C_n is the nonpoint pesticide concentration in µg/L, C_r is the downstream receiving water pesticide concentration in µg/L. p_n and p_d are the weights of WWTP effluent and nonpoint concentrations in the stream, ranging from 0 to 1. Finally, we performed a Monte Carlo simulation with 1000 iterations to evaluate the uncertainty in downstream pesticide concentrations (C_r) using Python 3.8. The simulation involved randomly sampling parameters related to the receiving stream flow and design effluent flows (see Table 5), considering both point and nonpoint sources. By incorporating these variabilities, we aimed to assess the potential fluctuations in C_r. This approach allowed us to model the system comprehensively and generate a distribution of C_r values, providing insights into the range of possible outcomes for both point and nonpoint scenarios. From these two scenario outcomes, we could compare the better ecological outcome from the upgraded Sac WWTP to the receiving stream.

5.4 RESULTS

5.4.1 SHADOW PRICE ESTIMATIONS FOR PESTICIDE REMOVAL

For this study, we estimated shadow prices for removing targeted pesticides to meet aquatic benchmarks using Python 3.8. Using the non-linear least squares (NLS) method, we estimated the parameters and found the total avoided cost to be $0.007 per liter of treated effluent. To determine shadow prices, we assigned a reference price of $0.0012 per unit, representing the total cost of treating wastewater, to the desirable output. The shadow price represents the avoided cost associated with the pesticide removals from ozonation and is negative since it is not a marketable output that can generate a direct income for the WWTP [23, 25]. The estimated shadow prices and environmental benefits for each of the undesirable outputs from implementing ozonation at the Sac WWTP are reported in Tables 6 and 7.

Table 6: Shadow prices for the undesirable outputs (\$/µg)

Output (Parameter Index)	Beta Parameter Value	Shadow Price (\$/µg)
Undesirable Output		
BOD_5	-2.08608	-0.00250
Nitrogen	1.11095	0.00133
TSS	-2.23265	-0.00267
Fipronil	-1.693345	-0.00203
Imidacloprid	0.685136	0.00082
Permethrin	-1.697229	-0.00203
Total		-0.00709

Table 7: Environmental benefit of treatment in \$/L

Pollutants	Shadow Prices (\$)	Share in Total (%)	Contribution to Total Value (million of \$)
BOD_5	0.00250	35.3	571
Nitrogen	(0.00133)	(18.8)	(304)
TSS	0.00267	37.8	611
Fipronil	0.00203	28.6	463
Imidacloprid	(0.00082)	(-11.5)	(187)
Permethrin	0.00203	28.7	464
Total Cost per liter	0.0071	100	
Total Value of Treated Wastewater (\$)	$0.0071 \times 2.2797 \times 10^{11} = 1,617,650,043.3$		

Total suspended solids (TSS), with a shadow price of -\$0.00267919 and the largest share of 37.76%, represents a significant environmental burden. With a shadow price of -\$0.00250331, biological oxygen demand (BOD_5) contributes 35.28% to the total shadow price and stands out as a pollutant whose removal can lead to significant environmental benefits. Investing in the removal of BOD_5 and TSS from wastewater can result in considerable cost savings, making it a worthwhile investment for environmental protection. Despite having a positive shadow price of

$0.00133314 and a -18.79% contribution, nitrogen's presence in treated effluent is associated with reduced costs, implying it may not provide as much environmental benefit upon removal. This suggests that investing in its removal might lead to less environmental savings and potentially higher costs.

For the pesticides, fipronil has a shadow price of -$0.00203201 and contributes a 28.64% share of the total amount, which is a major environmental concern. Similar to fipronil, permethrin has a shadow price of -$0.00203668 and a contribution of 28.70%. The negative shadow price indicates that investments in their removals will likely result in notable environmental benefits and potential savings in treatment costs. With a positive shadow price of $0.00082216 and a -11.59% contribution, the removal of imidacloprid appears to be less critical from a cost-saving perspective. Its positive shadow price suggests that it might not be as environmentally detrimental as other pollutants, or its removal might not lead to significant cost savings.

5.4.2 DOWNSTREAM COMPARISONS FOR WWTP AND OTHER PESTICIDE PATHWAYS

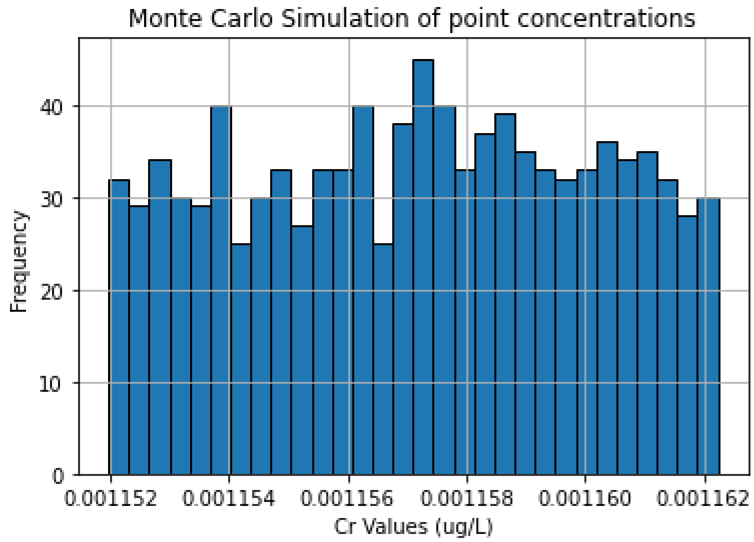
For the scenario analysis, the critical downstream concentrations of the three pesticides were evaluated under point-only contributions, and both point and nonpoint contributions. For the first scenario, we used a minimum 50% reduction in the WWTP effluent to a maximum of 95% pesticide residue removal for the three targeted pesticides. Ozonized wastewater effluent discharge yielded a downstream imidacloprid concentration of 0.0065µg/L, which was above the reporting limit (0.0002897µg/L). For fipronil, the downstream concentration was 0.0016µg/L, which also ranked above the reporting limit. Permethrin had values ranging from 0.0056µg/L to

