

FINAL REPORT

Project Information

Project Title	Quantifying California Municipal Wastewater Discharge Contributions to Streams for Pesticide Source Modeling
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Project Report

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PROJECT PURPOSE

Traditionally, agricultural runoff is a main contributor of pesticides entering the water supply. However, in urban areas wastewater can present one of the main routes of pesticide contamination into the environment. Recent studies have highlighted the occurrence of several pesticides within treated wastewater effluent at levels above U.S. EPA's aquatic life benchmarks for chronic exposure to invertebrates (Sutton et al., 2019). Yet, little is known regarding the ecological toll that wastewater treatment plants (WWTPs) may have taken on receiving streams, particularly those with higher levels of treated wastewater contributions. Knowledge of the relative contributions of pesticides to California surface waters is required to support source control and mitigation efforts, and to provide context regarding the frequency in which treated effluent serves as a potential threat to receiving waters. The overall goal of this project is to evaluate WWTP discharge contributions to California receiving streams under varying streamflow conditions and spatially identify watersheds that may be more susceptible to pesticide loadings. Outcomes of this study will be integrated into the California Department of Pesticide Regulation's (CDPR) modeling efforts and matched with CDPR's pesticide down-the-drain model to determine relative pesticide contributions from urban flows and agricultural runoff to California surface waters.

Completion of the following objectives support ongoing pesticide reduction programs:

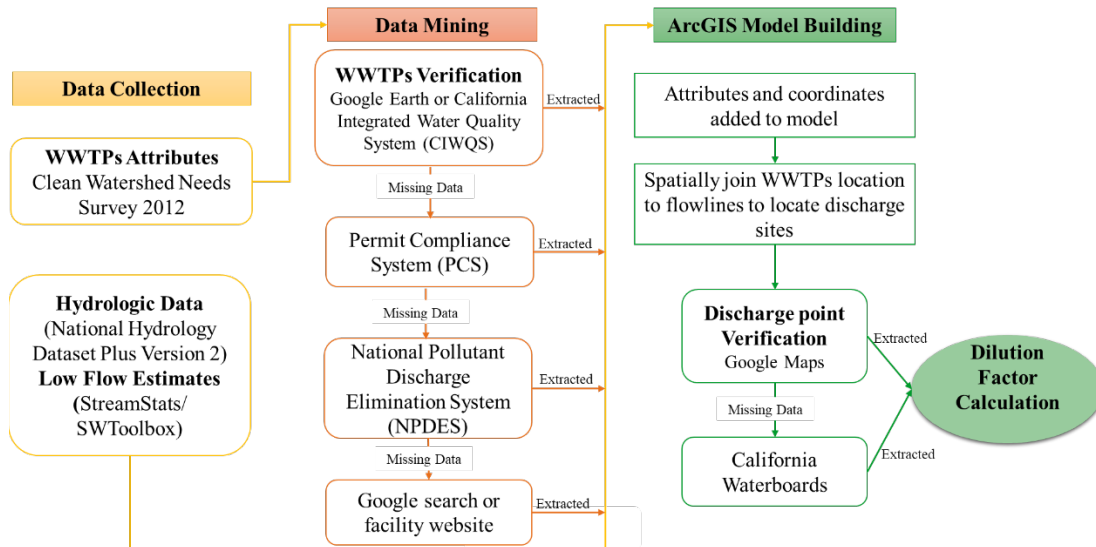
- (1) Develop and verify a spatial model estimating municipal wastewater discharges to California receiving streams under average streamflow conditions.
- (2) Determine temporal variation of dilution factors based on changes to historic streamflow data and climate change forecasts of future streamflow.
- (3) Identify CA streams most susceptible to WWTP discharges.
- (4) Create SWAT compatible input file templates for the incorporation of study results into ongoing DPR modeling.

ACCOMPLISHMENTS BY OBJECTIVE

Objective 1: Develop and Verify a Spatial Model Estimating Municipal Wastewater Discharges to California Receiving Streams Under Average Streamflow Conditions.

Development of Treated Wastewater Discharge Contribution Model Estimates

In-stream dilution for treated municipal WWTP discharges were estimated through development of an ArcGIS geospatial model with WWTP location and attribute data incorporated from multiple sources, as detailed below in Figure 1. Location data for WWTP discharges to surface water were initially collected and estimated from EPA's Clean Watershed Needs Survey (USEPA, 2016). These attributes were then verified using the Permit Compliance System (PCS), the National Pollutant Discharge Elimination System (NPDES), and California Integrated Water Quality System Project (CIWQS). Finally, these coordinates were validated using Google Earth or a Google search on each facility's website to obtain information regarding discharge location. Sites that could not be verified were contacted through email with request for location information. Once verified, sites discharging into estuaries were removed, leaving a total of 161 WWTPs. Within the selected sites, there are four surface discharge WWTP facilities with two outfall locations, bringing the total number of sites analyzed to 165. In addition to WWTPs with surface outfalls, roughly 440 non-surface water discharging WWTPs were verified through Google Earth. The verification process for these were slightly different; here we aimed to identify site locations instead of discharge locations. Figure 1 depicts the full methodology. Once complete, the database and respective coordinates were further verified through collaboration with C DPR.



CA WWTPs Discharge Method

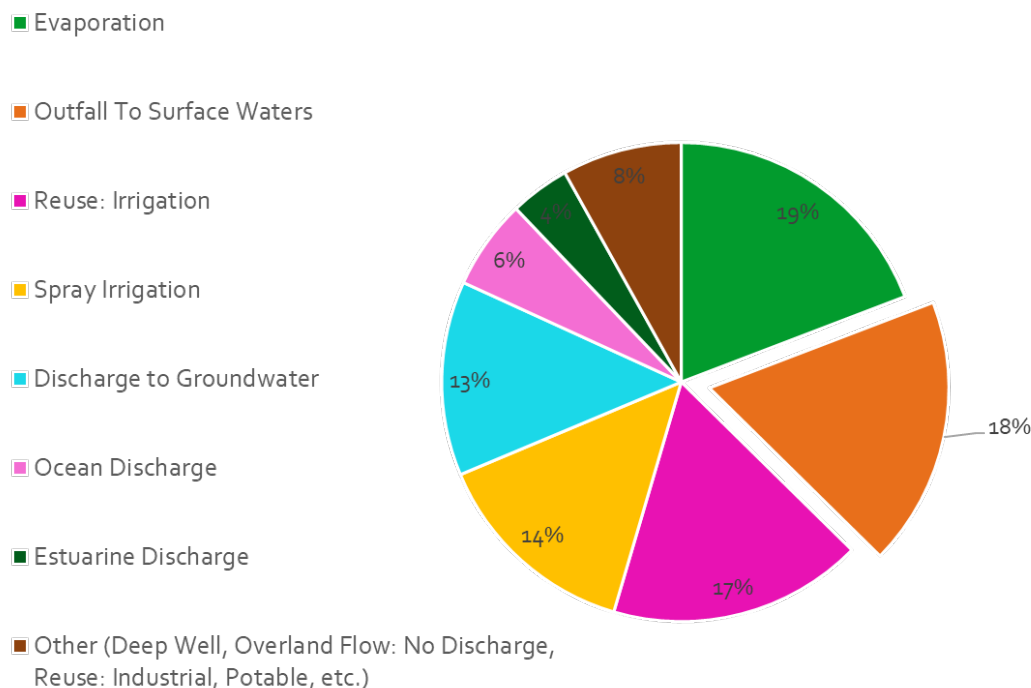


Figure 1: (A) Methodology for the geospatial analysis for WWTP discharge sites and (B) distribution of WWTPs by discharge type.

