

RESEARCH

Effects of Flow on Pesticides in Water and Zooplankton in the Northern Sacramento–San Joaquin Delta

James Orlando¹, Laura Twardochleb^{2,3}, David Bosworth², Michelle L. Hladik¹, Corey Sanders¹, Matthew De Parsia¹, Brittany E. Davis^{2*}

ABSTRACT

Zooplankton are a key food source for juvenile fishes in estuaries worldwide, including California’s Sacramento–San Joaquin Delta (hereafter Delta); both zooplankton quality and quantity are critical to ecosystem health. Zooplankton may be affected by pesticides in water and the food web, and the Delta is known to contain complex pesticide mixtures. In this study, we evaluated pesticide concentrations in water and zooplankton in the northern Delta during (1) the summer–fall of 2017, 2018, and 2019, which included periods of augmented pulse flows from agriculture tailwater, and (2) across a full seasonal cycle from May 2019 to March 2020. We quantified changes in pesticide concentration in response to environmental factors. We found that zooplankton showed more frequent detections

of hydrophobic pesticides compared to more frequent detections of hydrophilic compounds in water. Pesticide concentrations were influenced by flow, pesticide application, and season, but the effects of these environmental factors differed by habitat (Sacramento River or Yolo Bypass Toe Drain). Pesticides in water responded similarly to environmental factors in the Sacramento River and Yolo Bypass, whereas pesticides in zooplankton responded differently. In water, we found more detections and higher concentrations at higher flows in the Yolo Bypass and Sacramento River, but responses to pesticide application varied by habitat. Alternatively, pesticide concentrations in zooplankton increased in the Yolo Bypass with increasing flow (correlated with flow pulses) and changed seasonally; whereas, pesticide concentrations in zooplankton in the Sacramento River decreased at higher flows, and decreased with or did not respond to higher pesticide application in the watershed. Our study suggests that augmented flows—particularly those using agricultural tailwater—may have unintended negative ecological effects that could partially offset benefits to the food web and fishes in the northern Delta, underscoring the complex interplay among factors that drive increased pesticide exposure.

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* Corresponding author: brittany.e.davis@water.ca.gov

- 1 US Geological Survey
California Water Science Center
Sacramento, CA 95819 USA
- 2 California Department of Water Resources
Division of Integrated Science and Engineering
Sacramento, CA 95691 USA
- 3 State Water Resources Control Board
Division of Water Rights
Sacramento, CA 95814 USA

KEY WORDS

contaminants, pesticides, zooplankton, flow, discharge, season, summer–fall, food web

INTRODUCTION

Aquatic ecosystems have been influenced by a variety of ecosystem stressors such as alteration and degradation of aquatic habitats (Blann et al. 2009), introduction of invasive species (Ruiz et al. 1997; Strayer 2010), changes in climate (Poff et al. 2002; Comte and Olden 2017) and land use (Carpenter et al. 2011; Freeman et al. 2019). Urban and agricultural pesticides may exacerbate these stressors by bioaccumulating in aquatic organisms—through bioconcentration or biomagnification via trophic transfer—further affecting aquatic communities and food webs (Hoffman 2003; Jonker 2012). Pesticides can affect growth, abundance, and community composition (DeLorenzo et al. 1999; Lam et al. 2019). Pesticides can also reduce zooplankton survival and alter community composition (van Wijngaarden et al. 2014; Arenas-Sánchez et al. 2018; Hébert et al. 2021), and at lower exposure levels zooplankton may develop resistance to, and bioaccumulate pesticides, affecting native fish species that consume them (Bendis and Relyea 2014; Fong et al. 2016; Anzalone et al. 2024; Stillway et al. 2024). Fish exposed to pesticides in water, or their diet, display adverse genetic changes (Jeffries et al. 2015), organ lesions (Teh et al. 2005; Stillway et al. 2024), altered sex ratios (Brander et al. 2013), and changes in physiology and behavior (Baldwin et al. 2009; Renick et al. 2016). Moreover, bioaccumulation of pesticides in fish presents health risks for people who practice recreational and subsistence fishing (Kelly et al. 2007; De Vlaming 2008).

Zooplankton are a key food source for juvenile fishes in the Sacramento–San Joaquin Delta, California (hereafter Delta) including Chinook Salmon (*Oncorhynchus tshawytscha*) (Goertler et al. 2017) and the endangered Delta Smelt (*Hypomesus transpacificus*) (Slater and Baxter 2014). There have been long-term declines in total zooplankton biomass in the Delta as well as changes in zooplankton species composition, which are

hypothesized to have contributed to reductions in native fish populations (Sommer et al. 2007; Winder and Jassby 2011; FLOAT–MAST 2022). Pesticides in the Delta may have contributed to declines in zooplankton and fish through individual or population-level effects (Hanazato 2001; Fong et al. 2016). Studies have shown that Delta waters contain complex mixtures of current-use pesticides which vary in composition throughout the year (Orlando et al. 2014; De Parsia et al. 2018, 2019) and that these pesticides cause toxicity to native invertebrate (Werner et al. 2010; Weston and Lydy 2010) and fish species (Fong et al. 2016).

The Delta is a hydrologically complex region with a variety of constructed and natural interconnecting sloughs and channels that convey nearly one-half of California's total yearly runoff (CDWR 1993). Water reaches the Delta from the Sacramento and San Joaquin rivers, the Yolo Bypass, and several smaller tributaries. Together, these systems transport snowmelt and rainfall runoff, agricultural tailwater, municipal stormwater, and treated wastewater from multiple sources into the Delta. The Sacramento River is the largest source of fresh water to the Delta, conveying runoff from over 6 million hectares of land in northern California, including large tracts of agricultural land as well as multiple urban centers (Figure 1). During very wet winters and springs, Sacramento River flood flows can also enter the Yolo Bypass. The Yolo Bypass is a 60-kilometer-long, 24,000-hectare, partially-leveed basin that conveys rainfall runoff, agricultural tailwater, Sacramento River flood flows, municipal stormwater, and treated wastewater from multiple sources to the northwest portion of the Delta (Figure 1). The Yolo Bypass represents the largest remaining area of freshwater floodplain habitat in the Delta (Frantzich et al. 2018); however, during the drier summer–fall season the variable interannual floodplain area is reduced to the perennial Toe Drain channel. Detailed descriptions of the Yolo Bypass and Sacramento River watersheds, including land use types and primary agricultural crops, can be found in Orlando et al. (2020).