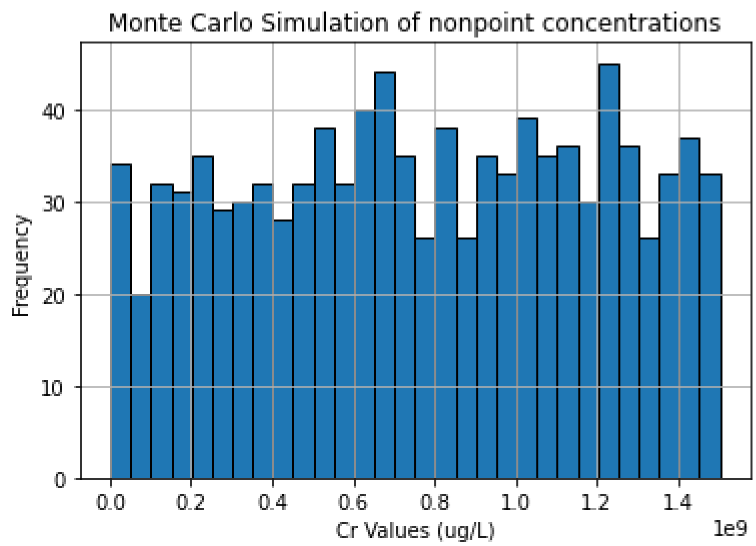
0.0021µg/L, which was slightly above the reporting limits. This range of values indicate that upgrading the Sac WWTP has an ecological benefit from permethrin reduction.

Table 8: Critical downstream concentrations of pesticides to model ecological impact

Pesticide	**Reporting Limit (µg/L)**	**Cr with no treatment**	**C_r at 50% reduction (µg/L)**	**C_r at 95% reduction (µg/L)**
Imidacloprid	9.9×10^{-6} to 2.89×10^{-4}	0.0001	0.0016	0.0016
Fipronil	4×10^{-7} to 2×10^{-5}	0.000095	0.0065	0.0065
Permethrin	1×10^{-4} to 0.001	0.043	0.0056	0.0021

Following the point model, we conducted a Monte Carlo simulation for both point and nonpoint sources for imidacloprid. From our results, the point source (WWTP discharge) exhibits a decreasing trend in the critical downstream concentration with increasing proportion. However, the nonpoint discharge did not display significant changes or trends associated with the downstream concentrations. Finally, the combination of both point and nonpoint discharges yielded no significant trends in downstream concentrations.


Monte Carlo Simulation of point concentrations
Frequency
0
10
20
30
40
0.001152
0.001154
0.001156
0.001158
0.001160
0.001162
Cr Values (ug/L)


Monte Carlo Simulation of nonpoint concentrations
Frequency
0
10
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1e9
Cr Values (ug/L)

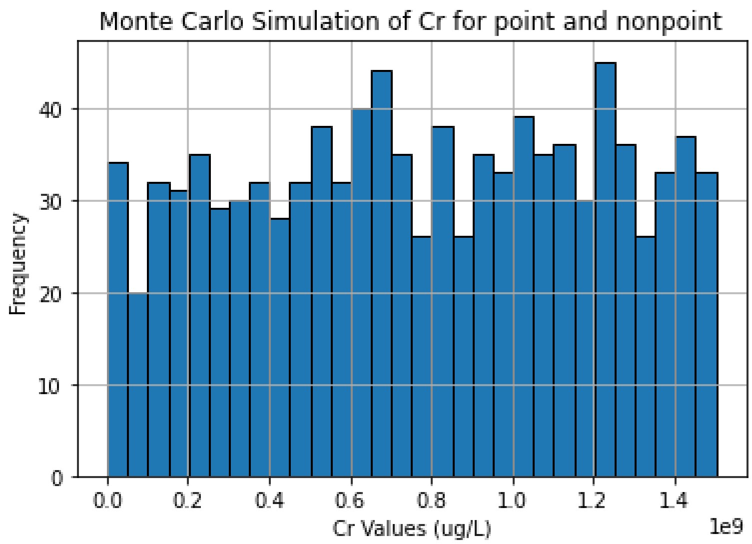


Figure 15: Chart showing the Monte Carlo simulations of imidacloprid downstream concentrations

5.5 DISCUSSION

This section summarizes the results from the shadow price estimation and aquatic benchmark comparisons for an upgraded Sac WWTP. Our objective was to provide an exemplary case study by estimating environmental benefits (expressed in monetary terms) from treating WWTP effluent with ozone. Ozonation is known for its efficiency in removing micropollutants and trace contaminants from wastewater [18]. These results were based on the WWTP characteristics and other factors such as pesticide concentrations, dilution factors, and projected costs per volume. We also assumed a steady flow state for the receiving stream to facilitate the critical downstream concentration estimates. By breaking down and oxidizing these harmful substances it helps protect aquatic ecosystems in Sacramento's streams. This, in turn, preserves the health and diversity of aquatic life, contributing to a more balanced and sustainable ecosystem.

From our shadow price estimations, fipronil and permethrin had shadow prices of \$0.002/μg and significantly larger shares for the environmental benefits when compared to imidacloprid (\$0.0008/μg). This price may be more effective for fipronil as it has the lowest dilution factor required to meet aquatic benchmarks from previous studies. However, this price may vary depending on the dynamics of pesticide usage and discharge within such a vulnerable watershed. Imidacloprid, along with nitrogen, showed positive shadow prices. The positive shadow price for imidacloprid is reasonable, given that their current concentration levels are already within aquatic benchmarks and further removal does not yield additional benefits. The positive shadow price for nitrogen may also suggest that its production is linked to other desirable outputs in a way that outweighs its negative aspects, leading to a positive shadow price. In summary, pollutants like BOD_5, TSS, fipronil, and permethrin, with their negative shadow prices, emerge as key targets for investment in advanced treatment processes. Their removal can lead to significant environmental benefits and cost savings. On the other hand, pollutants like nitrogen and imidacloprid, with positive shadow prices, suggest that their removal might not offer the same level of environmental or economic benefits.