After collecting the WWTP data, we turned our focus to hydrologic data, which were extracted from the National Hydrology Plus Version 2 Dataset (NHDPlus V2). Low flow estimates were obtained from iSTREEM (USEPA, 2019; ACI, 2022). These datasets served as the latest versions that could be incorporated successfully into the ArcGIS framework. WWTP attributes were spatially joined to hydrology flowlines representing discharge points for each receiving stream. At this stage, a second level of verification was completed verifying that the modeled spatial join was a good representation for each site. The dilution factor (DF) for each receiving stream site was calculated using Equation 1, where Q_w represents the WWTP design flow and Q_r represents receiving stream flow. Higher dilution factors signify a stream's ability to buffer effluent contaminants, while lower dilution factors may signify contaminant concentrations at levels of concern.

$$DF = \frac{Q_r + Q_w}{Q_w}, \quad [unitless] \quad (1)$$

Results for Dilution Factors under Average Streamflow

Dilution Factors (DFs) were calculated for 165 surface water discharging WWTPs across California under mean annual streamflow. The median DF across all sites was equal to 4.6, with 32% of the dataset having a DF less than 2.0 and 62% of the dataset having a DF below 10 (see Figure 2). Our prior work demonstrated the importance of instream flow conditions on contaminant concentrations, which is evaluated in Objective 2. In addition to streamflow

conditions, Strahler Stream Order (SSO) of the receiving stream greatly impacts a stream’s natural ability to buffer treated wastewater contributions. SSO is a widely used quantitative characterization of stream size based on the hierarchy of upstream tributaries. Tributaries that emerge from headwater channels are classified as first-order streams, and a second-order stream emerges from the confluence of two first-order streams. This continues with further classifications at confluences to the twelfth order (largest volume), with two streams of the same order increasing in SSO at the confluence. However, the confluence of two tributaries of different orders will retain the highest SSO from the confluence (Tarboton et al., 1991). In this analysis, California receiving streams were classified by Strahler Stream Order (SSO) ranging from first order to seventh. Our results indicate that roughly 40% of the discharge sites are into streams of an SSO equal to or less than three which are relatively more sensitive to climate-related variations.

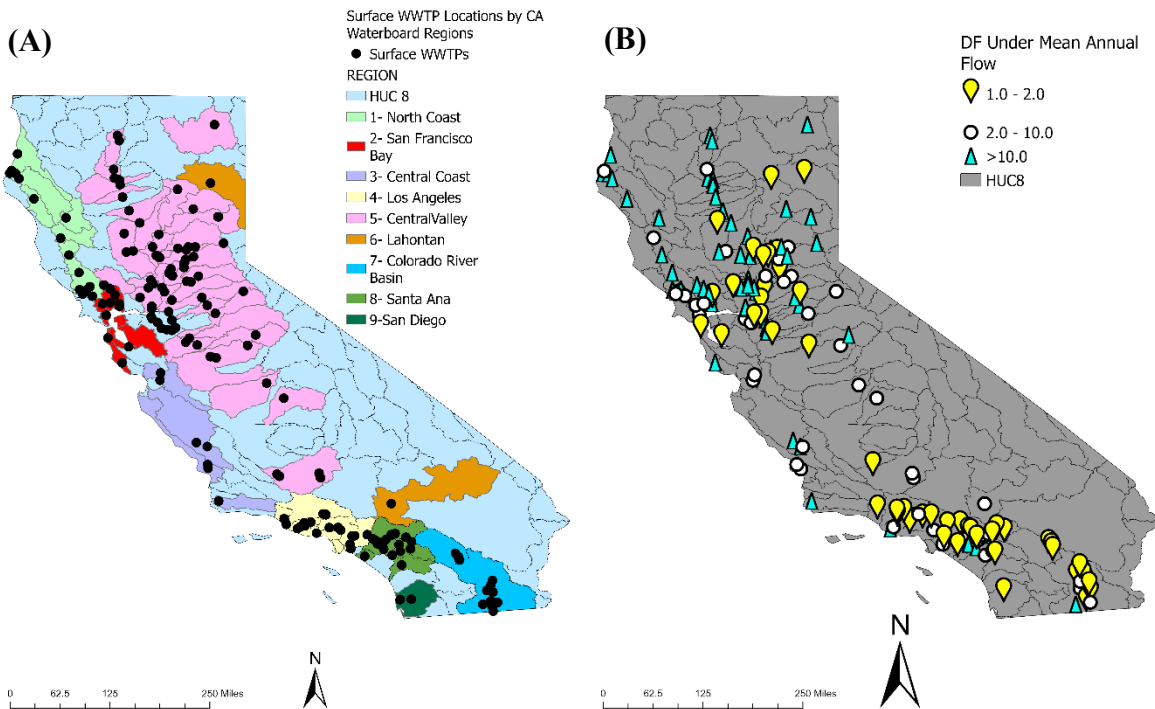


Figure 2: (A) Distribution of surface water discharging WWTP locations categorized by California Waterboards Region and (B) estimates for dilution factor under average streamflow conditions.

Objective 2: Determine Temporal Variation of Dilution Factors Based on Changes to Historic Streamflow Data and Climate Change Forecasts of Future Streamflow.

Methodology for Modeling Temporal Variation, DFs, and Resulting Pesticide Concentrations

In Objective 2, we expanded our analysis of dilution factors for additional streamflow conditions and compared the results to the outcomes under average streamflow conditions. Temporal variation was modeled in multiple stages, extreme low-flow events, including monthly variation (low vs. high monthly streamflow average), and predicted future conditions. Extreme low-flow event was modeled as the 7-day average streamflow with a 10-year recurrence interval (7Q10), based on iSTREEM data (ACI, 2022; Bondelid, 2018). The 7Q10 analysis represents an 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 (Rice, Via, & Westerhoff, 2015). It's important to note that iSTREEM data have an increased level of uncertainty for estimates within the state of California due to the complex hydrologic system and influence of manmade structures within the system. After quantifying dilution factors for each mean monthly streamflow, we identified March and October to serve as the min and max conditions respectively. Potential future impacts resulting from climate change predictions were developed for 165 sites based on the USDA Forest model, which estimates streamflow based on historical conditions and projected climate change scenarios (USDA Forest Service, 2022). Next, we evaluated how the role of temporal variation translates to expected in-stream pesticide concentrations and threats posed to aquatic life. In doing so, the required dilution factor was calculated for a suite of five (5) pesticides, which included bifenthrin, cypermethrin, fipronil, imidacloprid and permethrin to meet aquatic life benchmarks for chronic exposures to invertebrates within receiving surface water (as reported by USEPA OPP). These concentrations were calculated based upon CDPR monitoring data and available literary data (Xie et al., 2021) for secondary and tertiary treatment plants, due to data limitations the analysis was not separated by treatment level. The final dilution factors for the selected pesticides, supporting data, and equations are provided in Appendix A.

Resulting DFs for 7Q10 Indices and Monthly Streamflow

Under low-flow conditions (modeled as 7Q10), the median dilution factor across the sites is estimated to be slightly above 1 (1.01) for the 107 sites with available streamflow estimates. This is primarily due to 74% being below a DF of 10, and 66 of 107 sites having a DF below 2.0. Figure 3 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 forecasts.

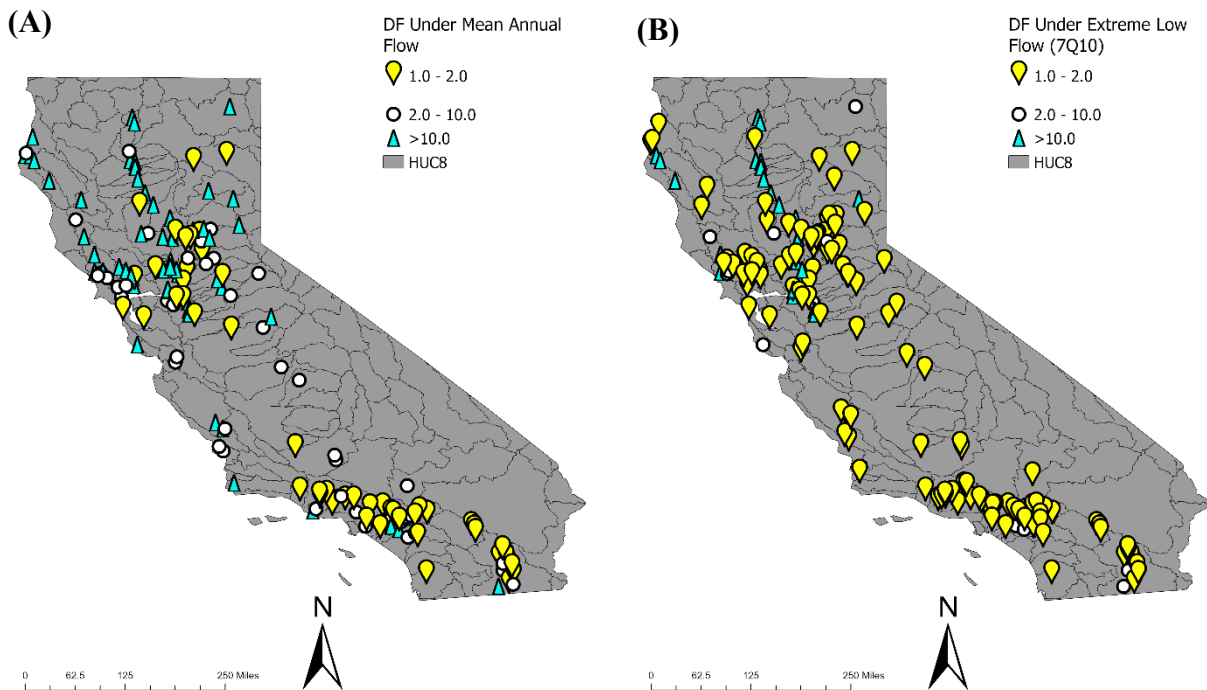


Figure 3: Color-coded maps of dilution factors for receiving streams at WWTPs' discharge sites under a) mean annual flow and b) low flow (7Q10).