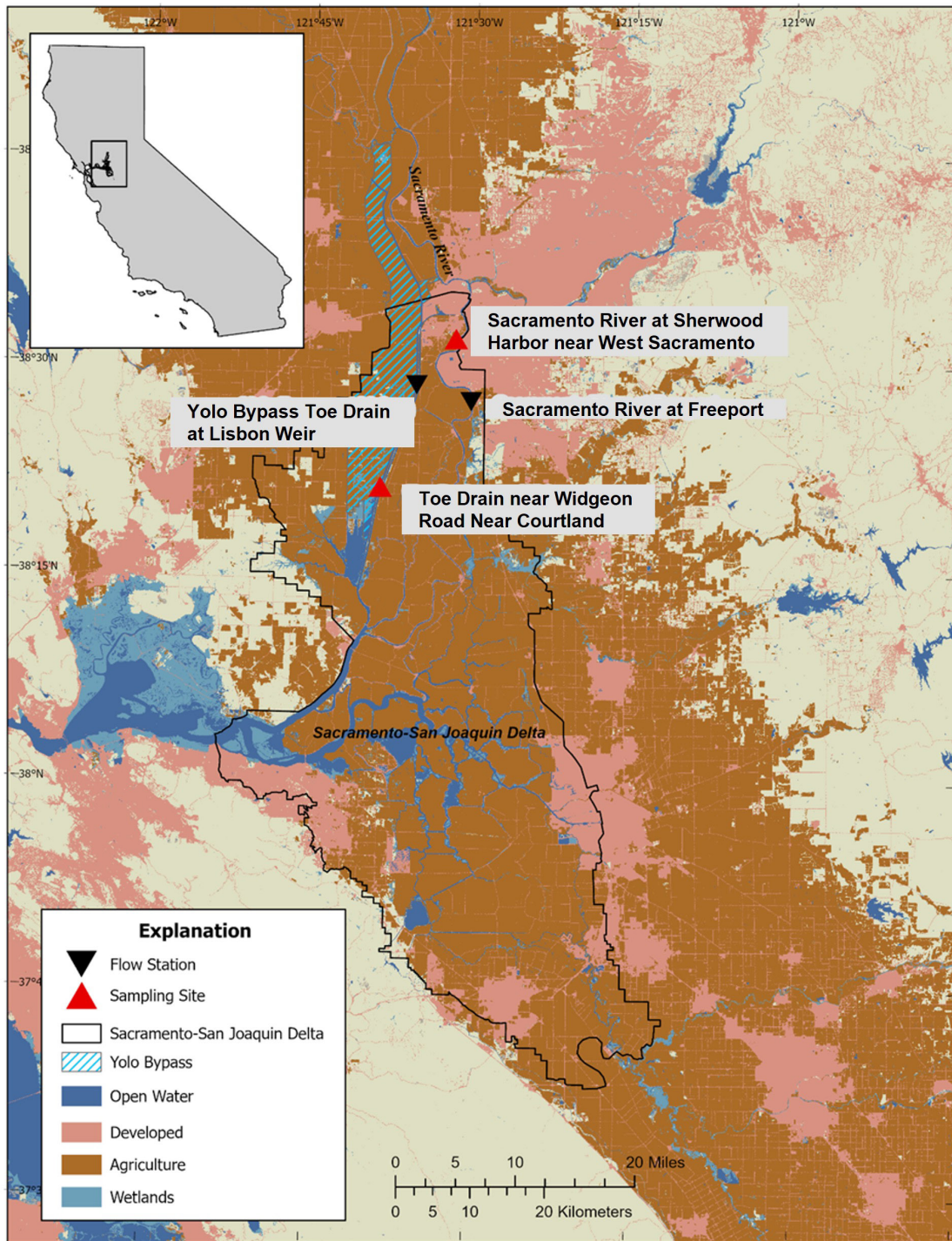


Figure 1 Map showing sampling site locations in the Sacramento–San Joaquin Delta, California. *Pale yellow* indicates other land-cover classifications. *Source:* Base layer is modified from US Geological Survey National Land Cover Database, 2021.

The Sacramento and San Joaquin rivers carry pesticides from agricultural and urban runoff into the Delta throughout the year, and the types and concentrations of these pesticides vary, based on their use in the upstream watersheds (Weston and Lydy 2010; Orlando et al. 2014; Weston et al. 2014; Stout et al. 2018; De Parsia et al. 2018, 2019). Pesticides associated with rice agriculture along with some urban-use pesticides are often detected in water in the Yolo Bypass and Sacramento River in the spring and summer seasons (Orlando et al. 2020). In addition, recent studies reported several legacy and current-use insecticides in zooplankton from the Yolo Bypass and Sacramento River in 2019 and 2020 (Anzalone et al. 2022, 2024). Despite this recent evidence, more research can aid in understanding how pesticide detections and concentrations may differ between habitats, and their effects on the Delta food web. Floodplain and riverine habitats may be affected differently by pesticide loading, based on pesticide application in the watersheds, the timing and types of water inputs (urban vs. agricultural return flows), flow magnitude, and water residence time. Understanding how contaminants vary between the Sacramento River and Yolo Bypass is particularly important to evaluate potential negative effects on threatened and endangered species in the Delta such as Chinook Salmon and Delta Smelt.

Resource managers are interested in how flow augmentation affects pesticide detections and concentrations, to evaluate if negative ecological effects of management actions may outweigh their intended benefits. In the fall of 2012, a large-magnitude flow pulse occurred in the Yolo Bypass Toe Drain after changes in normal water operations, which may have contributed to a rare fall phytoplankton bloom in the lower Sacramento River and western Delta (Frantzich et al. 2018). After this event, researchers began experimenting with the augmentation of summer–fall flow pulses in the Yolo Bypass, using either agricultural tailwater or Sacramento River water, and exploring the effects of these pulses on phytoplankton production, plankton densities in historical Delta Smelt habitat, and water quality. Pesticides in water samples collected before,

during, and after augmented summer–fall flow pulses in 2016 (Sacramento River water), 2018 and 2019 (agricultural tailwater), and a flow pulse from normal agricultural drainage in 2017 are reported in Orlando et al. (2020) and Uychutin et al. (2024). The 2018 and 2019 augmented flow pulses using agricultural tailwater were shown to increase pesticide concentrations in water in the Yolo Bypass, particularly pesticides associated with rice agriculture (Orlando et al. 2020; Stillway et al. 2024; Uychutin et al. 2024). To further characterize pesticides in this sensitive ecosystem, supplemental research began to explore pesticide concentrations detected in zooplankton in the Sacramento River and Yolo Bypass during years with (2018, 2019) and without (2017) experimental augmented flow pulses (Orlando et al. 2021).

The goal of this study was to describe pesticide concentrations in the Yolo Bypass and Sacramento River, and potential effects on the food web in the northern Delta. We assessed how pesticide concentrations in water and zooplankton respond to pesticide application, season, river flow, and augmented flow pulses in summer–fall. We examined the following study questions:

1. How do classes of pesticides detected differ in water vs. zooplankton?
2. How do pesticide application, flow, and season affect pesticide detections and concentrations in the Yolo Bypass and Sacramento River?
3. How do augmented summer–fall flow pulses in the Yolo Bypass affect pesticide detections and concentrations in the Yolo Bypass Toe Drain?

Studies have shown that zooplankton bioaccumulate hydrophobic pesticides, which concentrate in sediments and organisms in the Yolo Bypass because of the importance of benthic detrital energy sources to floodplain consumers (Fong et al. 2016; Anzalone et al. 2024). Accordingly, we hypothesize the following: (1) Pesticide detections and concentrations in water and zooplankton would differ based on

the pesticide class, with zooplankton having more detections and higher concentrations of hydrophobic pesticides compared with water. (2) Flow and pesticide application rates would correspond with increased pesticide concentrations in water and zooplankton. Moreover, we hypothesized that increased pesticide detections and concentrations would follow increases in flow during fall rainstorms that mobilize contaminants and increase stormwater runoff, with larger increases in concentrations in the Yolo Bypass than the Sacramento River. In addition, we expected the types of pesticides to vary in detection frequency and concentration by location, given reported differences in annual pesticide applications. (3) The greatest increases in pesticide detections and concentrations would be observed in the Yolo Bypass after rapid changes in flow during augmented summer–fall flow pulses.

MATERIALS AND METHODS

Sample Collection

Water and zooplankton samples were collected biweekly in the summer–fall of 2017 (August–November), 2018 (July–October), and from May 2019 to March 2020 from US Geological Survey (USGS) stations on the Yolo Bypass Toe Drain (Yolo Bypass) and the Sacramento River in the northern region of the Delta. (Figure 1, Table A1). At the first station, Toe Drain near Widgeon Road near Courtland, California (USGS station ID 382113121383501), only zooplankton samples were collected in 2017 ($n = 6$) and 2018 ($n = 10$) whereas in 2019–2020 water and zooplankton samples were collected concurrently ($n = 21$). At the second station, Sacramento River at Sherwood Harbor near West Sacramento, California (USGS station ID 383155121314101), water and zooplankton samples were collected concurrently for all sampling events ($n = 6$ [2017], 9 [2018], and 21 [2019–2020]).

California Department of Water Resources (CDWR) personnel collected surface-water grab samples, from a boat at the center of the channel, for analysis of dissolved pesticides. At each site, two 1-L baked, amber glass bottles were

submerged 0.5 meters below the water surface, allowed to fill completely, and then capped while still submerged. The samples were labeled with identifying information and immediately placed on wet ice. After collection, samples were transported to the USGS Organic Chemistry Research Laboratory (OCRL) in Sacramento, California for extraction and analysis. Water-quality parameters (temperature, specific conductance, dissolved oxygen concentration, turbidity, and pH) were recorded when samples were collected using a handheld multi-parameter sonde (ProDSS, Yellow Spring Instruments, Ohio, USA) (Orlando et al. 2020; Uychutin et al. 2024).

Zooplankton samples were collected using a 150- μ m-mesh conical plankton net that was 2 m long and had a 0.50-m-diameter mouth (IEP et al. 2021). The zooplankton net was submerged just below the surface and towed for a minimum of 10 minutes. The contents of the nets were immediately transferred to 1-L plastic (HDPE) bottles, labeled, and placed on wet ice. Samples were then transported to the USGS OCRL for extraction and analysis.

Hydrologic Conditions

To assess the effect of summer–fall flows and seasonal changes in hydrology and precipitation on pesticide concentrations, we used daily average discharge data from the Sacramento River at Freeport and the Yolo Bypass Toe Drain at Lisbon Weir stream gauges located in the northern Delta. Tidally filtered daily average discharge data collected at Sacramento River at Freeport, California (USGS station ID 11447650) were obtained from the USGS National Water Information System (USGS c2023) using the ‘dataRetrieval’ R package (DeCicco et al. 2022). For the Yolo Bypass Toe Drain at Lisbon Weir station (Water Data Library [WDL] station ID B91560Q), we acquired instantaneous discharge data, collected at 15-minute intervals, from the CDWR Water Data Library (CDWR c2023). The instantaneous discharge data collected at Lisbon Weir was processed through a low-pass filter to calculate net discharge (Godin 1972) and then aggregated as daily averages. Before applying the filter, we imputed values for gaps

up to 2 hours in the instantaneous data using linear interpolation. We acquired precipitation data from the California Irrigation Management Information System for multiple stations within the Yolo Bypass and Sacramento River watersheds (CIMIS c2023).