The scenario analysis conducted to evaluate critical downstream concentrations of pesticides under different contribution scenarios (point-only and point-and-nonpoint) provides valuable insights into the potential ecological impacts and the effectiveness of wastewater treatment plant (WWTP) upgrades. The study investigated two distinct scenarios: point-only contributions and both point and nonpoint contributions for a more accurate assessment of the environmental impact. The observed ranges of values for imidacloprid and fipronil downstream concentrations indicate that upgrading the Sac WWTP can have a positive ecological benefit for aquatic life in the long term. While some pesticides remain a concern within this watershed, the findings imply that targeted improvements can lead to reduced pesticide pollution in the receiving waters in the end. This steady-state model can be extended to incorporate other pesticides of concern, thereby providing a versatile tool for understanding and addressing water quality issues associated with various pesticides.

From the Monte Carlo simulations, the findings reveal a decreasing trend in the critical downstream concentration of imidacloprid with an increasing proportion of WWTP discharge. This suggests that as a higher proportion of the effluent from the WWTP contributes to the water body, the downstream concentration of imidacloprid tends to decrease. In contrast to the point model, the simulation of nonpoint discharge did not reveal significant changes or trends associated with the downstream concentrations. This means that variations in nonpoint sources (such as stormwater runoff and agricultural or urban discharge) may not have a significant impact on the downstream concentration of imidacloprid based on their relative loads within the receiving stream. Additionally, the interactions between point and nonpoint sources may be influenced by various factors, making it difficult to predict their combined effects. These results warrant a focus on optimizing point source discharge, where wastewater pollution control efforts can be maximized for greater efficiency.

5.6 CONCLUSIONS

Meeting California's aquatic standards for water quality is of paramount importance to protect and sustain aquatic ecosystems [13, 44]. In this study, we estimated the shadow price for pesticide removal in a large-scale WWTP in a highly urbanized watershed. Based on our estimations, the shadow price for the proposed upgrade was $0.007 per volume of treated effluent. Also, our results from simulating scenario analyses highlighted the impact of point source discharges on aquatic life. The results from this study show that WWTP upgrades are a promising avenue for achieving said standards, as they have a decreasing trend in downstream pesticide concentrations. This underscores the necessity of continued investments in wastewater treatment infrastructure to reduce pesticide contamination's ecological impact and align with California's stringent water quality regulations. The lack of significant trends in the combined point and nonpoint sources also highlights the complexity of interactions between different pollution sources. Understanding these interactions may require further investigation as several assumptions about pesticide chemistry, transport, and fate were not fully represented in the model. Additional real-world data, including best management practices, can help to refine the model’s accuracy and complement WWTP upgrades in reducing nonpoint source pollution. This work provides a foundation for understanding the behavior of pesticides in water bodies and the potential benefits of upgrading wastewater treatment facilities. Sharing these results with stakeholders can enhance the effectiveness of pollution control efforts to ensure that they align with California’s ecological goals.

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5.8 APPENDIX

Table A 3: Table showing the financial cost breakdown data used for estimating the shadow prices from advanced WWTP treatment targeting pesticide removals [37]

Cost Classifications	**2022/23 Expenditure ($)**	**2023/24 Budgeted Expenditure ($)**
Operating expenses		
Electricity	12,000,000	14,000,000
Other utilities	608,643	743,747
Equipment	300,000	367,000
Chemicals	21,377,475	26,309,000
Data processing	8,678,893	10,222,179
Laboratory	5,102,982	5,960,265
Services and supplies	2,736,069	92,535,239
Program Management	834,417	872,944
Other upgrades	659,664	717,173
Other Charges	9,621	7,146,000
Sac WWTP Labor	11,171,392	12,128,192
Sac WWTP Staff	18,893,706	20,814,903
Consultants	5,162,970	6,310,751
Sac WWTP Maintenance	24,942,909	27,974,486
Interceptor maintenance	9,211,903	9,978,700

Land Maintenance	1,417,201	1,612,580
Capital Expenditures		
Acquisition and construction of capital assets	40,204,596	156,532,051
Landfill closure and post closure care	1,075,686	-
Insurance	1,209,483	-
Investment Expenditures		
Depreciation and amortization	2,354,283	2,400,000
Bonds/Loans	62,000,000	100,000,000
Debt (Principal + Interest)	125,000,000	134,000,000
Contingency	0	2,000,000
Other expenses	1,500,068	-
Total Expenditure	356,451,961	632,625,210

Table A 4: Parameters and their corresponding coefficients from the parameterization of the output distance function. The α values correspond to the inputs, the β values correspond to the outputs, the γ values correspond to the interactions between inputs and output

Parameter Type	**Description**	**Values**
Alpha	Input-related parameters	$\alpha_0 = 4.80090853$; $\alpha_1 = 6.17679482$; $\alpha_2 = 21.648646$; $\alpha_3 = -3.85740535$
Beta	Output-related parameters	$\beta_0 = 3.20925499$; $\beta_1 = -2.08608991$; $\beta_2 = 1.11095315$; $\beta_3 = -2.23265706$; $\beta_4 = -1.693345$; $\beta_5 = 0.685136425$; $\beta_6 = -1.69722944$
Gamma	Interaction between inputs and outputs	$\gamma_0 = 1.05871864$; $\gamma_1 = -1.52415151$; $\gamma_2 = -0.0843684582$; $\gamma_3 = -0.506167726$; $\gamma_4 = 0.395777731$ ... (28 values in total)
Delta	Interaction between outputs	$\delta_0 = 6.78254092$; $\delta_1 = 0.634311074$; $\delta_2 = -0.489169895$; $\delta_3 = 0.703029071$; $\delta_4 = -5.5357494$ ... (49 values in total)

CHAPTER 6: SUMMARY, CONCLUSIONS AND FUTURE WORK

6.1 SUMMARY OF FINDINGS AND CONCLUSIONS

The overall goal of this research was to develop a geospatial analysis of wastewater-derived pesticides in California's urban receiving streams and to explore the potential environmental benefits of improving their wastewater infrastructure. This goal was achieved through completion of three studies. The first study was conducted by quantifying pesticide concentrations at WWTP discharge points and identifying the most vulnerable streams to pesticide loads. The second study involved the generation of a multimetric index using climatic and hydrologic data to model pesticide transport and fate within watersheds. Lastly, the third study assessed the environmental impacts associated with the upgrade of a selected WWTP to meet stipulated aquatic benchmarks for targeted pesticide loads.