After quantifying dilution factors for each mean monthly streamflow, we identified March and October to serve as the maximum and minimum conditions for mean dilution factors respectively. For further comparison, results for the month of August (representing a common hydrologic statistic) are provided in Appendix C. These are juxtaposed in Figure 4. March represents the wettest month for much of California and historically the highest monthly streamflow average. The median dilution factor is estimated to be 9.3. Roughly 20% of receiving streams have a dilution factor below 2, and half of discharge sites fell below a DF of 10. In contrast, during the dry weather season, the median dilution factor is estimated to be 1.5. Approximately 58% of sites fall below a dilution factor of 2, and over 75% fall below 10. Differences in results between March and October illustrate the impact that seasonal streamflow variation, particularly seasonal drought can have on instream pollutant concentrations.

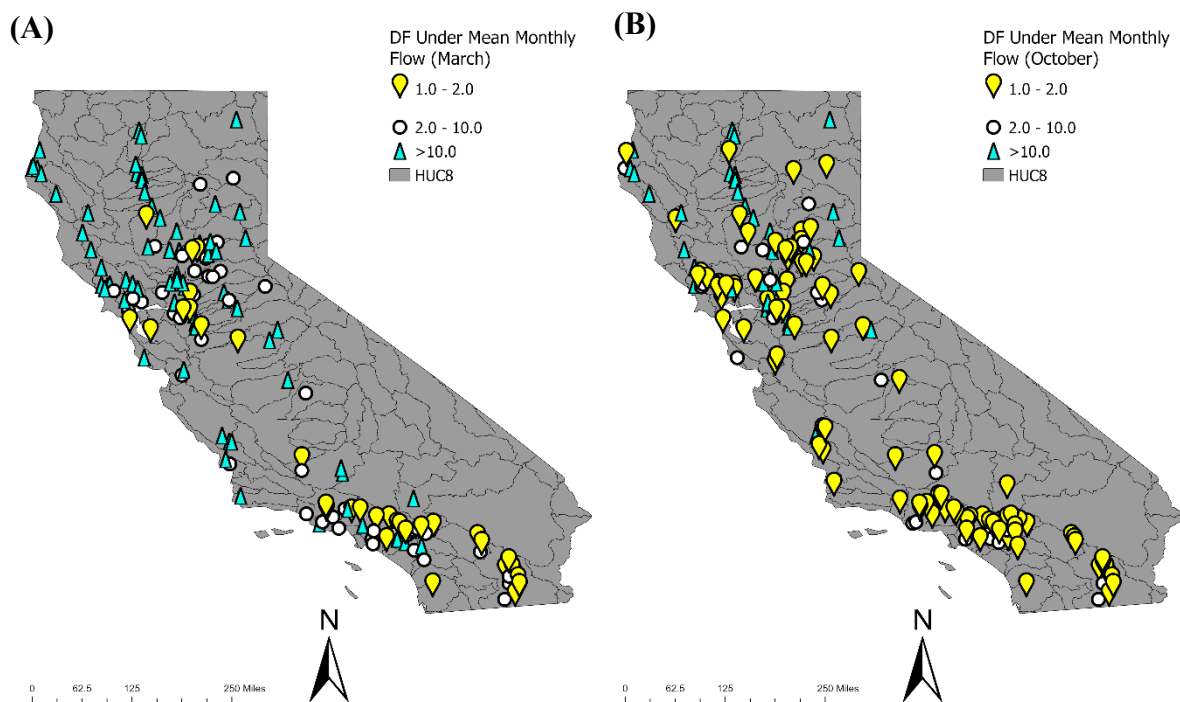


Figure 4: Color-coded maps of dilution factors for receiving streams at WWTPs' discharge sites under mean monthly flow conditions in (A) March and (B) October.

Resulting DFs for Future Streamflow Conditions (2040 and 2080)

California's future streamflow conditions are anticipated to change due to projected warming and expected changes in precipitation and snow patterns. Current estimates are limited to potential changes in average annual, or seasonal streamflow estimates obtained from gridded runoff products. Prior work has predicted changes to future streamflow conditions; however, there is no consensus on the direction (sign) of change for the flow regime. Based on the assumptions inherited in the Western U.S. Stream Flow Metrics Analysis (USDA), average annual streamflow

is generally expected to increase for much of California. With the USDA model, five (5) global climate models are incorporated into the National Hydrography Dataset Plus Version 2 (NHDPlus V2), providing a comparison of seasonal, peak, and low flow events across the NHD watershed scales (USDA Forest Service, 2022). Miller et. al (2021) highlighted uncertainties associated with current streamflow projections. In a study containing seven different climate models, roughly half of the models projected streamflow decreases for southeastern California in the 2080s relative to the historic time-period. However, the multimodel mean projected a modest increase (2.4%) in streamflow. Using the USDA dataset, we observed that there was roughly a two-fold increase in the predicted median dilution factors across receiving streams when comparing projected mean annual flow in 2040 (15.6) and 2080 (14.8) against current USGS average annual flow estimates (6.7). Further evaluations were made for August flows to determine if future projections result in larger seasonal streamflow variations. When compared to the historic August flow, projected August flows of 2040 resulted in a doubling of the calculated DF (3.0). It is important to note that the work presented here is limited by the modeling assumptions inherited within the streamflow dataset and are aggregated in time (such as annual averages) and space (state-level), which is not a representation of less frequent extreme events. However, prior research highlights the important role that extreme conditions will play for California due to lower low flows and higher high flows (Mallakpour et. al, 2018).