Summer-Fall Conditions

Summertime flows on the Sacramento River were generally slightly above historical average daily flows at the Sacramento River at Freeport (USGS c2023) in 2017, and 2019, while flows in 2018 were close to average (Figure 2A). Summertime flows at the Yolo Bypass Toe Drain at Lisbon Weir were variable, with ambient flows in 2017, and augmented flow pulses in both 2018 and 2019 (CDWR c2023). A flow pulse was implemented from late August to late September 2018 which reached a maximum discharge of 551 cubic feet per second ($\text{ft}^3 \text{s}^{-1}$). The flow pulse in 2019 occurred over the same period, and reached a peak flow of just over $700 \text{ ft}^3 \text{ s}^{-1}$. Both the 2018 and 2019 flow pulses were created by releasing stored agricultural tailwater into the Yolo Bypass (Figure 2B). California receives approximately 75% of its annual precipitation between November and March so precipitation during the summer to fall is generally minimal. Precipitation in the study area was normal to below-normal in the summer-fall sampling windows in 2017, 2018, and 2019.

Seasonal Conditions

For the period of May 2019 to March 2020, Sacramento River flows were at their peak in June 2019 and remained above average through early January 2020, after which flows were consistently below average through the winter (Figure 2C). In the Yolo Bypass, peak flows reached just over $1,500 \text{ ft}^3 \text{ s}^{-1}$ after a storm in May; no Sacramento River flows entered the bypass during this period (Figure 2D). Precipitation between May 2019 and March 2020 was normal to below normal, except for May 2019 and December 2020, which were both above normal with monthly cumulative precipitation of roughly 70 mm and 180 mm, respectively.

Pesticide Use

Data on pesticides applied to agriculture and on those applied by professional applicators in urban areas were obtained from the California Department of Pesticide Regulation (CDPR) (CDPR c2022). Applications of synthetic pesticides analyzed in this study in the Sacramento River watershed for 2017, 2018, 2019, and 2020 were 949,748 kg, 991,129 kg, 1,012,281 kg, and 1,186,224 kg, respectively. For the Yolo Bypass watershed, applications in 2017, 2018, 2019, and 2020 were 908,244 kg, 919,685 kg, 913,814 kg, and 886,017 kg, respectively (Figure A1). The CDPR does not track pesticide applications by private homeowners, and this may be a significant route of use for certain pesticide classes such as pyrethroids. Pesticide applications to rice account for the largest percentage of use in the summer-fall in the Sacramento River (approximately 30%) and Yolo Bypass (approximately 50%) watersheds. More detailed pesticide application information can be found in Orlando et al. (2020).

Sample Processing

Within 24 hours of collection, water samples were filtered through $0.7\text{-}\mu\text{m}$ glass-fiber filters (Grade GF/F, Whatman, Piscataway, New Jersey) into pre-cleaned glass bottles to remove suspended material. Each zooplankton sample was filtered through a $63\text{-}\mu\text{m}$ sieve to separate the zooplankton and vegetation/detritus from the water. Large sticks, twigs, rocks, and leaves were rinsed with organic free water into the sieve and then discarded. The remaining zooplankton and detritus retained on the sieve was transferred into 50-mL plastic centrifuge tubes and frozen overnight at $-20\text{ }^\circ\text{C}$. The samples were then dehydrated completely using a freeze dryer, and stored at $-20\text{ }^\circ\text{C}$ until further processing and analysis. The “zooplankton” sample does not consist entirely of zooplankton but includes detritus and other suspended particles, based on the operational size cut-off. Methods used in this study to quantify pesticide concentrations in zooplankton tissue are comparable to those used in other studies (e.g., Anzalone et al. 2022).

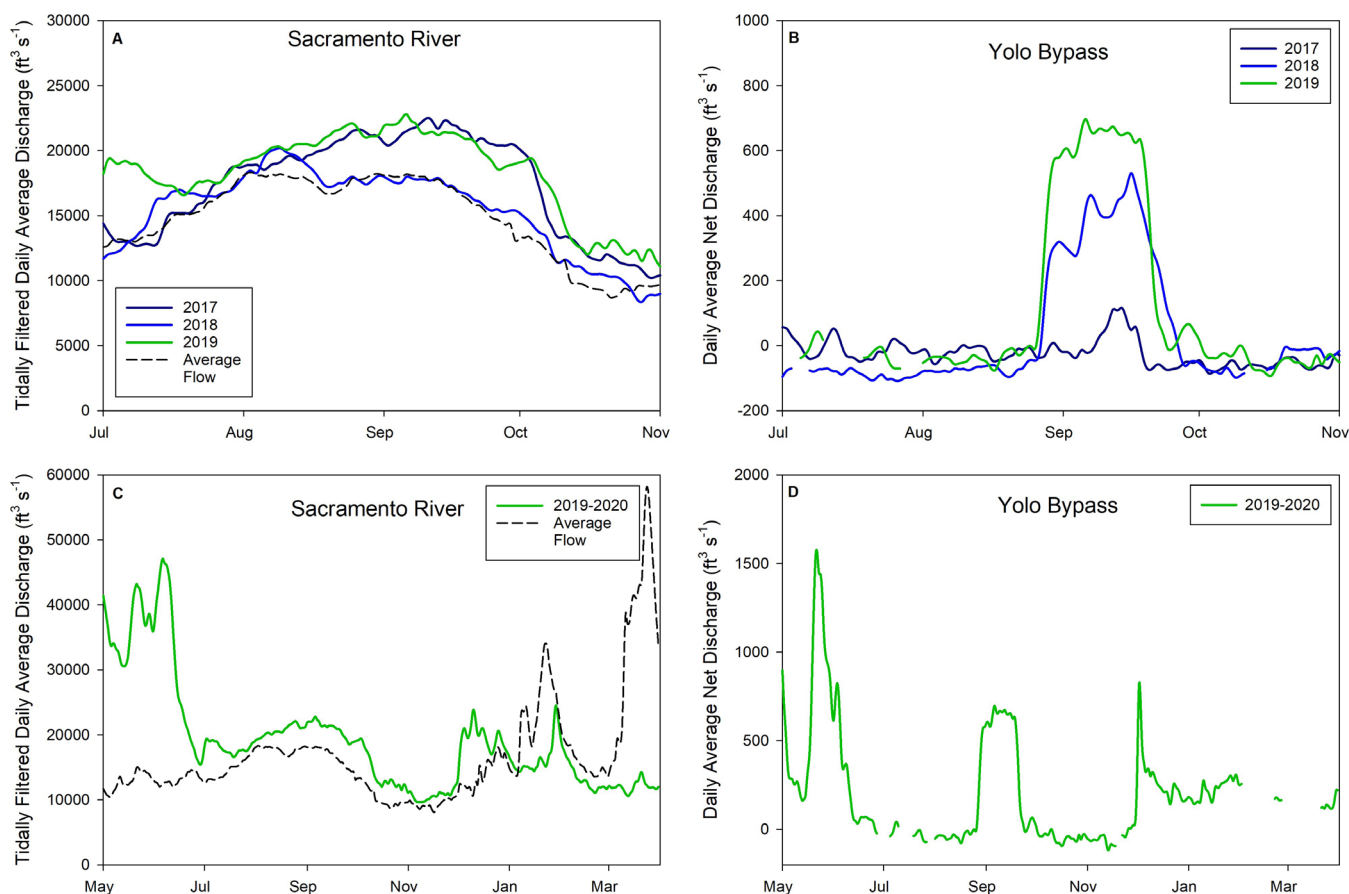


Figure 2 Hydrographs from 2017–2020 at the Sacramento River at Freeport and the Yolo Bypass Toe Drain at Lisbon Weir, California. Discharge (flow) measurements are in cubic feet per second ($\text{ft}^3 \text{s}^{-1}$).

Sample Analysis

Water

Water samples were analyzed using gas chromatography–mass spectrometry (GC–MS) and liquid chromatography–tandem mass spectrometry (LC–MS/MS) analytical methods (Hladik et al. 2008, 2009; Hladik and Calhoun 2012; Sanders et al. 2018) for a suite of 177 pesticides and pesticide degradates (Table A2). Details of the sample extraction and analysis can be found in Orlando et al. (2020).

Pesticide concentrations in water were validated using performance-based quality-control samples, including trip blanks, field replicates, laboratory matrix spikes, matrix-spike replicates, laboratory blanks, and surrogate recoveries (Orlando et al. 2020). Quality-control samples collected in

2019 consisted of two each of trip blanks, field replicates, and laboratory matrix spikes with matrix-spike replicates. Each trip blank consisting of 1 L of organic-free blank water was opened to the atmosphere when environmental samples were collected at one site. Samples were processed in the same manner as environmental samples. One trip blank was analyzed by GC–MS and one by LC–MS/MS, and no pesticides were detected in any of the trip blanks.