A geospatial model using Geographic Information System (GIS) was created by incorporating 165 surface-discharging California WWTP characteristics across the state. From the developed model framework, selected pesticide concentrations were quantified at the discharge sites, and streams at higher risks of benchmark exceedance were identified by comparing the modeled pesticide concentrations to aquatic safety thresholds. Under mean annual flow conditions, 32% of the median pesticide concentration across all sites was less than 0.0001 µg/L and 62% of the sites concentrations fell below 0.0005 µg/L. Under low stream flow conditions (modeled as 7-day 10-year low), the median pesticide concentrations across the sites were estimated to be up to ten times below the benchmark. Our results indicated that streams with a lower Strahler stream order (≤ 3) have lower buffering abilities due to the high required DF to meet or exceed the aquatic thresholds. This increase is worsened by seasonal droughts such as the 7Q10 that lead to lower stream volumes and higher instream pesticide concentrations. Based on our results, we accept the hypothesis that California WWTPs are a significant contributor of pesticide residue into streams.

Next, a multimetric pesticide vulnerability index (PVI) was developed using stream characteristics and climatic data identify the most impacted watershed by point and nonpoint pesticide pollution sources in California. In addition, hot spots analysis was performed to elucidate regions of high likelihood of pesticide discharges. Our modeling results suggest that point pesticide loads are most likely to occur in highly urbanized watersheds such as the San Francisco Bay. Nonpoint pesticide loads are more likely to emanate from agricultural usage, hence their notable hotspots in the Sacramento Valley watersheds. Overall, the current and projected PVI indicate an increasing likelihood of worsening loads due to the impact of increased precipitation and runoff. Based on our results, we accept the hypothesis that highly vulnerable watersheds are positively correlated with endangered species.

Finally, an environmental benefits analysis for upgrading a secondary WWTP towards targeted pesticide removals was conducted based on budgeted costs. From these input costs, shadow price parameters were incorporated into the output distance function for estimating the avoided cost per liter of treated wastewater. Our results show that our estimated shadow price of $0.007 per liter of treated effluent has some merit for pesticide removals. This analysis indicates that the environmental benefits of upgrading the secondary wastewater treatment plant for targeted pesticide removal outweigh the budgeted costs, signifying a favorable cost-benefit ratio. Our study also found that critical downstream pesticide concentrations were more likely to meet aquatic benchmarks when oxidation was factored into our steady state models. This has the potential to improve protection of aquatic ecosystems located downstream of the WWTP effluent discharges. Based on our results, we accept the hypothesis that advanced WWTP implementation has positive ecological and economic merit within vulnerable watersheds.

6.2 LIMITATIONS

The presented model serves as a valuable framework for assessing the ecological consequences of pesticide pollution and evaluating the efficacy of pollution control measures. It can be extended to incorporate other pesticides of concern, providing a versatile tool for understanding and addressing water quality issues associated with various pesticides. This study is, however, limited by the availability of data for model inputs at the watershed level. The study also relies on numerous assumptions about pesticide behavior, transport, and fate, which may not fully represent real-world conditions. In addition, some of the data obtained is dated and may not be updated enough to meet current stream conditions. Data quality and availability can vary, and discrepancies in monitoring and reporting at different WWTPs may introduce uncertainties in the analysis.

This study focuses on mean annual and low stream flow conditions that may not fully capture the temporal variability of pesticide pollution across watersheds. Pesticide concentrations can fluctuate depending on changing weather patterns and seasonal variations. Therefore, a more comprehensive understanding of these dynamics is needed. Finally, this study is on pesticides, which are of critical emerging concern due to changing uses by consumers. However, future research could consider a broader range of contaminants and look into their combined effects on watershed health to provide a more comprehensive assessment of water quality.

The presented model of estimating the shadow prices and ecological impacts of upgrading a secondary WWTP to incorporate advanced treatment methods is limited to one sample size and by availability of cost data. Several assumptions were also made to model the production cycle and output parameter values. Future work can involve scaling for both small and large scale WWTPs and can be adapted for various locations depending on each plant's requirements. This model can be extended for environmental impact assessments on a wider array of WWTPs and watersheds across the state for multiple treatment upgrades.

6.3 FUTURE WORK

Future work should incorporate long-term field monitoring of pesticide concentrations and other non-pesticides to capture seasonal and climatic variations while understanding their dynamics fully. Incorporating up-to-date data on wastewater treatment plants (WWTPs), stream attributes, and pesticide concentrations will enhance our model accuracy. Additionally, this study could extend the assessment of environmental impacts to a wider array of WWTPs and watersheds across the state. Evaluating various WWTP upgrade scenarios and quantifying potential benefits could help streamline future feasibility studies for decision-makers.

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CHAPTER 7: APPENDICES

7.1 SUPPLEMENTARY INFORMATION FOR CHAPTER 2

Table A 5: Pesticide removal rates from ATPs in pilot studies.

Pesticide	**Study Type**	**Advanced Treatment Process**	**Removal Rate (%)**	**Reference**
Fipronil Imidacloprid	Pilot (5 full-scale facilities)	Ozone; Reverse Osmosis	80-97% 44-74%	King et al. 2020 [96]
Dieldrin DDx	Pilot (1 full-scale facility model)	Ozone	61-78% 58-71%	Kenny et al. 2018 [97]
Sulfamethoxazole	Pilot	Membrane	80%	Lopes et al. 2020 [98]
Imidacloprid	Pilot	UV	90%	Cerreta et al. 2019 [99]
Chlorpyrifos, Diazinon, Carbofuran	Pilot	Bio-filtration; Granular Activated Carbon (GAC) filter	66.5%-81.3%	Pham et al. 2013 [100]
Herbicide Terbuthylazine	Pilot	Constructed Wetlands (CWs) and	58.4%-73.7%	Gikas et al. 2018 [101]