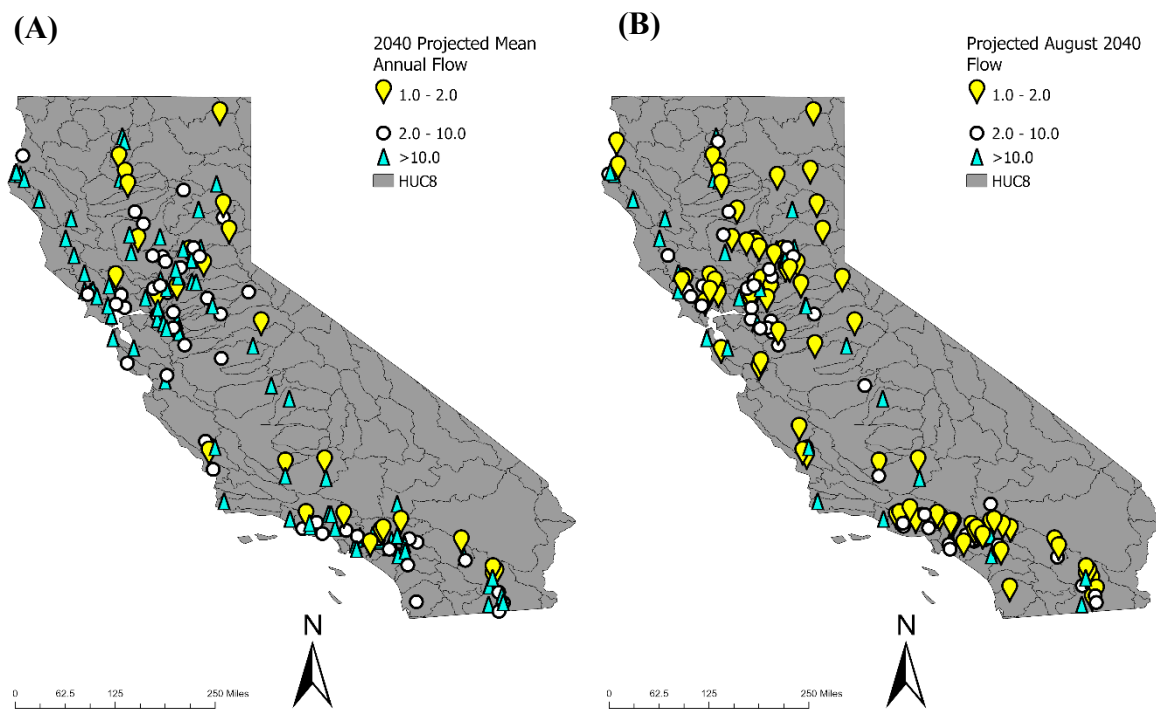
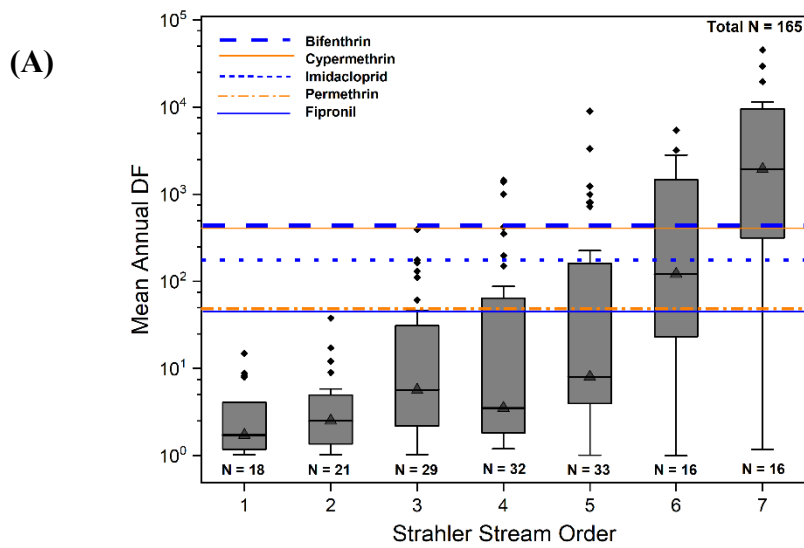


Figure 5: Color-coded maps of dilution factors for receiving streams at WWTPs' discharge sites for the year 2040 under projected (A) mean annual flow and (B) August flow.

Exceedance of Pesticide Aquatic Life Benchmarks

Five pesticides are investigated at levels in secondary WWTP effluent that require dilution to meet the aquatic life benchmark within receiving streams, with an applied safety factor of 10. Listed in

order of highest to lowest required dilution factor, these include bifenthrin, cypermethrin, fipronil, imidacloprid, and permethrin (full detail provided in Appendix A). Exceedance was analyzed with and without an applied safety factor, several sites (as displayed in Figure 6) are estimated to exceed aquatic life benchmarks for three pesticides under mean annual and low instream flow conditions. Due to a high required DF, bifenthrin concentrations within receiving streams are estimated to exceed the aquatic life benchmark in over 83% of sites under mean annual streamflow conditions, increasing to over 94% during low-instream flow events (7Q10). Additionally, roughly 78% and 85% of sites exceed the threshold for three modeled pesticides (bifenthrin, cypermethrin, and imidacloprid) during mean annual and 7Q10 streamflow respectively. These results highlight the potential threats posed by pesticides characterized by relatively lower aquatic life benchmark concentrations and persistent in treated wastewater effluent at levels of concern.



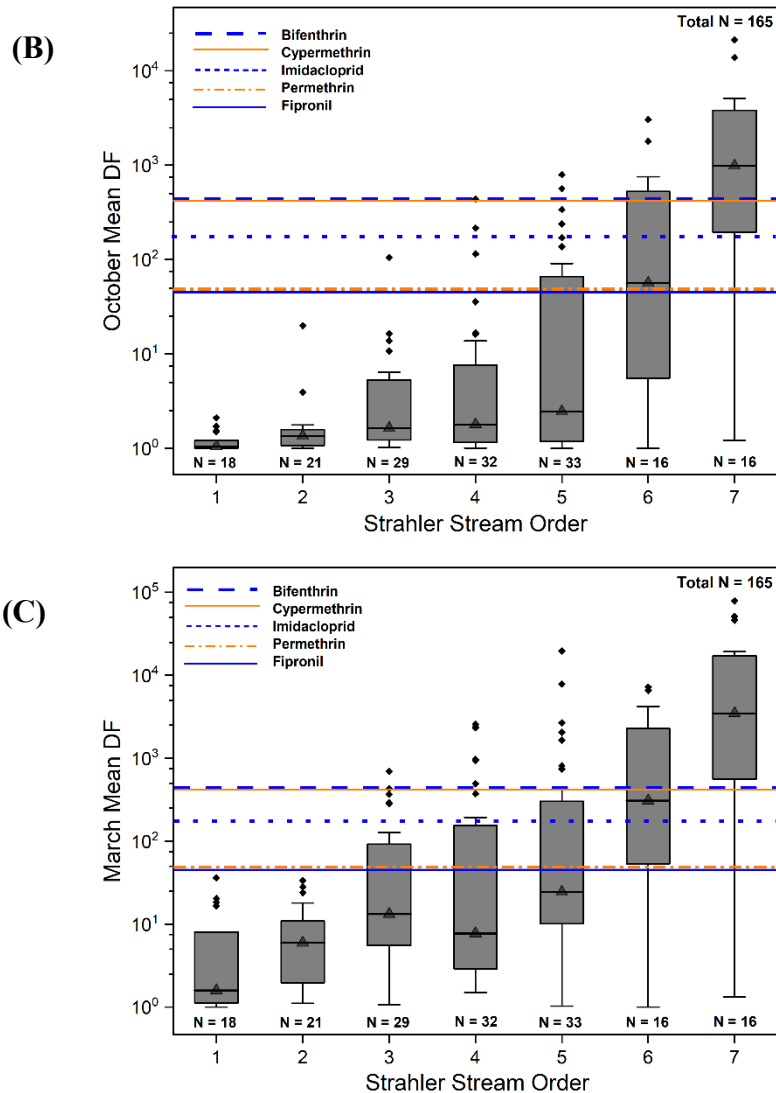


Figure 6: Boxplots displaying dilution factors (DF) for surface WWTPs’ receiving streams and the required dilution factors do not exceed aquatic health benchmarks (bifenthrin, cypermethrin, fipronil, imidacloprid, and permethrin) under (A) mean annual conditions, (B) low monthly streamflow conditions, 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.

Objective 3: Identify California Streams Most Susceptible to WWTP Discharges.

Pesticide Vulnerability Index Development

For Objective 3, a multi-metric index was developed to assess the relative vulnerability of watersheds across the state to the potential discharge of pesticides from point and non-point sources (see Figure 7). These metrics were selected in consultation with the California Integrated Assessment of Watershed Health (2013) report. Surface WWTP data from the previously developed geospatial model (Objectives 1 and 2) were incorporated into the index along with

selected pesticide use data to characterize point and non-point source metrics respectively. For the hydrologic conditions, the dam storage ratio was selected, and for environmental sensitivity, threatened species proximity was used. A full description can be found in Appendix B.