Two field-replicate sample pairs (one each by GC–MS and LC–MS/MS) were collected to test the reproducibility of results. There were 35 detections of pesticides in the sample pairs, and the relative percent difference (RPD) ranged from 0.0% to 2.5%. The correlation of pesticide detections between the paired environmental and replicate samples was 100%.

Three matrix spikes each paired with a matrix-spike replicate sample were analyzed (one by GC–MS and two by LC–MS/MS). Spike recoveries ranged from 70.2% to 124.0%, and the RPD ranged from 0.0% to 3.4%. Recoveries of surrogate compounds in both environmental and quality-control samples ranged from 70.3% to 129.8%.

Zooplankton

Extraction and analysis procedures were adapted from a published sediment method (Hladik and McWayne 2012) previously applied to the extraction of biofilms (Mahler et al. 2020). Each freeze-dried zooplankton sample was homogenized and sub-sampled before extraction, with 0.5 to 1 grams as the targeted mass per sample. For samples with a total mass of less than 0.5 grams, the entire sample was extracted. The weighed sample was further homogenized with sodium sulfate, and surrogates were added. The sample was then extracted with dichloromethane at 100°C and 1,500 PSI using an Accelerated Solvent Extractor 200 (Dionex Corporation, Sunnyvale, California). Extracts were cleaned up using activated carbon, evaporated to 200 μ L in ethyl acetate, had internal standards added, and were analyzed by GC–MS/MS; Hladik et al. 2016) for 86 pesticides and pesticide degradates (Table A2).

Pesticide concentrations in zooplankton samples were validated using laboratory replicates, matrix spikes, and blank samples. Eight laboratory-replicate samples were analyzed; there were 166 detections of pesticides in the environmental/laboratory-replicate sample pairs, and the RPD ranged from 0.1% to 7.8%. The correlation of pesticide detections between the paired environmental and replicate samples was 100%. Four laboratory matrix-spike samples were analyzed to assess pesticide recoveries for all compounds, and these ranged from 70.2% to 124.6%. Six laboratory blank samples consisting of baked sand/sodium sulfate were analyzed; no pesticides were detected. Recoveries of surrogate compounds added to all environmental and quality-control samples ranged from 71.0% to 128.2%.

Statistical Analyses

Using a zero-inflated negative binomial model, we evaluated how classes of detected pesticides (measured in both matrices) differ in water vs. zooplankton. Pesticide detection frequency was modeled according to:

$$\text{Pesticide detection frequency} \sim \begin{cases} \log K_{ow} * \text{Matrix, Detection} = 0/1 \\ \log K_{ow} * \text{Matrix, Detection Frequency} > 0 \end{cases} \quad \text{Eq 1}$$

Pesticide detection frequency was natural-log ($x+1$)-transformed, and the model included an interaction between pesticide hydrophobicity (measured as $\log K_{ow}$, a water partitioning coefficient) and a categorical term for matrix (water or zooplankton). Zero-inflated negative binomial models were run using R (R Core Team c2022) with the ‘glmmTMB’ package, version 1.1.7 (Brooks et al. 2023) and model fit was assessed using functions in the ‘DHARMA’ package, version 0.4.6 (Hartig 2022).

We used linear models or generalized additive models (GAMs) to examine how pesticide application, flow, and season affect total pesticide concentrations in water (ng L^{-1}) and zooplankton (ng g^{-1}) in the Yolo Bypass and Sacramento River. We conducted analyses on two time-periods: (1) summer–fall (to inform effects of pulse flows), using data collected from July 1–October 31 in 2017–2019; and (2) data collected biweekly between June 2019 and February 2020, to examine effects of season. For each period, we modeled pesticide concentrations separately for water and zooplankton, and separately for the Yolo Bypass and Sacramento River, for a total of eight models. We examined the fit of each model using diagnostic plots, including histograms of residuals, quantile–quantile (QQ) plots of residuals, and plots of observed vs. fitted values. Pesticide concentration data were natural-log-, \log_{10} –, or square-root-transformed as needed, to achieve normality and homoscedasticity of model residuals.

For each of the eight models, we included terms for daily average net discharge ($\text{ft}^3 \text{ s}^{-1}$) and pesticide application standardized by watershed

area (Yolo Bypass or Sacramento River) (kg mi^{-2}), to account for the difference in size between the two watersheds. We used daily average net discharge measured at the Yolo Bypass Toe Drain at Lisbon Weir station in the Yolo Bypass model, and at the Sacramento River at Freeport station for the Sacramento River model, respectively. We ran separate models including either the total monthly pesticide application for the month of or month before sample collection to investigate which of the two was a better predictor of pesticide concentrations in water or zooplankton. For seasonal zooplankton models, we also included a term for pesticide concentration in water and the previous 1- or 2-month's pesticide concentration in water. Model selection procedures are described below.

All linear models and GAMs were run in R version 4.3.1 (R Core Team c2022). For each of the four seasonal models using data from June 2019 to February 2020, we built all models as GAMs, including a smooth term for day of year as a cyclic cubic regression spline, using restricted maximum likelihood (REML) as the smoothing parameter estimation method to account for the effects of seasonality (Pedersen et al. 2019) not captured by discharge or pesticide application. In models for which the smooth term for day of year was not significant, we also ran a linear model including all other model terms except the smooth term for day of year. For the GAMs, we did not specify the number of basis functions, K . We fit GAMs with a Gaussian distribution using the 'mgcv' package, version 1.8-42 (Wood 2023), and assessed overall model fit and adequacy—and overfitting of the value of K —using diagnostic functions in the 'gratia' package, version 0.8.1 (Simpson 2023). For all models, we compared simpler models to more complex models using Akaike's Information Criterion (AIC), and selected a model as the best fitting if it had an AIC value of at least 4 less than the next-best model.

RESULTS

Comparison of Pesticides Detected in Water and Zooplankton

We found a significant interaction between pesticide hydrophobicity ($\log K_{ow}$) and matrix (water vs. zooplankton) on pesticide detection frequency (Figure 3) using a zero-inflated negative binomial model (Table 1). Zooplankton samples had significantly more detections of hydrophobic pesticides than water samples, and water samples had significantly more non-detections of hydrophobic pesticides than zooplankton samples. Overall, 29 pesticides were detected in zooplankton samples, and 96% of zooplankton samples contained multiple pesticides (up to 17 per sample). However, several moderately hydrophobic pesticides ($\log K_{ow}$ between 2 and 4) which are applied primarily to rice (thiobencarb, 3,4-dichloroaniline, and azoxystrobin), were also frequently detected in zooplankton samples (Figure 3).

Summer-Fall Pesticides

Summer-Fall 2017, 2018, 2019

All water samples in summer-fall contained multiple pesticides (from 3 to 18), and a total of 30 pesticides were detected during these periods (Table A3). The most frequently detected pesticides, which were detected in every sample, included 3,4-dichloroaniline (a degradate of the rice herbicide propanil and the widely applied herbicide diuron), the fungicide azoxystrobin, and the herbicide hexazinone. The insecticide methoxyfenozide was also frequently detected (94%), as well as the herbicide metolachlor (61%). Pesticide concentrations reached a maximum of $1,090 \text{ ng L}^{-1}$ (azoxystrobin) (Orlando et al. 2020; Uychutin et al. 2024). In 2019, total water pesticide concentrations were greater in Yolo Bypass samples than in Sacramento River samples during seven of the eight sampling events (Figure 4E and 4F), with nearly a 6-fold increase in concentrations in the bypass during the September pulse flow period. When comparing concentrations measured to the US Environmental Protection Agency (USEPA) aquatic life benchmarks, one Sacramento River water sample (8/23/2018) contained the organophosphate

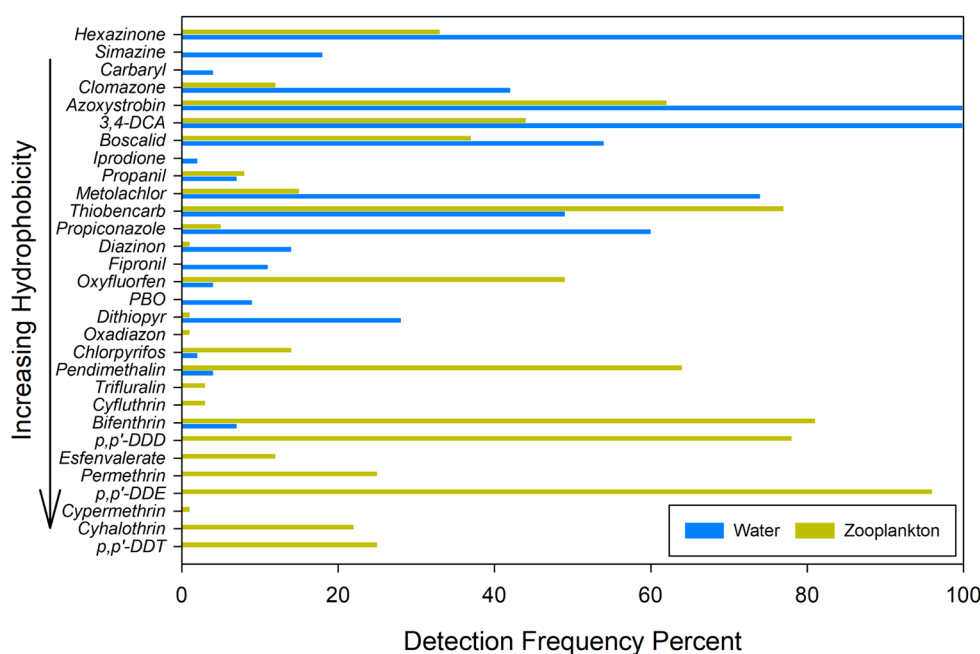


Figure 3 Detection frequencies ordered by increasing hydrophobicity ($\log K_{ow}$) for pesticides analyzed in both water and zooplankton and detected in either matrix, 2017-2020