		Biopurificaton systems (BPS)		
Diazinon, Phosalone, and Chlorpyrifos	Pilot	Adsorption; Mixed hemimicelle SDS-coated magnetic chitosan nanoparticles (MHMS-MCNPs)	96%-98%	Bandforuzi & Hadjmohamma 2019[102]
Alachlor, atrazine, chlorfenvinphos, diuron, and isoproturon	Pilot	Ozone	26%	Saleh et al. 2020[95]
Atrazine	Pilot	Submerged biological aerated filter (SBAF)	97.9%	Saleh et al. 2020[95]

7.2 SUPPLEMENTARY INFORMATION FOR CHAPTER 4

7.2.1 DEVELOPMENT OF GROUPED SPEARMAN'S RANK CORRELATION

After generating the simulated index values, we conducted Spearman's rank correlation analysis to determine the correlation between each watershed's selected pesticide concentration and their corresponding point, nonpoint, and PVI values. Field concentrations for five selected pesticides (bifenthrin, cypermethrin, permethrin, fipronil, and imidacloprid) were extracted from the SURF database[1] and spatially joined to associated watersheds to establish the correlations. The datasets ranged from 2016 to 2021 for the following pesticides: bifenthrin (n=5006), cypermethrin (n=4202), fipronil (n=2511), permethrin (n=6543), and imidacloprid (n=2380). Watershed PVI values were split based on the median PVI score (i= 6.206) into less and more vulnerable watersheds to pesticide loads and analyzed using IBM SPSS Statistics 29 software.

a. BIFENTHRIN

Table A 6: Spearman's rank correlations across all watersheds

Correlations

			PI_wHydro	BifenthrinConc	NPIwHydro	PVI
Spearman's rho	PI_wHydro	Correlation Coefficient	1.000	-.044**	.371**	.703**
		Sig. (2-tailed)	.	.003	<.001	.000
		N	4419	4419	4419	4419
	BifenthrinConc	Correlation Coefficient	-.044**	1.000	-.168**	-.168**
		Sig. (2-tailed)	.003	.	<.001	<.001
		N	4419	5006	4894	4419
	NPIwHydro	Correlation Coefficient	.371**	-.168**	1.000	.874**
		Sig. (2-tailed)	<.001	<.001	.	.000
		N	4419	4894	4894	4419
	PVI	Correlation Coefficient	.703**	-.168**	.874**	1.000
		Sig. (2-tailed)	.000	<.001	.000	.
		N	4419	4419	4419	4419

**. Correlation is significant at the 0.01 level (2-tailed).

b. CYPERMETHRIN

Correlations

			CypermethrinConc	NPIwHydro	PI_wHydro	PVI
Spearman's rho	CypermethrinConc	Correlation Coefficient	1.000	-.194**	-.087**	-.221**
		Sig. (2-tailed)	.	<.001	<.001	<.001
		N	4202	4090	3652	3652
	NPIwHydro	Correlation Coefficient	-.194**	1.000	.352**	.879**
		Sig. (2-tailed)	<.001	.	<.001	.000
		N	4090	4090	3652	3652
	PI_wHydro	Correlation Coefficient	-.087**	.352**	1.000	.671**
		Sig. (2-tailed)	<.001	<.001	.	.000
		N	3652	3652	3652	3652
	PVI	Correlation Coefficient	-.221**	.879**	.671**	1.000
		Sig. (2-tailed)	<.001	.000	.000	.
		N	3652	3652	3652	3652

**. Correlation is significant at the 0.01 level (2-tailed).

c. FIPRONIL

Correlations

			PVI	FipronilConc	PI_wHydro	NPIwHydro
Spearman's rho	PVI	Correlation Coefficient	1.000	-.155**	.883**	.885**
		Sig. (2-tailed)	.	<.001	.000	.000
		N	2307	2307	2307	2307
	FipronilConc	Correlation Coefficient	-.155**	1.000	-.135**	-.134**
		Sig. (2-tailed)	<.001	.	<.001	<.001
		N	2307	2511	2307	2460
	PI_wHydro	Correlation Coefficient	.883**	-.135**	1.000	.603**
		Sig. (2-tailed)	.000	<.001	.	<.001
		N	2307	2307	2307	2307
	NPIwHydro	Correlation Coefficient	.885**	-.134**	.603**	1.000
		Sig. (2-tailed)	.000	<.001	<.001	.
		N	2307	2460	2307	2460

**. Correlation is significant at the 0.01 level (2-tailed).

d. IMIDACLOPRID

Correlations

			PVI	Imidacloprid	NPIwHydro	PI_wHydro
Spearman's rho	PVI	Correlation Coefficient	1.000	-.394**	.896**	.861**
		Sig. (2-tailed)	.	<.001	.000	.000
		N	2120	2120	2120	2120
	Imidacloprid	Correlation Coefficient	-.394**	1.000	-.332**	-.401**
		Sig. (2-tailed)	<.001	.	<.001	<.001
		N	2120	2380	2339	2120
	NPIwHydro	Correlation Coefficient	.896**	-.332**	1.000	.592**
		Sig. (2-tailed)	.000	<.001	.	<.001
		N	2120	2339	2339	2120
	PI_wHydro	Correlation Coefficient	.861**	-.401**	.592**	1.000
		Sig. (2-tailed)	.000	<.001	<.001	.
		N	2120	2120	2120	2120

**. Correlation is significant at the 0.01 level (2-tailed).

e. PERMETHRIN

Correlations

			PVI	Permethrin	NPIwHydro	PI_wHydro
Spearman's rho	PVI	Correlation Coefficient	1.000	-.186**	.864**	.714**
		Sig. (2-tailed)	.	<.001	.000	.000
		N	5892	5892	5892	5892
	Permethrin	Correlation Coefficient	-.186**	1.000	-.149**	-.256**
		Sig. (2-tailed)	<.001	.	<.001	<.001
		N	5892	6543	6363	5892
	NPIwHydro	Correlation Coefficient	.864**	-.149**	1.000	.359**
		Sig. (2-tailed)	.000	<.001	.	<.001
		N	5892	6363	6363	5892
	PI_wHydro	Correlation Coefficient	.714**	-.256**	.359**	1.000
		Sig. (2-tailed)	.000	<.001	<.001	.
		N	5892	5892	5892	5892