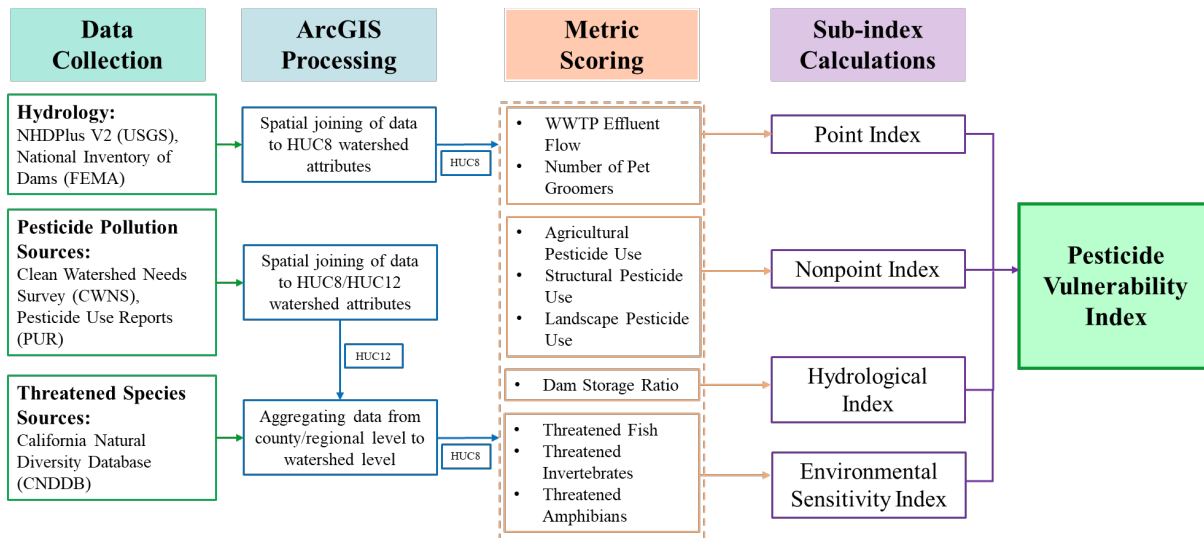


Figure 7: Methodology for the calculation of the pesticide vulnerability index (PVI) for the California receiving watersheds.

Pesticide Vulnerability Index Results

Based on the ranking system adopted for the study, sites with lower values are comparatively more vulnerable to pesticide concentrations due to the combined effects of pollution sources, hydrologic conditions, and environmental sensitivity. Figure 8 displays the pesticide vulnerability index values across California. Based on our model estimates, the most vulnerable HUC8 watersheds to pesticide loading were San Francisco Bay, San Joaquin Delta, Lower Sacramento, and San Gabriel respectively. This was largely due to the major cities having the largest number of pet groomers and WWTPs in the area, leading to higher levels of estimated pesticide use and potential release into the environment. It is important to note that the quantitative loading estimates are not integrated into this assessment at a level where differences in pesticide loading across sources can be evaluated. Despite this, the results draw attention to watersheds where combined factors relatively may be of more concern.

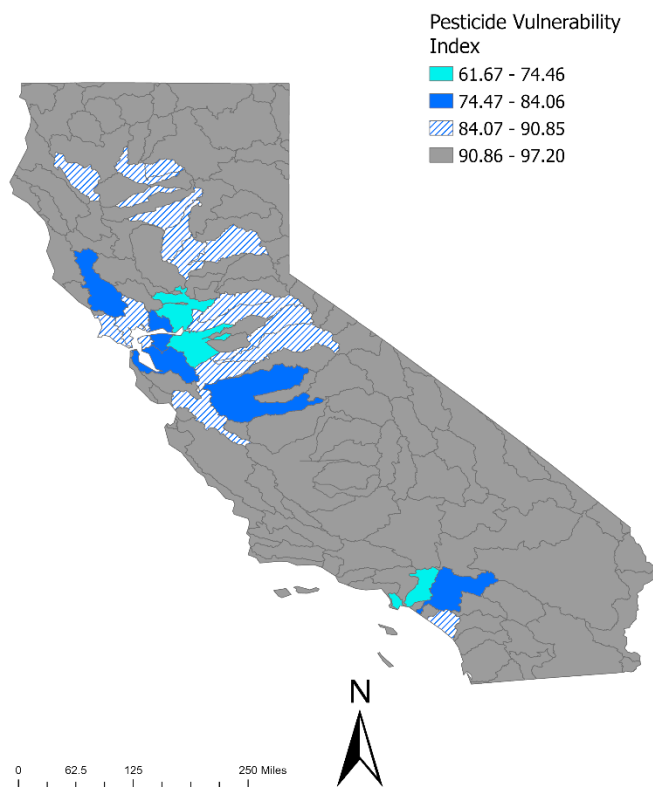


Figure 8: Color-coded Map Showing the Most Vulnerable Watersheds to Pesticide Discharge.

Objective 4: Create SWAT Compatible Input File Templates for The Incorporation of Study Results into Ongoing DPR Modeling.

In collaboration with CDPR, the means for data transfer has been identified as a Microsoft Excel workbook and Microsoft Access Database. These file types include spatial data and unique identifiers (CWNS Number) to support integration into CDPR’s modeling efforts. Several sites were identified through CIWQS that did not contain CWNS identities. In the MS workbook, these sites have been given fictitious CWNS IDs that start with the prefix ‘CDPR’. To accommodate formatting requirements for unique identifiers within the Access database, the CDPR prefix was replaced by ‘9999’ which still allows for the sites to be matched across the two datasets by the latter numerical values. For illustration, CDPR000002 (MS Excel) relates to 9999000002 (MS Access).

SUMMARY OF SIGNIFICANT FINDINGS AND IMPACT

Significant Scientific Contributions

Results of this work highlight the potential contributory role of WWTP effluent to pesticide occurrence within streams at levels that may pose threats by way of chronic exposures to

invertebrates. Traditionally, non-point pesticide sources have been the focus for pesticide loadings to streams, routed through stormwater runoff. However, results of this study suggest that pesticide concentrations within streams receiving treated municipal wastewater can be at levels that threaten invertebrates even in the absence of land-applied pesticides. In this study the likelihood of a pesticide presenting a chronic exposure threat to invertebrates within a specific watershed is largely dependent on its concentration within wastewater effluent and the aquatic life benchmark. We expect this trend to hold true for other pesticide compounds with similar characteristics. All pesticides included in this study pose concern for aquatic life, these risks were heightened during periods of low instream flow. Outcomes from this work align with prior studies noting ecological risks posed by fipronil and imidacloprid. This study also demonstrated the importance of streamflow conditions on expected pesticide concentrations and presents DF as a useful metric for estimating instream concentrations for other pesticides in streams receiving municipal wastewater discharges. In addition, this study took the first steps in comparing cumulated point and non-point pesticide sources across CA watersheds. Indices were calculated by assigning equal weights across each metric; however, this can be improved in the future by setting more representative weights based on expert opinion or literary justification.

Impact

Ultimately outcomes of the model will be integrated into CDPR's modeling efforts and used to inform policy decisions for pesticides within the state of California. The project has also enabled significant opportunities for skill and professional development of two female PhD students, one who graduated in December 2021.

REFERENCES

- American Cleaning Institute (ACI) iSTREEM (2022). <https://www.istreem.org/>
- Budd, R., Wang, D., Ensminger, M., & Phillips, B. (2020). An evaluation of temporal and spatial trends of pyrethroid concentrations in California surface waters. *Science of the Total Environment*, 718, 137402. <https://doi.org/10.1016/j.scitotenv.2020.137402>
- Chow, R., Scheidegger, R., Doppler, T., Dietzel, A., Fenicia, F., & Stamm, C. (2020). A review of long-term pesticide monitoring studies to assess surface water quality trends. *Water Research X*, 9, 100064. <https://doi.org/10.1016/j.wroa.2020.100064>
- Clean Watersheds Needs Survey (CWNS) | US EPA. (2015, April 24). US EPA. <https://www.epa.gov/cwns>
- California Integrated Assessment Of Watershed Health A Report on the Status and Vulnerability of Watershed Health in California. (2013). https://www.mywaterquality.ca.gov/monitoring_council/healthy_streams/docs/ca_hw_report_111213.pdf
- Cryder, Z., Greenberg, L., Richards, J., Wolf, D., Luo, Y., & Gan, J. (2019). Fiproles in urban surface runoff: Understanding sources and causes of contamination. *Environmental Pollution*, 250, 754–761. <https://doi.org/10.1016/j.envpol.2019.04.060>
- Definition and Characteristics of Low Flows | US EPA. (2018, October 17). US EPA. <https://www.epa.gov/ceam/definition-and-characteristics-low-flows>
- Delcour, I., Spanoghe, P., & Uyttendaele, M. (2015). Literature review: Impact of climate change on pesticide use. *Food Research International*, 68, 7–15. <https://doi.org/10.1016/j.foodres.2014.09.030>
- DeMars, C., Wang, R., Grieneisen, M. L., Steggall, J., & Zhang, M. (2021). Assessment of pyrethroid contamination and potential mitigation strategies in California Central Coast surface waters. *Journal of Environmental Management*, 278, 111507. <https://doi.org/10.1016/j.jenvman.2020.111507>
- Bondelid, T. (2018). Development of 7Q10 Flows for the iSTREEM 2.0 Model. American Cleaning Institute. https://www.istreem.org/help/iSTREEM_7Q10_flow_development.pdf
- LOW FLOW STATISTICS TOOLS A How-To Handbook for NPDES Permit Writers. (2018). https://www.epa.gov/sites/default/files/2018-11/documents/low_flow_stats_tools_handbook.pdf
- Luo, Y., & Deng, X. (2015). Methodology for Prioritizing Pesticides for Surface Water Monitoring in Agricultural and Urban Areas III: Watershed-Based Prioritization. https://www.cdpr.ca.gov/docs/emon/pubs/ehapreps/analysis_memos/luo_prioritization_3.pdf
- Mallakpour, I., Sadegh, M., & AghaKouchak, A. (2018). A new normal for streamflow in California in a warming climate: Wetter wet seasons and drier dry seasons. *Journal of hydrology*, 567, 203-211.