Table 1 Model results for classes of pesticides in water vs. zooplankton

Model	Model term	Estimate	Standard error	Z-value	P-value
Conditional model (pesticide detection frequency > 1)	Intercept	5.549	0.5410	10.26	< 0.001
	Hydrophobicity ($\log K_{ow}$)	-0.5413	0.1513	-3.578	< 0.001
	Matrix (zooplankton)	-2.093	0.6861	-3.050	0.002
	Hydrophobicity ($\log K_{ow}$) * Matrix (zooplankton)	0.6131	0.1743	3.517	< 0.001
Zero-inflation model (pesticide detection = 0/1)	Intercept	-6.891	1.859	-3.708	< 0.001
	Hydrophobicity ($\log K_{ow}$)	7.873	2.077	3.790	< 0.001
	Matrix (zooplankton)	1.363	0.3698	3.685	< 0.001
	Hydrophobicity ($\log K_{ow}$) * Matrix (zooplankton)	-1.854	0.4368	-4.244	< 0.001

insecticide dichlorvos at a concentration of 9.6 ng L^{-1} , which is above the chronic invertebrate toxicity benchmark of 5.8 ng L^{-1} , and concentrations of bifenthrin surpassed both the chronic freshwater vertebrate (4.0 ng L^{-1}) and acute freshwater invertebrate (0.25 ng L^{-1}) toxicity benchmarks in one Sacramento River water sample (10/28/2019) and one Yolo Bypass water sample (10/29/2019) (USEPA 2020). USEPA toxicity benchmarks were not surpassed in any other water samples during this period.

Multiple pesticides were detected in 44 of the 47 zooplankton samples analyzed. Sacramento River samples contained an average of ten pesticides per sample, whereas Yolo Bypass zooplankton contained an average of six pesticides per sample (Table A3 and Figure A2). A total of 26 pesticides were detected in zooplankton during these periods, and the most frequently detected pesticides were the p,p'-DDT degradates, p,p'-DDE (94% of the samples analyzed) and p,p'-DDD (77%), the pyrethroid insecticide bifenthrin

(72%), and the fungicide azoxystrobin (72%). Several pesticides including three pyrethroid insecticides (cyhalothrin, cypermethrin, and esfenvalerate) were detected only in Sacramento River zooplankton (Figure 3, Table A3, and Figure A2). Maximum pesticide concentrations were 838.7 ng g^{-1} (azoxystrobin) (Orlando et al. 2021). In general, total zooplankton pesticide concentrations were higher in Sacramento River than in Yolo Bypass samples in summer–fall (Figures 4 and 5); however, zooplankton pesticide concentrations substantially increased (Figure 4D and 4F; Figure 5D and 5F) in the Yolo Bypass in 2018 and 2019 during the managed pulse flow periods.

Summer–Fall Models

For all four summer–fall models, a linear model that included pesticide application for the same month of sample collection provided the best fit to the data. We found that total pesticide concentrations in water and zooplankton increased significantly with daily average net discharge in the Yolo Bypass ($p < 0.001$, Table 2, Figure 4D and F), while the relationship between concentrations and monthly pesticide application was not significant ($p = 0.52$ [water] and $p = 0.78$ [zooplankton]). In the Sacramento River, pesticide concentrations in water increased significantly with both net discharge ($p = 0.001$) and pesticide application ($p = 0.028$), whereas concentrations in zooplankton decreased significantly with both net discharge ($p < 0.001$) and pesticide application ($p < 0.001$).

Seasonal Pesticides

2019–2020

From May 2019 to March 2020, 47 pesticides were detected in the water samples (Table A3). For Sacramento River samples, 29 unique pesticides were detected, whereas 45 pesticides were detected in Yolo Bypass samples (Table A3). All samples contained mixtures of multiple pesticides (6 to 35), and the average number of pesticides detected was 10 in Sacramento River samples and 18 in Yolo Bypass samples. The most frequently detected pesticides in water samples are shown in Table A3. Pesticide concentrations in water

ranged from below method reporting limits to 315 ng L^{-1} (3,4-dichloroaniline) in Sacramento River samples, and from below method reporting limits to $1,100 \text{ ng L}^{-1}$ (azoxystrobin) in Yolo Bypass samples (Uychutin et al. 2024). In addition to the USEPA aquatic life benchmarks exceedances discussed previously under “Summer–Fall Pesticides” for the October 2019 samples (bifenthrin exceeding both the acute invertebrate and chronic vertebrate benchmarks for both the Sacramento River [10/28/2019] and Yolo Bypass [10/29/2019]), there were two more exceedances. An additional Sacramento River sample (12/10/2019) contained bifenthrin above the chronic invertebrate benchmark of 1.3 ng L^{-1} , and an additional Yolo Bypass water sample (12/9/2019) contained both bifenthrin and the neonicotinoid insecticide imidacloprid at concentrations above their benchmarks for chronic invertebrate toxicity (1.3 and 10 ng L^{-1} , respectively).

Twenty-five pesticides were detected in zooplankton samples (note that zooplankton were analyzed for 86 pesticides vs. the 177 pesticides in water) collected from the Sacramento River and Yolo Bypass ($n = 21$ samples each), including four pyrethroid insecticides and the organophosphate insecticide diazinon (Table A3). By site, 21 different pesticides were detected in Sacramento River zooplankton samples, and 23 were detected in Yolo Bypass samples. As many as 16 pesticides were detected in every sample, and the average number of pesticides detected was 9 in Yolo Bypass and 10 in Sacramento River samples. The most frequently detected pesticides in zooplankton included azoxystrobin, bifenthrin, pendimethalin, and thiobencarb (Figure 3, Table A3). Pesticide concentrations ranged from 3.8 ng g^{-1} (fluxapyroxad) to 920 ng g^{-1} (cyhalothrin) (Orlando et al. 2021).

2019–2020 Models

For samples collected between June 2019 and February 2020, we found that a linear model best explained pesticide concentrations in water in the Yolo Bypass and Sacramento River and in zooplankton in the Sacramento River, and a GAM including a smooth term for day of year best explained pesticide concentrations in zooplankton