**. Correlation is significant at the 0.01 level (2-tailed).

7.2.2 RESULTS FROM THE SPEARMAN'S RANK CORRELATIONS

Table A5 displays the outcomes from the PVI scores against field monitoring results for bifenthrin, cypermethrin, permethrin, fipronil, and imidacloprid. Overall, there is no statistically significant correlation between the PVI and the pesticide concentrations. In-depth differences from Tables A6 and A7 show the outcomes of the Spearman's rank correlations for the point, nonpoint, and PVI scores based on two groups of watersheds (less and more vulnerable). Overall, the less vulnerable watersheds demonstrated statistically significant positive correlations to the index values, with bifenthrin (ρ (PVI) = 0.349, $p < .001$) and imidacloprid (ρ (PVI) = 0.282, $p < .001$) having the highest positive correlations. Additionally, the pesticide with the least positive correlation was permethrin, with ρ(PVI) of -0.24, $p < .001$. For the more vulnerable watersheds, Spearman's rank correlation showed negative correlations for all the field pesticide data, with the best value shown for cypermethrin (ρ (PVI) = -0.237, $p < .001$). From these results, it is inferred that the PVI is more likely to highlight less vulnerable watersheds for pesticides such as bifenthrin and imidacloprid loadings and less likely to highlight more vulnerable watersheds for all the selected pesticide loadings. When comparing the point and nonpoint indices against the field values, the results varied across the pesticides. For the less vulnerable watersheds, higher statistically significant correlations were observed for nonpoint index values against the point index values. The only exception was bifenthrin, where the point index displayed a higher correlation against the nonpoint index values (ρ (PI) = 0.300, $p < .001$; ρ (NPI) = 0.204, $p < .001$). There were no statistically significant correlations observed between the field data and the point and nonpoint indices for the more vulnerable watersheds. The correlations between the field pesticide data and the indices demonstrate its effectiveness in identifying less vulnerable watersheds while determining the relative contributions of point vs nonpoint pesticide pollution sources.

a. BIFENTHRIN

Table A 7: Spearman's rank correlations for less vulnerable watersheds

Correlations

			NPI	PVI	PI	Bifenthrin
Spearman's rho	NPI	Correlation Coefficient	1.000	.442**	-.327**	.204**
		Sig. (2-tailed)	.	<.001	<.001	<.001
		N	2263	2263	2263	2263
	PVI	Correlation Coefficient	.442**	1.000	.463**	.349**
		Sig. (2-tailed)	<.001	.	<.001	<.001
		N	2263	2263	2263	2263
	PI	Correlation Coefficient	-.327**	.463**	1.000	.300**
		Sig. (2-tailed)	<.001	<.001	.	<.001
		N	2263	2263	2263	2263
	Bifenthrin	Correlation Coefficient	.204**	.349**	.300**	1.000
		Sig. (2-tailed)	<.001	<.001	<.001	.
		N	2263	2263	2263	2263

**. Correlation is significant at the 0.01 level (2-tailed).

b. CYPERMETHRIN

Correlations

			Cypermethrin	NPI	PVI	PI
Spearman's rho	Cypermethrin	Correlation Coefficient	1.000	.187**	.190**	.132**
		Sig. (2-tailed)	.	<.001	<.001	<.001
		N	1944	1944	1944	1944
	NPI	Correlation Coefficient	.187**	1.000	.493**	-.300**
		Sig. (2-tailed)	<.001	.	<.001	<.001
		N	1944	1944	1944	1944
	PVI	Correlation Coefficient	.190**	.493**	1.000	.440**
		Sig. (2-tailed)	<.001	<.001	.	<.001
		N	1944	1944	1944	1944
	PI	Correlation Coefficient	.132**	-.300**	.440**	1.000
		Sig. (2-tailed)	<.001	<.001	<.001	.
		N	1944	1944	1944	1944

**. Correlation is significant at the 0.01 level (2-tailed).

c. FIPRONIL

Correlations

			Fipronil	NPI	PVI	PI
Spearman's rho	Fipronil	Correlation Coefficient	1.000	.291**	.189**	.098**
		Sig. (2-tailed)	.	<.001	<.001	.004
		N	853	853	853	853
	NPI	Correlation Coefficient	.291**	1.000	.616**	-.308**
		Sig. (2-tailed)	<.001	.	<.001	<.001
		N	853	853	853	853
	PVI	Correlation Coefficient	.189**	.616**	1.000	.349**
		Sig. (2-tailed)	<.001	<.001	.	<.001
		N	853	853	853	853
	PI	Correlation Coefficient	.098**	-.308**	.349**	1.000
		Sig. (2-tailed)	.004	<.001	<.001	.
		N	853	853	853	853

**. Correlation is significant at the 0.01 level (2-tailed).

d. IMIDACLOPRID

Correlations

			Imidacloprid	NPI	PVI	PI
Spearman's rho	Imidacloprid	Correlation Coefficient	1.000	.181**	.282**	-.069*
		Sig. (2-tailed)	.	<.001	<.001	.045
		N	839	839	839	839
	NPI	Correlation Coefficient	.181**	1.000	.750**	-.507**
		Sig. (2-tailed)	<.001	.	<.001	<.001
		N	839	839	839	839
	PVI	Correlation Coefficient	.282**	.750**	1.000	-.062
		Sig. (2-tailed)	<.001	<.001	.	.075
		N	839	839	839	839
	PI	Correlation Coefficient	-.069*	-.507**	-.062	1.000
		Sig. (2-tailed)	.045	<.001	.075	.
		N	839	839	839	839

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

e. PERMETHRIN

Correlations

			Permethrin	NPI	PVI	PI
Spearman's rho	Permethrin	Correlation Coefficient	1.000	-.035	-.024	-.003
		Sig. (2-tailed)	.	.051	.181	.852
		N	3112	3112	3112	3112
	NPI	Correlation Coefficient	-.035	1.000	.459**	-.340**
		Sig. (2-tailed)	.051	.	<.001	<.001
		N	3112	3112	3112	3112
	PVI	Correlation Coefficient	-.024	.459**	1.000	.446**
		Sig. (2-tailed)	.181	<.001	.	<.001
		N	3112	3112	3112	3112
	PI	Correlation Coefficient	-.003	-.340**	.446**	1.000
		Sig. (2-tailed)	.852	<.001	<.001	.
		N	3112	3112	3112	3112