- Miller, O. L., Putman, A. L., Alder, J., Miller, M., Jones, D. K., & Wise, D. R. (2021). Changing climate drives future streamflow declines and challenges in meeting water demand across the southwestern United States. *Journal of Hydrology X*, 11, 100074. <https://doi.org/10.1016/j.hydroa.2021.100074>
- NHD Plus - NHDPlus Home. (2012). Nhdplus.com. <https://nhdplus.com/NHDPlus/>
- NPDES Permit Basics | US EPA. (2015, September 23). US EPA. <https://www.epa.gov/npdes/npdes-permit-basics>
- PCS-ICIS Overview | US EPA. (2015, August 31). US EPA. <https://www.epa.gov/enviro/pcs-icis-overview>
- Rice, J., Via, S. H., & Westerhoff, P. (2015). Extent and Impacts of Unplanned Wastewater Reuse in US Rivers. *Journal American Water Works Association*, 107(11), 93-93. doi:10.5942/jawwa.2015.107.0178
- USEPA. (2016). *Clean Watershed Needs Survey, 2012, Report to Congress*. Retrieved from Washington, DC:
- StreamStats. (2022). Usgs.gov. <https://streamstats.usgs.gov/ss/>
- Sadaria, A. M., Sutton, R., Moran, K. D., Teerlink, J., Brown, J. V., & Halden, R. U. (2016a). Passage of fiproles and imidacloprid from urban pest control uses through wastewater treatment plants in northern California, USA. *Environmental Toxicology and Chemistry*, 36(6), 1473–1482. <https://doi.org/10.1002/etc.3673>
- Sadaria, A. M., Supowit, S. D., & Halden, R. U. (2016b). Mass Balance Assessment for Six Neonicotinoid Insecticides During Conventional Wastewater and Wetland Treatment: Nationwide Reconnaissance in United States Wastewater. *Environmental Science & Technology*, 50(12), 6199–6206. <https://doi.org/10.1021/acs.est.6b01032>
- Sutton, R., Xie, Y., Moran, K. D., & Teerlink, J. (2019). Occurrence and Sources of Pesticides to Urban Wastewater and the Environment. *Pesticides in Surface Water: Monitoring, Modeling, Risk Assessment, and Management* (Vol. 1308, pp. 63-88): American Chemical Society.
- State of California Natural Resources Agency Department Of Fish And Wildlife Biogeographic Data Branch California Natural Diversity Database State And Federally Listed Endangered And Threatened Animals Of California. (2018). <https://nrm.dfg.ca.gov/FileHandler.ashx?DocumentID=109405&inline>
- Tarboton, D. G., R. L. Bras, and I. Rodriguez-Iturbe. (1991). On the Extraction of Channel Networks from Digital Elevation Data. *Hydrological Processes*. 5: 81–100.
- Teerlink, J., Hernandez, J., & Budd, R. (2017). Fipronil washoff to municipal wastewater from dogs treated with spot-on products. ResearchGate; Elsevier. https://www.researchgate.net/publication/316897783_Fipronil_washoff_to_municipal_wastewater_from_dogs_treated_with_spot-on_products
- The Nine Regional Water Quality Control Boards in California. (n.d.). https://www.waterboards.ca.gov/publications_forms/publications/factsheets/docs/region_brds.pdf

- USEPA. (2019). NHDPlus (National Hydrology Dataset Plus). Retrieved from:
<https://www.epa.gov/waterdata/get-nhdplus-national-hydrography-dataset-plus-data#Download>
- USDA Forest Service. (2022). U.S. Stream Flow Metric Dataset: Modeled Flow Metrics for Stream Segments in the United States Under Historical Conditions and Projected Climate Change Scenarios: Data Guide
- USGS Water Data for the Nation. (2022). Usgs.gov. <https://waterdata.usgs.gov/nwis>
- Wang, D., Singhasemanon, N., & Goh, K. S. (2016). A statistical assessment of pesticide pollution in surface waters using environmental monitoring data: Chlorpyrifos in Central Valley, California. *Science of the Total Environment*, 571, 332–341. <https://doi.org/10.1016/j.scitotenv.2016.07.159>
- Xie, Y., Budd, R., Teerlink, J., Luo, Y., & Singhasemanon, N. (2021). Assessing pesticide uses with potentials for down-the-drain transport to wastewater in California. *Science of the Total Environment*, 773, 145636. <https://doi.org/10.1016/j.scitotenv.2021.145636>
- Xu, E. G., Bui, C., Lamerdin, C., & Schlenk, D. (2016). Spatial and temporal assessment of environmental contaminants in water, sediments and fish of the Salton Sea and its two primary tributaries, California, USA, from 2002 to 2012. *Science of the Total Environment*, 559, 130–140. <https://doi.org/10.1016/j.scitotenv.2016.03.144>

APPENDIX A: AQUATIC BENCHMARK SUPPORTING INFORMATION

Table A1-1: Selected pesticides with estimated aquatic benchmarks and required DF.

Pesticide	Classification	Median WW Effluent Concen- trations (ug/L)	90th Percentile WW Effluent Concen- trations (ug/L)	Aquatic Benchmark (ug/L)^a	DF Required (w/ SF)^b	DF Required^c
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	45.1	4.5
Imidacloprid	Neonicotinoid	0	0.1741	0.01	174.1	17.4
Permethrin	Pyrethroid	0	0.0220	0.0042	48.6	4.9

^aEPA OPP Aquatic Life Benchmarks (ug/L) for chronic exposure for sensitive aquatic invertebrates

^bMinimum dilution factor required to meet the aquatic benchmark (based on 90th percentile effluent conc.) with a safety factor of 10

^cMinimum dilution factor required to meet the aquatic benchmark (based on 90th percentile effluent conc.) with no safety factor applied.

Explanation of DF Required Methodology

Hazard quotients were calculated for each pesticide by Equation (A-1), based on estimated environmental concentrations (EECs), modeled as the 90th percentile reported values, and aquatic life benchmarks (ALB) for chronic exposure to invertebrates. The dilution factor required to meet the hazard quotient for each pesticide was estimated using Equation (A-2), 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.

$$HQ_{eff} = \frac{EEC}{ALB} \quad (A-1)$$

$$DF_{req} = \frac{HQ_{eff}}{LOC} \quad (A-2)$$

APPENDIX B: PESTICIDE VULNERABILITY INDEX SUPPORTING INFORMATION

Overview of Approach

A comprehensive Pesticide Vulnerability Index (PVI) was created to profile and assess the most vulnerable streams to point and non-point sources of pesticide loadings as well as their environmental factors and impacts within a spatial model. This PVI presents an index-based framework for comparing the likelihood of negative impacts to aquatic health from cumulative pesticide sources which persist in California’s watersheds. The metric indicators for the PVI include pesticide pollution sources (point and non-point), hydrological conditions, and environmental sensitivity to capture the environmental impacts of pesticides on wildlife in these areas. These metric indicators are further broken down into 1) aggregated WWTP effluent flow, pet groomers per watershed for point sources; 2) aggregated agricultural, structural and landscape use per watershed for non-point sources; 3) dam storage per watershed for modelling watershed conditions; and 4) aggregated targeted fish, amphibians, and invertebrates per watershed to model wildlife proximity to pesticide loadings. 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.