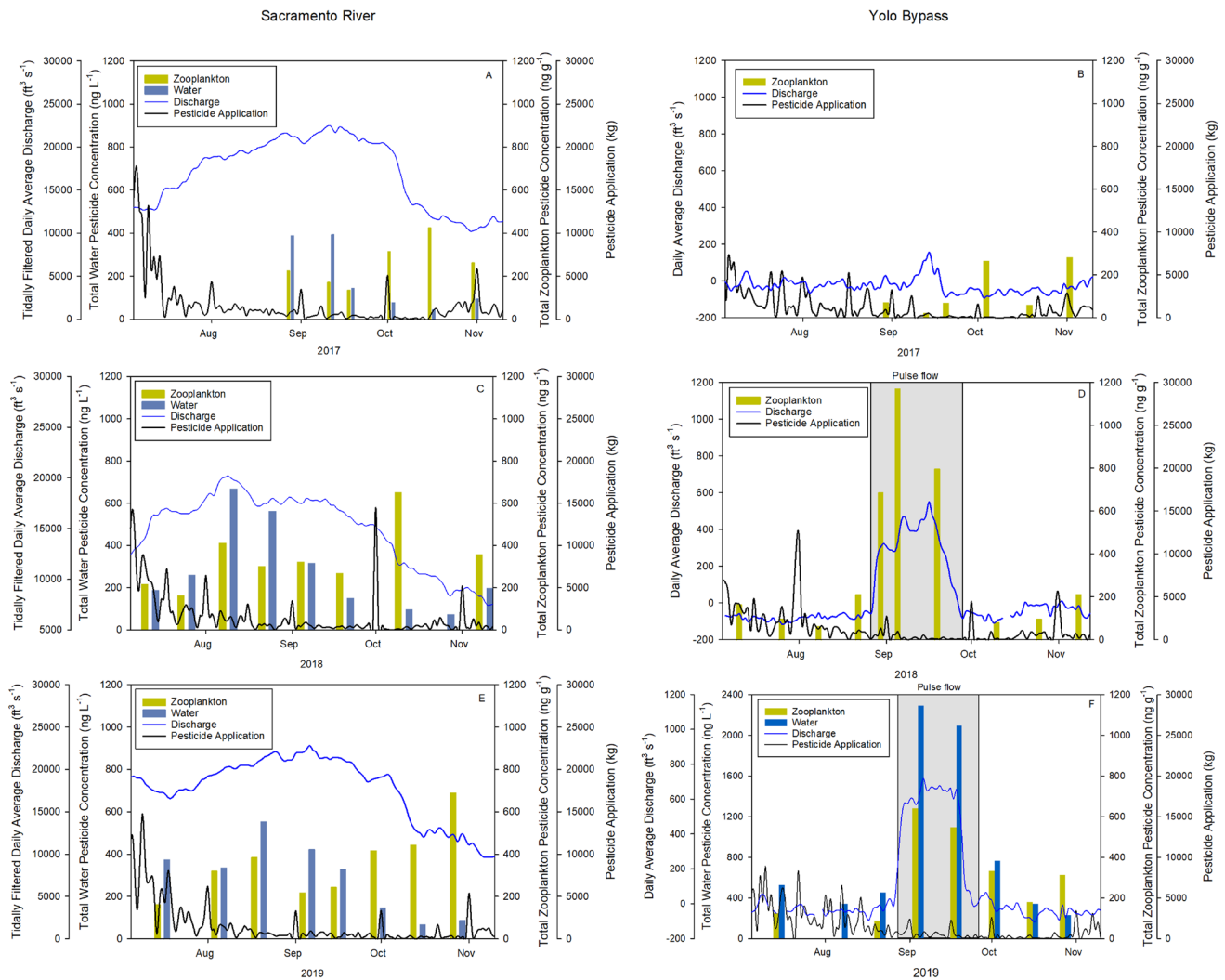


Figure 4 Total pesticide concentrations in water (ng L^{-1}) and zooplankton (ng g^{-1}) samples collected from the Sacramento River at Sherwood Harbor (A, C, and E) and the Yolo Bypass at the Toe Drain, California (B, D, and F) in the summer-fall periods in 2017, 2018 and 2019 (corresponding to summer-fall models in Table 2). Note the increased scale of water pesticide concentrations in Figure 4F. Discharge data ($\text{ft}^3 \text{s}^{-1}$) are from Sacramento River at Freeport and the Yolo Bypass Toe Drain at Lisbon Weir represented by a blue line; pesticide application (kg) is the black line; the shaded region represents the period of an augmented pulse flow in the Yolo Bypass.

in the Yolo Bypass (Figure 6, Table 3). Pesticide concentrations in water and zooplankton in the Yolo Bypass were positively correlated with daily average net discharge. For water samples from the Sacramento River, pesticide concentrations also increased with pesticide application during the month before sample collection. Pesticide concentrations in zooplankton from the Yolo Bypass increased with pesticide applications in the month of sample collection. There was also a significant seasonal effect on pesticide

concentrations in zooplankton in Yolo Bypass independent of discharge or pesticide application; concentrations were higher during the months of October to December when both application and discharge were relatively low (Figure 6, Table 3). For zooplankton in the Sacramento River, pesticide concentrations were negatively correlated with daily average net discharge. Zooplankton models that included terms for the previous 1- or 2-month's pesticide concentration in water were not supported by AIC.

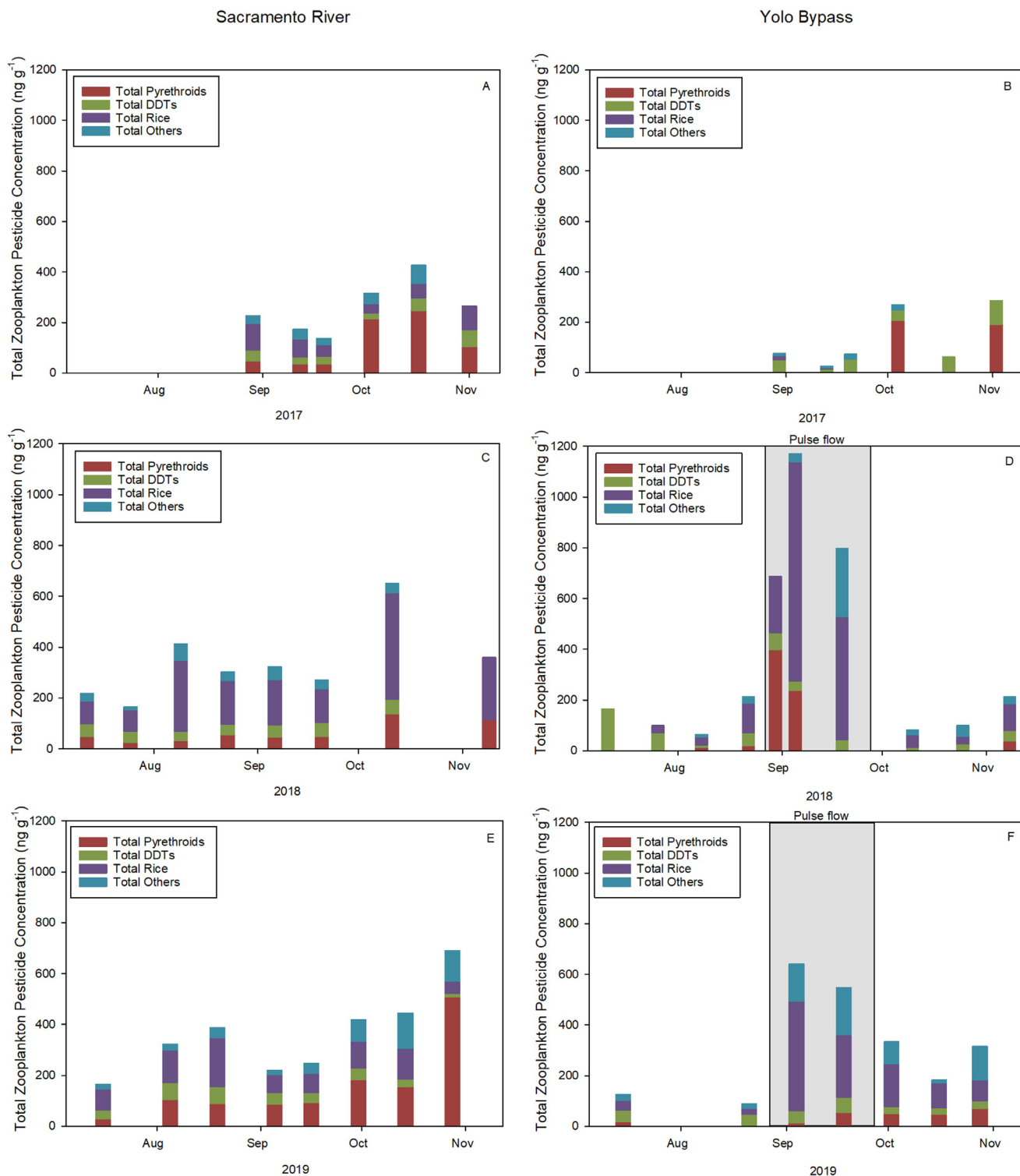


Figure 5 Zooplankton pesticide concentrations (in ng g^{-1}) by type (pyrethroids, DDTs, rice herbicides, and others) in the Sacramento River at Sherwood Harbor (A, C, and E) and the Yolo Bypass at the Toe Drain (B, D, and F) in the summer-fall periods of 2017, 2018, and 2019. The shaded region represents the period of an augmented pulse flow in the Yolo Bypass.