**. Correlation is significant at the 0.01 level (2-tailed).

a. BIFENTHRIN

Table A 8: Spearman's rank correlations for more vulnerable watersheds

Correlations

			Bifenthrin	NPI	PVI	PI
Spearman's rho	Bifenthrin	Correlation Coefficient	1.000	-.223**	-.309**	-.182**
		Sig. (2-tailed)	.	<.001	<.001	<.001
		N	2912	2800	2325	2325
	NPI	Correlation Coefficient	-.223**	1.000	.697**	.253**
		Sig. (2-tailed)	<.001	.	.000	<.001
		N	2800	2800	2325	2325
	PVI	Correlation Coefficient	-.309**	.697**	1.000	.825**
		Sig. (2-tailed)	<.001	.000	.	.000
		N	2325	2325	2325	2325
	PI	Correlation Coefficient	-.182**	.253**	.825**	1.000
		Sig. (2-tailed)	<.001	<.001	.000	.
		N	2325	2325	2325	2325

**. Correlation is significant at the 0.01 level (2-tailed).

b. CYPERMETHRIN

Correlations

			Cypermethrin	NPI	PVI	PI
Spearman's rho	Cypermethrin	Correlation Coefficient	1.000	-.174**	-.237**	-.092**
		Sig. (2-tailed)	.	<.001	<.001	<.001
		N	2402	2290	1852	1852
	NPI	Correlation Coefficient	-.174**	1.000	.662**	.342**
		Sig. (2-tailed)	<.001	.	<.001	<.001
		N	2290	2290	1852	1852
	PVI	Correlation Coefficient	-.237**	.662**	1.000	.883**
		Sig. (2-tailed)	<.001	<.001	.	.000
		N	1852	1852	1852	1852
	PI	Correlation Coefficient	-.092**	.342**	.883**	1.000
		Sig. (2-tailed)	<.001	<.001	.000	.
		N	1852	1852	1852	1852

**. Correlation is significant at the 0.01 level (2-tailed).

c. FIPRONIL

Correlations

			Fipronil	NPI	PVI	PI
Spearman's rho	Fipronil	Correlation Coefficient	1.000	-.395**	-.406**	-.241**
		Sig. (2-tailed)	.	<.001	<.001	<.001
		N	1658	1607	1454	1454
	NPI	Correlation Coefficient	-.395**	1.000	.687**	.194**
		Sig. (2-tailed)	<.001	.	<.001	<.001
		N	1607	1607	1454	1454
	PVI	Correlation Coefficient	-.406**	.687**	1.000	.808**
		Sig. (2-tailed)	<.001	<.001	.	.000
		N	1454	1454	1454	1454
	PI	Correlation Coefficient	-.241**	.194**	.808**	1.000
		Sig. (2-tailed)	<.001	<.001	.000	.
		N	1454	1454	1454	1454

**. Correlation is significant at the 0.01 level (2-tailed).

d. IMIDACLOPRID

Correlations

			Imidacloprid	NPI	PVI	PI
Spearman's rho	Imidacloprid	Correlation Coefficient	1.000	-.434**	-.436**	-.342**
		Sig. (2-tailed)	.	<.001	<.001	<.001
		N	1541	1500	1281	1281
	NPI	Correlation Coefficient	-.434**	1.000	.742**	.253**
		Sig. (2-tailed)	<.001	.	<.001	<.001
		N	1500	1500	1281	1281
	PVI	Correlation Coefficient	-.436**	.742**	1.000	.800**
		Sig. (2-tailed)	<.001	<.001	.	<.001
		N	1281	1281	1281	1281
	PI	Correlation Coefficient	-.342**	.253**	.800**	1.000
		Sig. (2-tailed)	<.001	<.001	<.001	.
		N	1281	1281	1281	1281

**. Correlation is significant at the 0.01 level (2-tailed).

e. PERMETHRIN

Correlations

			Permethrin	NPI	PVI	PI
Spearman's rho	Permethrin	Correlation Coefficient	1.000	-.210**	-.358**	-.436**
		Sig. (2-tailed)	.	<.001	<.001	<.001
		N	3431	3251	2780	2780
	NPI	Correlation Coefficient	-.210**	1.000	.662**	.072**
		Sig. (2-tailed)	<.001	.	.000	<.001
		N	3251	3251	2780	2780
	PVI	Correlation Coefficient	-.358**	.662**	1.000	.738**
		Sig. (2-tailed)	<.001	.000	.	.000
		N	2780	2780	2780	2780
	PI	Correlation Coefficient	-.436**	.072**	.738**	1.000
		Sig. (2-tailed)	<.001	<.001	.000	.
		N	2780	2780	2780	2780

**. Correlation is significant at the 0.01 level (2-tailed).

7.2.3 PESTICIDE CONCENTRATIONS ACROSS WATERSHEDS

Mean and median concentrations of the pesticides were assessed across watersheds in this study (Tables A8 and A9). From the results, more vulnerable sites in the urban watersheds, such as San Francisco Bay, Sacramento, and Los Angeles, had lower concentrations overall but were more clustered within the watersheds. The sites located in the less vulnerable watersheds were sparsely distributed but yielded higher concentrations. Across the less vulnerable watersheds, the pesticide with the highest mean and median concentrations was imidacloprid (mean = 0.626ppb; median = 0.046ppb). The highest recorded concentration from one site was as high as 165ppb for imidacloprid, with a standard deviation of 6.524. Cypermethrin had the lowest mean and median concentrations across the watersheds (mean = 0.009ppb; median = 0.001ppb). For the more vulnerable watersheds, the pesticide with the highest mean concentration and standard deviation was also imidacloprid (mean = 0.099ppb; median = 0.008ppb; $\sigma = 0.5$). The pesticide with the lowest mean and median concentrations was cypermethrin (mean = 0.005ppb; median = 0.0005ppb). From these results, we can infer that imidacloprid has the highest detection rate across all watersheds and locations. As such, imidacloprid usage should be reduced to limit the hazard that is incurred by aquatic ecosystems located downstream from the pesticide discharges.