Table B1-1: Table displaying the indices and metrics for the Pesticide Vulnerability Index (PVI).

Index	Sub-index	Metric
Pesticide Pollution Sources	Point sources of pesticides	<ul style="list-style-type: none"> Aggregated WWTP effluent flow (existing flow) normalized by HUC8 watershed area Estimated number of pet groomers per watershed
Pesticide Pollution Sources	Non-point sources of pesticides	<ul style="list-style-type: none"> Agricultural use per watershed Structural use per watershed Landscape use per watershed
Hydrologic Conditions	Watershed condition	<ul style="list-style-type: none"> Estimated dam storage ratio per watershed
Environmental Sensitivity	Wildlife proximity	<ul style="list-style-type: none"> Aggregated targeted animal (fish, amphibians, invertebrates) per watershed

Description of Metric Data Collection and Spatial Data Processing

Point Source Pesticide Pollution

For point source metrics, WWTP discharge flow values were obtained from the prior analysis. By incorporating WWTP size, community factors such as housing density and ratio of population on centralized sewer systems are inherently taken into account. In addition to surface

discharging WWTPs, pet groomers were included as point sources of pesticide discharges to watersheds due to their copious use of pet products thereby serving as another critical pathway for pesticides entry into municipal wastewater systems. Pesticides such as fipronil and imidacloprid are prevalent in pet products and are consistently used in grooming pets and preventing the transmission of diseases (Wise et al., 2020, 2022). These products are absorbed through the users' skin or fur and remain persistent in their systems for extended periods of time even after they are washed off (Teerlink et al., 2017; Aerts et al., 2018; Wise et al., 2020). Therefore, watersheds with a higher density of grooming locations were expected to have higher pesticide loadings to WWTPs. To characterize these point source metrics, pet groomer locations across the state were obtained through web scraping, which is the use of a programming software (Apify was utilized for this analysis) to automatically obtain data from multiple websites. Through this process, 975 pet groomer locations across the state were collated into a spatial map in ArcGIS with about 5% (50) of them visually verified via Google Maps.

Non-Point Source Pesticide Pollution

To control and monitor agricultural and non-agricultural use of pesticides within the state, the California Department of Pesticide Regulation (CDPR) established the Pesticide Use Report (PUR) in 1990 for assessing health risks associated with several pesticides (Flint et al., 2005; Nuckols et al., 2007). The PUR contains pesticide use data from professional applications including application time, location, and amount in pounds, and provides an annual snapshot of cumulative trends in agricultural, structural, landscape and right of way pesticide applications. The PUR database, however, does not include use data from consumers. These reports were collated and categorized for selected pesticides (bifenthrin, cypermethrin, fipronil, imidacloprid, permethrin, zeta-cypermethrin) based on the following use patterns: agricultural, structural, landscape, and right of way across multiple years (2016-2018). Over 50% of the right of way data had null values, therefore this metric was removed from the analysis.

Watershed Conditions (Dam Storage Ratio)

To characterize the hydrological condition of CA watersheds, dam storage ratio was calculated utilizing data obtained from the National Inventory of Dams (NID, 2020). Dams are considered as a significant anthropogenic stressor on streams because of altered natural flow, stream temperature, and downstream water quality. This metric incorporates the impact from anthropogenic hydrologic conditions to watershed vulnerability, by estimating the ratio of dam normal storage (impoundment) to the highest mean annual outlet flow within each watershed. Since the mean annual flow was extracted from the CWNS 2012 dataset, both factors were aggregated at the HUC8 watershed level in ArcGIS. The HUC8 scale is the lowest scale available to maintain the resolution of the datasets in this case.

Wildlife Proximity Metric (Threatened Species)

For the wildlife proximity metric, three categories of threatened wildlife data (fish, invertebrates, and amphibians) were extracted from the California Natural Diversity Database (CNDDDB) to model their proximity to the impacted watershed streams. The authors would like to thank Catherine Bilheimer from CDPR's Endangered Species Program for helping UNCC obtain and preprocess the dataset. The CNDDDB database compiles a comprehensive list of state and federally threatened/endangered species that inhabit each region of the state. To identify species

assumed to be more sensitive to pesticide exposures, the top endangered and threatened wildlife species data were aggregated and mapped in ArcGIS for amphibians, fish, and invertebrates across the state for further analysis. The environmental sensitivity metric does not account for seasonal fluctuations in wildlife populations due to diseases, migration, etc.

Table B1-2: Table showing the selected state and federally endangered and threatened species of wildlife selected for the PVI.

Amphibians	Fish	Invertebrates
<p>Salamanders: Santa Cruz long-toed California Tiger Desert slender Kern Canyon slender Tehachapi slender Limestone Shasta Siskiyou Mountains Scott Bar</p> <p>Toads: Yosemite toad Black Arroyo</p> <p>Frogs: CA red-legged Foothill yellow-legged Cascades Oregon spotted Southern mountain yellow-legged Sierra Nevada yellow-legged</p>	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	<p>Fairy shrimp: Conservancy Longhorn San Diego Riverside Vernal pool</p> <p>Vernal pool tadpole shrimp CA freshwater shrimp Shasta crayfish Trinity bristle snail</p>

Spatial Data Processing and Calculations

Following the California Integrated Assessment of Watershed Health (CIAWH) methodology, pesticide usage, hydrologic and aquatic species data were aggregated on a HUC8 watershed scale and normalized per watershed area to ensure uniform weighting and equal directional scaling for analysis (CIAWH, 2013). Normalization ensures that multiple metrics are converted into uniform, unitless scores for even scaling. The PVI scores range from 0 to 100, with lower scores indicating a higher estimated vulnerability to pesticide concentrations and vice versa.

Metric and Sub-Index Scores

Sub-index scores were calculated for each sub-index (i.e., point source, non-point source, watershed condition, and wildlife proximity). Surface WWTP effluent flow and pet groomer locations were aggregated and normalized per HUC8 watershed to calculate their metric scores (see equations B-1 and B-2). These two metrics were then equally weighted (see equation B-3) to calculate the point source pesticide pollution sub-index. For the non-point source metric, pesticide use data were aggregated from the HUC12 watershed level and converted to HUC8 level in ArcGIS due to the lack of relevant feature class data for the other metrics at the smaller watershed level (HUC12). Since the pesticides were assumed to have the same mobilities within the environment, the pesticide use data were combined and normalized within each HUC8 watershed. The normalized metric scores were categorized by agricultural, structural and landscape use and equally weighted to calculate the sub-index score and ranking for non-point pesticide index. After a spatial join in ArcGIS, the geographical area of each wildlife species location (fish, invertebrates, amphibians) was aggregated and normalized per corresponding HUC8 watershed area. These ratios were then equally weighted to calculate the metric scores for the wildlife proximity sub-index. For the watershed conditions metric, the ratio of the total volume of impounded water and the annual flow volume were aggregated and calculated per each watershed. The ratios were then normalized and ranked for the watershed conditions sub-index.

(B-1)

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

(B-2)

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

(B-3)

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

PVI Scoring

Finally, the Pesticide Vulnerability Index (PVI) was calculated as the average of all the sub-index scores of the point and non-point pesticide pollution sources, hydrologic conditions, and environmental sensitivity (Equation B-4). The PVI model was then spatially displayed on a color-coded map using ArcGIS (Figure 8) to identify the most vulnerable watersheds to pesticide loadings from point and non-point sources.