Table 2 Summary of linear models for water and zooplankton samples collected during summer–fall of 2017, 2018, and 2019 (summer–fall models)

Response	Station	Parameter	Estimate	Standard error	T-value	P-value
Water (ng L ⁻¹)	Yolo Bypass	Intercept	613.1	121.5	5.048	0.007
		Net discharge	2.624	0.2426	10.82	<0.001
		Pesticide application	-4.915	6.903	-0.7121	0.516
log(Water) (ng L ⁻¹)	Sacramento River	Intercept	2.334	0.5277	4.423	0.004
		Net discharge	1.632 × 10 ⁻⁴	2.827 × 10 ⁻⁵	5.772	0.001
		Pesticide application	4.076 × 10 ⁻²	1.416 × 10 ⁻²	2.878	0.028
sqrt(Zooplankton) (ng g ⁻¹)	Yolo Bypass	Intercept	13.76	1.921	7.165	<0.001
		Net discharge	2.510 × 10 ⁻²	5.822 × 10 ⁻³	4.311	<0.001
		Pesticide application	-2.126 × 10 ⁻²	7.423 × 10 ⁻²	-0.2864	0.778
log(Zooplankton) (ng g ⁻¹)	Sacramento River	Intercept	7.364	0.3196	23.04	<0.001
		Net discharge	-8.287 × 10 ⁻⁵	1.712 × 10 ⁻⁵	-4.841	<0.001
		Pesticide application	-4.318 × 10 ⁻²	9.271 × 10 ⁻³	-4.657	<0.001

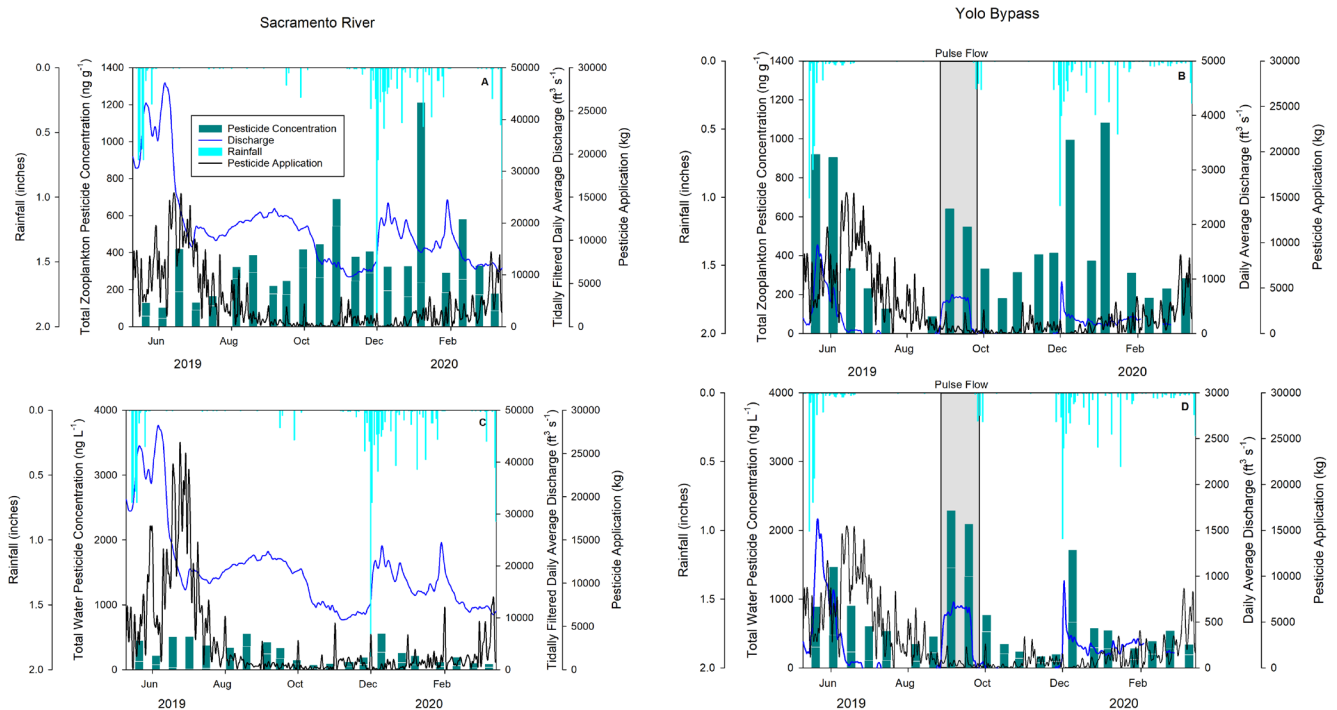


Figure 6 Total pesticide concentrations in zooplankton (A, B, in ng g⁻¹) and water (C, D, in ng L⁻¹) from 2019–2020 at Sacramento River at Sherwood Harbor, and the Yolo Bypass at the Toe Drain, California (corresponding to seasonal models in Table 3). Discharge (ft³ s⁻¹) is shown as the blue lines; pesticide application (kg) is indicated by black lines; precipitation (rainfall in inches) is light blue extending from the top; and the shaded region represents the pulse flow period in the Yolo Bypass.

Table 3 Best-fitting models testing effects of flow, pesticide application, and seasonality (day of year) on total pesticide concentration in water and zooplankton in the Yolo Bypass and Sacramento River for samples collected between June 2019 and February 2020 (seasonal models). For each model, we list the response variable, the parameters, the parameter estimate, standard error (SE) of the estimate, the test statistic, and the *P*-value that indicates the significance of the effect of each term on the response variable. The test statistic for linear models is a *t*-value, and the test-statistic for the generalized additive model (GAM) is an *F*-value.

Linear model	Response	Parameter	Estimate	Standard error	Test statistic	<i>P</i> -value
Water in Yolo Bypass	Log ₁₀ Total Pesticide Concentration (ng L ⁻¹)	Intercept	6.045	0.1887	32.02	< 0.001
		Discharge (ft ³ s ⁻¹)	1.381 × 10 ⁻⁰³	4.245 × 10 ⁻⁰⁴	3.254	0.005
Water in Sacramento River	Total Pesticide Concentration (ng L ⁻¹)	Intercept	- 167.0	86.56	- 1.964	0.067
		Discharge (ft ³ s ⁻¹)	2.287 × 10 ⁻⁰²	5.060 × 10 ⁻⁰³	4.519	< 0.001
		Previous month pesticide application (kg mi ⁻²)	5.750	1.981	2.903	0.010
Zooplankton in Sacramento River	Log ₁₀ Total Pesticide Concentration (ng g ⁻¹)	Intercept	2.828	1.092	25.91	< 0.001
		Discharge (ft ³ s ⁻¹)	- 1.719 × 10 ⁻⁰⁵	5.043 × 10 ⁻⁰⁶	- 3.408	0.003
Generalized additive model	Response	Parameter	Estimate ^a	Standard error ^a	Test statistic	<i>P</i> -value
Zooplankton in Yolo Bypass	Square root Total Pesticide Concentration (ng g ⁻¹)	Intercept	10.82	2.593	4.175	0.002
		Discharge (ft ³ s ⁻¹)	1.954 × 10 ⁻⁰²	4.000 × 10 ⁻⁰³	4.885	< 0.001
		Current month pesticide application (kg mi ⁻²)	0.1325	5.579 × 10 ⁻⁰²	2.374	0.037
		Smooth (day of year)	2.951	8	2.898	0.003

a. For the smooth term for day of year, the value shown under the “Estimate” column is the effective degrees of freedom, indicating the complexity of the smooth (higher values indicate more wiggly curves), and the value shown under the “Standard error” column is the degrees of freedom used in the analysis of variance (ANOVA) to test the significance of the smooth term.

DISCUSSION

This study evaluated pesticide concentrations in the northern Delta region of the Sacramento–San Joaquin Delta. We found more frequent detections of hydrophobic compounds in zooplankton compared to more frequent detections of hydrophilic and moderately hydrophobic compounds in both water and zooplankton. The bioaccumulation of hydrophobic pesticides such as pyrethroid insecticides in zooplankton may negatively affect the food web and partially negate intended benefits of pulse flow experiments for fishes. We also showed that pesticide concentrations in the North Delta region from 2017 to 2020 were influenced by flow, pesticide application, and season, but the effects of these environmental factors differed based on habitat (Sacramento River or Yolo Bypass Toe Drain) (Table 4). Pesticide increases in the bypass aligned with managed pulse flows using agriculture tailwater (Figures 4 and 6) indicating

a strong correlation between flow increases and pesticide exposure.

Concentrations of several pesticides in both locations and across time-frames exceeded EPA benchmarks for toxicity; this included exceedances once each for dichlorvos and imidacloprid (chronic invertebrate benchmarks), and four sample exceedances for bifenthrin (two for chronic invertebrate, two for acute invertebrate/chronic vertebrate benchmarks). The EPA benchmarks are tested for single pesticides, while all water samples in this study contained complex mixtures of pesticides (Orlando et al. 2020; Uychutin et al. 2024). Previous research has demonstrated that the toxicity of pesticide mixtures can be additive and possibly even synergistic (Laetz et al. 2009; Rico et al. 2018), and therefore the presence of these complex pesticide mixtures in the Sacramento River and Yolo

Table 4 Summary of relationships from summer–fall and seasonal models that assessed the effects of three predictors—flow rate, pesticide application, and season—on pesticide concentrations in water and zooplankton in the Yolo Bypass and Sacramento River. Significant relationships are indicated by “+” or “–” when the predictor significantly increased or decreased pesticide concentrations, respectively. “NS” denotes no significant effect, and blank cells indicate that the predictor was not retained in the top-performing model.

Habitat	Model	Predictor	Pesticides in water	Pesticides in zooplankton
Yolo Bypass	Summer–Fall (2017, 2018, 2019)	Flow	+	+
		Application	NS	NS
	Seasonal (June 2019 to Feb 2020)	Flow	+	+
		Application		+
		Season		+ in Oct–Dec
Sacramento River	Summer–Fall (2017, 2018, 2019)	Flow	+	–
		Application	+	–
	Seasonal (June 2019 to Feb 2020)	Flow	+	–
		Application	+	
		Season		

Bypass may have significant implications for the food web and fishes in the northern Delta.