Table A 9: Mean pesticide concentrations across less vulnerable watersheds

Statistics

Bifenthrin

N	Valid	2263
	Missing	0
Mean		.0272891511
Median		.0020700000
Std. Deviation		.10380582499
Range		2.59995000
Minimum		.00005000
Maximum		2.60000000

Statistics

Cypermethrin

N	Valid	1944
	Missing	0
Mean		.0096751666
Median		.0010000000
Std. Deviation		.07944567353
Range		2.63152895
Minimum		.00005000
Maximum		2.63157895

Statistics

Fipronil

N	Valid	853
	Missing	0
Mean		.01728738
Median		.00200000
Std. Deviation		.044389135
Range		.685950
Minimum		.000050
Maximum		.686000

Statistics

Imidacloprid

N	Valid	839
	Missing	0
Mean		.62690326
Median		.04600000
Std. Deviation		6.524276472
Range		164.998100
Minimum		.001900
Maximum		165.000000

Statistics

Permethrin

N	Valid	3112
	Missing	0
Mean		.0118266287
Median		.0020000000
Std. Deviation		.07653441897
Range		2.63147895
Minimum		.00010000
Maximum		2.63157895

Table A 10: Mean pesticide concentrations across more vulnerable watersheds

Statistics

Bifenthrin

N	Valid	2912
	Missing	2
Mean		.014742316
Median		.001000000
Std. Deviation		.1850887969
Range		5.6334770
Minimum		.0000500
Maximum		5.6335270

Statistics

Cypermethrin

N	Valid	2402
	Missing	0
Mean		.004820746
Median		.000500000
Std. Deviation		.0350622447
Range		1.2528800
Minimum		.0000500
Maximum		1.2529300

Statistics

Fipronil

N	Valid	1658
	Missing	0
Mean		.00832179
Median		.00200000
Std. Deviation		.032726503
Range		.999900
Minimum		.000100
Maximum		1.000000

Statistics

Imidacloprid

N	Valid	1541
	Missing	0
Mean		.09946666
Median		.00800000
Std. Deviation		.500505760
Range		9.303010
Minimum		.001900
Maximum		9.304910

Statistics

Permethrin

N	Valid	3431
	Missing	0
Mean		.02057810
Median		.00200000
Std. Deviation		.378583227
Range		17.735080
Minimum		.000100
Maximum		17.735180

7.2.4 GEOSPATIAL MODEL BUILDING

For the point source sub-index metric, the effluent flow for 165 WWTPs was aggregated and normalized per HUC8 watershed using Equation (1). WWTP effluent flows were summarized within each NHDPlus V2 HUC-8 watershed by a spatial join followed by merging the sum of the effluent flow. A similar approach was used for the pet groomer location data, where the density of the sum of locations was spatially joined to the model and normalized per watershed (equation 1). These individual metrics were converted into metric scores per watershed using equation 2 and then equally weighted to calculate the point pesticide sub-index scores. Non-point pesticide use data was aggregated from the HUC12 level and converted to the HUC8 level in GIS due to the lack of other relevant data available at the smaller watershed level (HUC12). Since the pesticides were assumed to have identical mobilities within the environment, the metric values were combined and normalized per watershed to calculate their metric scores using Equation 2. Metric scores were then categorized by agricultural, structural, and landscape use before being averaged to calculate the non-point sub-index score (equation 3).

To characterize the hydrological conditions within California watersheds, average precipitation and runoff change were joined to each NHDPlusV2 HUC8 watershed in ArcGIS. After joining the precipitation and runoff data to each representative watershed, their metric scores were calculated using equations 5 and 6. The average precipitation and runoff data were assumed to be inversely proportional to the non-point source volumes, thereby modeling pesticide dilution rates from seasonal changes (i.e., rain and droughts) (equation 5). For the point sources, the projected precipitation and runoff change were assumed to be directly proportional to the streamflow volume, indicating the impact of seasonal changes on instream pesticide concentrations (equation 6). In other words, increased precipitation and runoff positively affect the dilution of point-source pesticides but harm non-point-source pesticide dilutions [57, 147].

7.3 DATA DIRECTORY

Table A 11: Data Directory used in this study.

Data Set	**Description**	**Data Source**	**Data Source Agency**	**Period**	**Methodology**
WWTPs	Coordinates, Flow, Discharge Methods, Level of Treatment	Clean Watersheds Needs Survey (CWNS); Permit Compliance System (PCS)	U.S. EPA	January 2012 - December 2012	Survey
Mean Annual and Monthly Flow Estimates	Flow	National Hydrography Dataset Plus (NHDPlus) V2	USGS; U.S. EPA	CONUS EROM: 1971 to 2000	Enhanced Unit Runoff Method (EROM) Gage-Adjusted Flow Estimates
7Q10 Flow Estimates	Flow	iSTREEM V2.1	American Cleaning Institute (ACI)	CONUS EROM: 1971 to 2000	7Q10 Flows at Gages: The Basis For the iStreem 7Q10 Flows Nhdplus-Based Routing Method

Stream Gage	Gage Location and Flow Statistics	National Hydrography Dataset Plus (NHDPlus) V2	USGS; U.S. EPA	Real-Time Data	
Watershed Boundary Dataset	Hydrologic Unit Map	National Hydrography Dataset Plus (NHDPlus) V2	USGS	2012	
Precipitation and Runoff	Average Precipitation and Runoff (mean annual)	National Climate Change Viewer (NCCV)	USGS	Baseline: 1950-2005 Projected: 2030-2045	20 downscaled CMIP5 climate models for the RCP8.5 emissions scenarios
Pesticide Concentrations	Concentrations	Standardized Urban Riverine Framework (SURF)	CDPR	2012 to 2019	
Climate Change	Projected Minimum Temperature Change (Mean Annual)	National Climate Change Viewer (NCCV)	USGS	Baseline: 1950-2005 Projected: 2030-2045	20 downscaled CMIP5 climate models for the RCP8.5 emissions scenarios