(B-4)

$$\text{Final PVI score} = \frac{\sum_{j=1}^m \text{Sub_indexScore}_j}{m}$$

References:

- Aerts, R., Joly, L., Szternfeld, P., Tsilikas, K., De Cremer, K., Castelain, P., Aerts, J. M., Van Orshoven, J., Somers, B., Hendrickx, M., Andjelkovic, M., & Van Nieuwenhuysse, A. (2018). Silicone Wristband Passive Samplers Yield Highly Individualized Pesticide Residue Exposure Profiles. *Environmental Science and Technology*, 52(1), 298–307. <https://doi.org/10.1021/acs.est.7b05039>
- California Integrated Assessment of Watershed Health A Report on the Status and Vulnerability of Watershed Health in California. (2013). https://www.mywaterquality.ca.gov/monitoring_council/healthy_streams/docs/ca_hw_report_11_1213.pdf
- Flint, M. L., Ph, D., Wilen, C. A., & Zhang, M. (2005). Tracking Non-residential Pesticide Use in Urban Areas of California Submitted by. Environmental Protection.
- Nuckols, J. R., Gunier, R. B., Riggs, P., Miller, R., Reynolds, P., & Ward, M. H. (2007). Linkage of the California Pesticide Use Reporting Database with spatial land use data for exposure assessment. *Environmental Health Perspectives*, 115(5), 684–689. <https://doi.org/10.1289/ehp.9518>
- National Inventory of Dams. <https://nid.usace.army.mil/#/>
- Pur, A. G. (2020). 2018 Pesticide Use Maps -. https://water.usgs.gov/nawqa/pnsp/usage/maps/show_map.php?year=2018&map=PARAQUAT&hilo=H
- State of California Natural Resources Agency Department of Fish And Wildlife Biogeographic Data Branch California Natural Diversity Database State And Federally Listed Endangered And Threatened Animals Of California. (2018). <https://nrm.dfg.ca.gov/FileHandler.ashx?DocumentID=109405&inline>
- Teerlink, J., Hernandez, J., & Budd, R. (2017). Fipronil washoff to municipal wastewater from dogs treated with spot-on products. ResearchGate; Elsevier. https://www.researchgate.net/publication/316897783_Fipronil_washoff_to_municipal_wastewater_from_dogs_treated_with_spot-on_products
- Wise, C. F., Wise, C. F., Hammel, S. C., Herkert, N., Ma, J., Ma, J., Motsinger-Reif, A., Stapleton, H. M., Stapleton, H. M., Breen, M., Breen, M., Breen, M., Breen, M., & Breen, M. (2020). Comparative Exposure Assessment Using Silicone Passive Samplers Indicates That Domestic Dogs Are Sentinels to Support Human Health Research. *Environmental Science and Technology*, 54(12), 7409–7419. <https://doi.org/10.1021/acs.est.9b06605>
- Wise, C. F., Hammel, S. C., Herkert, N. J., Ospina, M., Calafat, A. M., Breen, M., & Stapleton, H. M. (2022). Comparative Assessment of Pesticide Exposures in Domestic Dogs and Their Owners Using Silicone Passive Samplers and Biomonitoring. *Environmental Science and Technology*, 56(2), 1149–1161. <https://doi.org/10.1021/acs.est.1c06819>

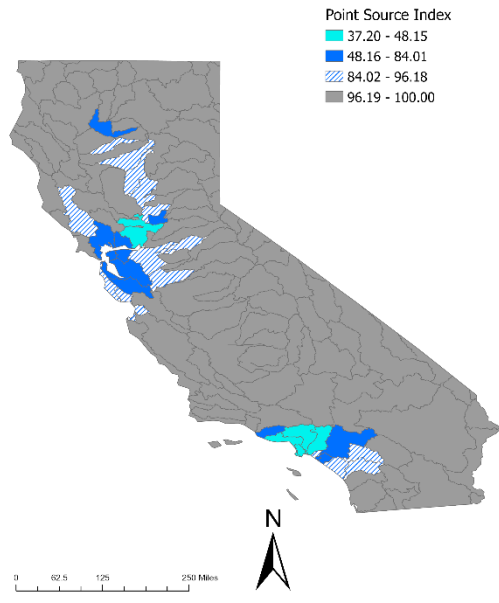


Figure B-1: Color-coded Map Displaying Spatial Distribution of Index Score Values for Point Pesticide Sources.

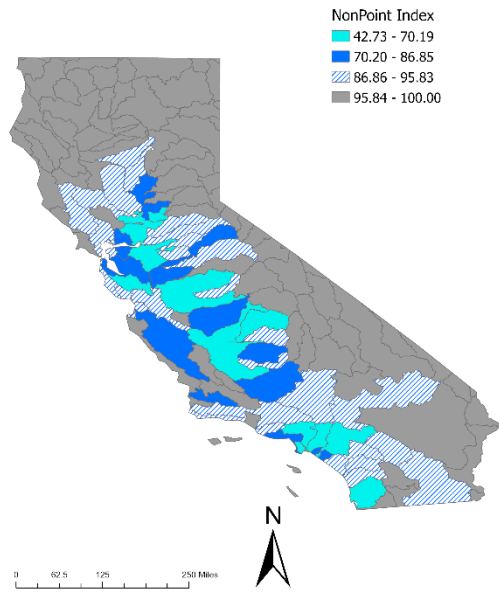


Figure B-2: Color-coded Map Displaying Spatial Distribution of Index Score Values for Nonpoint Pesticide Sources.

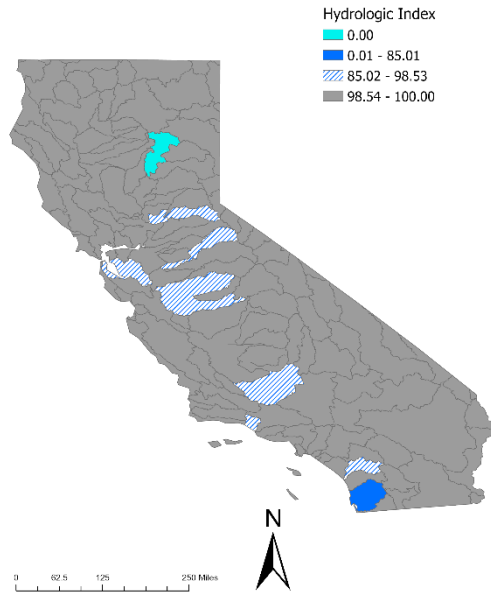


Figure B-3: Color-coded Map Displaying Spatial Distribution of Index Score Values for Hydrologic Conditions.

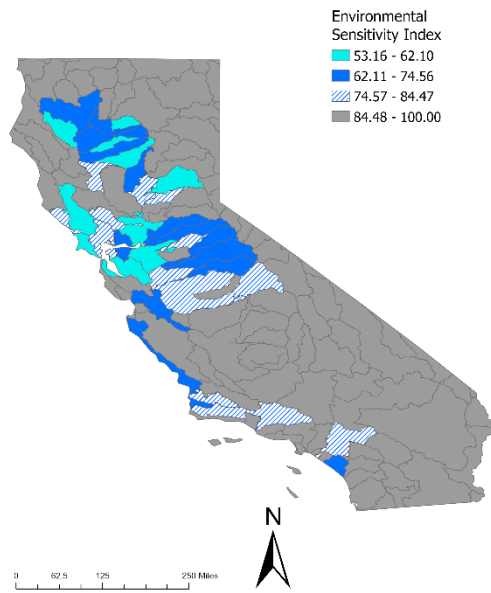


Figure B-4: Color-coded Map Displaying Spatial Distribution of Index Score Values for Environmental Sensitivity.

APPENDIX C: AUGUST MEAN MONTHLY DILUTION FACTORS

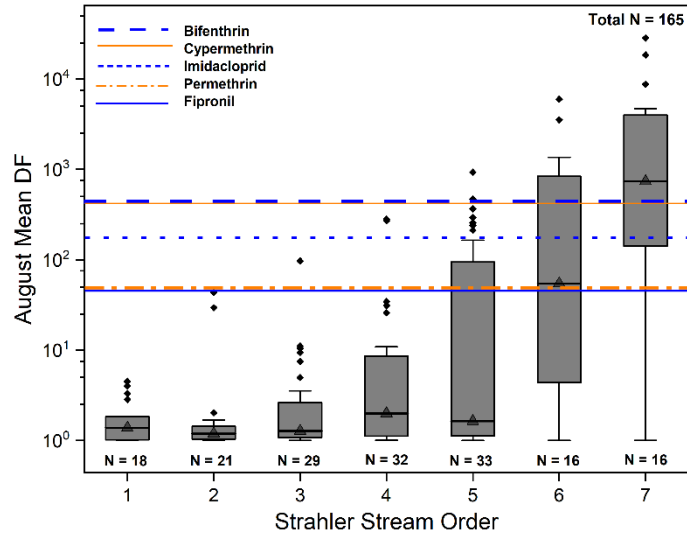


Figure C-1: Color-coded Map of Dilution Factors for Receiving Streams at WWTPs’ Discharge Sites under Mean Monthly Flow conditions in August.