Zooplankton samples accumulated more hydrophobic pesticides than water samples (Figure 3). This result is not surprising given that hydrophobic chemicals tend to bioconcentrate (their rate of uptake exceeds their rate of elimination) and biomagnify (increase in concentration at higher trophic levels through trophic transfer) in aquatic organisms (Hoffman 2003; Jonker 2012; Mackay et al. 2016). Pesticide concentrations in zooplankton are also affected by diet composition and interaction with sediment (e.g., demersal behavior) (Mackay et al. 2016). Although we did not examine pesticide concentrations in phytoplankton or other zooplankton food sources, zooplankton likely bioaccumulated pesticides through their diet and through absorption across their gill surfaces and other membranes (Hoffman 2003; Jonker 2012). We recognize that zooplankton taxa were not specifically identified in our samples, which also included detritus and suspended material that may accumulate hydrophobic chemicals (samples include material > 63 μm , similar to Anzalone et al. 2022). Five pyrethroid insecticides that were detected in zooplankton samples and not in water (cyfluthrin, cyhalothrin, cypermethrin,

esfenvalerate, permethrin) are highly toxic to aquatic invertebrates (Werner et al. 2010; Weston and Lydy 2010). Biomagnification of pesticides in zooplankton may also affect zooplanktivorous fish species, which are particularly susceptible to hydrophobic pesticides. These pesticides can also accumulate in birds and humans because of trophic transfer, potentially causing wide-ranging effects to ecological and human health in the Delta (Kelly et al. 2007; Fong et al. 2016). Because pyrethroids are rarely detected in water as a result of their hydrophobicity, characterizing their presence in zooplankton and detritus is important to understanding how these compounds could potentially affect the Delta food web.

Pesticide concentrations increased in response to discharge after rainfall or managed flow pulse actions during the summer–fall that used agricultural tailwater (Figures 4 and 6). These results align with our initial hypotheses and other studies in the Delta that have found increased pesticide concentrations in water and higher exposure or effects on the food web with higher runoff and flow that results from precipitation, agricultural drainage, or flow management actions. (Weston et al. 2019; Anzalone et al. 2022; Stillway et al. 2024). However, we found one exception to this trend in the Sacramento River

where pesticides in zooplankton decreased with increasing discharge, suggesting that different mechanisms control pesticide concentrations in zooplankton at this location. Discharge in the Sacramento River is primarily affected by rainfall, snowmelt, and reservoir releases (Singer 2007), while discharge in the Yolo Bypass is primarily influenced by agricultural runoff and rainfall, except during inundation periods, which can also result from flood-control releases from upstream reservoirs (Sommer et al. 2001, 2004). Accordingly, two hypothesized mechanisms that underlie these findings include these two points:

1. High flows in the Sacramento River reduced pesticide concentrations in zooplankton samples through dilution by snowmelt and reservoir release water that is relatively low in pesticides; and higher flows in the Yolo Bypass increased pesticide concentrations because agricultural runoff and managed flow pulses using agricultural tailwater have higher pesticide concentrations (Figures 4 and 6).
2. During periods of high discharge, hydrophobic pesticides may have adsorbed to suspended sediments instead of bioconcentrating in zooplankton in the Sacramento River. This is because hydrophobic pesticides have both (1) an affinity for organic carbon in sediments (Domagalski and Kuivila 1993; Hoke et al. 1997; Pehkonen et al. 2010) and (2) observed increases in suspended sediment during periods of high discharge in the Sacramento River (Wright and Schoellhamer 2005; McKee et al. 2006; Figure A3).

Application rates of pesticides were not a consistent predictor of pesticide concentrations. Only pesticides in water in the Sacramento River and in zooplankton in the Yolo Bypass (seasonal model only) increased with pesticide application in the watershed (Tables 2 and 3). This did not align with our hypothesis that pesticide concentrations would increase with watershed application, and could have resulted from uncertainties in the location and timing

of pesticide application, as well as a paucity of information about urban pesticide use (CDPR 2000). These findings suggest the relationship between application rates and pesticide exposure are complex, and inconsistent with previous studies that showed application rates were strongly correlated with effects at a broader scale (Fong et al. 2016). The pesticide application data used in our analysis does not include pesticides purchased and used by individual homeowners, and this is likely a significant source of pesticides, especially in urban environments (Sutton et al. 2019), which are characteristic of the Sacramento River sampling location near the city of Sacramento (Figure 1), and of the Yolo Bypass, which receives urban wastewater from the cities of Davis and Woodland. Next, we looked at pesticide applications on a full watershed basis rather than considering the point locations where pesticides were applied or discharged to waterways. Such a fine-scale analysis could be conducted for agricultural pesticide applications because they are identified to the section level (1 square mile), but this would not be possible for urban pesticide applications. Pesticides applied in urban settings are only reported at the county level, and typically once per month, resulting in an entire month of use reported as occurring on the first day of the month (CDPR 2000).

Rice pesticides and pyrethroid insecticides made up the bulk of the total pesticide burden in zooplankton collected from the Sacramento River and Yolo Bypass. The rice pesticides detected most frequently and at the highest concentrations included the fungicide azoxystrobin, the herbicide thiobencarb, and 3,4-dichloroaniline, which is a degradate of the very heavily used rice herbicide propanil (Table A3). Zooplankton—especially copepods and cladocerans—are sensitive to exposure to azoxystrobin, as are some phytoplankton taxa (Gustafsson et al. 2010; van Wijngaarden et al. 2014). The proportion of rice pesticides was greatest during the summer–fall period, consistent with the timing of application of these compounds, and was elevated in the Yolo Bypass during augmented flow pulses in 2018 and 2019 (Figures 4 and 5). This suggests that exposure to rice pesticides may affect the food web in the

North Delta during the summer–fall agricultural drainage periods and could be further affected by augmented flow pulses that leverage agricultural drainage water. Other studies support higher pesticide exposure in the food web of the Yolo Bypass relative to the Sacramento River, particularly during winter and spring runoff and floodplain inundation. For example, Anzalone et al. (2022) found higher concentrations of organochlorines in floodplain-rearing juvenile Chinook Salmon than those from the Sacramento River, and prey-item detection frequencies also were higher during high-flow periods compared to drought conditions. Fish inhabiting the North Delta may also be exposed to higher levels of legacy pesticides, including DDT, through their diet. Diet is a major exposure route of DDT degradates (DDE, DDD) for juvenile Chinook Salmon in the Yolo Bypass compared with the Sacramento River, with chironomid larvae and zooplankton implicated as contaminated prey sources (Anzalone et al. 2024).

After the 2019 augmented flow pulse, pesticide concentrations in zooplankton remained elevated throughout the fall period in the Yolo Bypass (Figure 5), especially compared to 2018, when native and imperiled fish species (such as Delta Smelt) in the upper estuary are assumed to be food limited (Smith and Nobriga 2023). Previous studies found histopathological signs of contaminant exposure in wild Delta Smelt collected from the Cache Slough complex (Hammock et al. 2015; Teh et al. 2020), and fish from that region showed the worst signs of food limitation and contaminant exposure stress (Hammock et al. 2015). Similarly, Delta Smelt exposed to agricultural drainage water used in the 2019 augmented fall flow pulse had more organ lesions than fish exposed to water collected from other regions of the estuary (Stillway et al. 2024). Recent research suggests the North Delta food web may be more affected by agricultural pesticides during wet years because more water is available to support increased agricultural plantings (Anzalone et al. 2022; Anzalone et al. 2024; Stillway et al. 2024). Bioaccumulation of pesticides may be increased when rainfall occurs during or shortly after summer–fall pesticide

applications and before major flow events (compare concentrations in October of 2019 to 2018 in Figure 6) and could further affect the food web.

Urban pesticides such as pyrethroid insecticides made up a significant proportion of the total pesticide burden in zooplankton, and were detected in greater variety and frequency in samples collected from the Sacramento River than from the Yolo Bypass (Table A3), consistent with the urban setting of our Sacramento River sampling site (Figure 1). The pyrethroids bifenthrin and permethrin, which are used extensively in urban settings and are present in a wide variety of home-use pesticides (NPIRS c2023), were frequently detected in both Sacramento River and Yolo Bypass zooplankton (Table A3). Pyrethroids are highly toxic to aquatic invertebrates, and are detected more frequently from urban runoff than from agricultural drainage in the Delta (Werner et al. 2010; Weston and Lydy 2010). Pyrethroids are endocrine-disrupting chemicals that can affect organisms and populations (Brander et al. 2013; Riar et al. 2013; Tadesse and Kasa 2017), including skewed sex ratios in Mississippi Silverside at sites with high urban runoff (Brander et al. 2013), altered feeding behavior in juvenile salmon (Baldwin et al. 2009), and histopathological lesions and stress responses in Sacramento Splittail (Teh et al. 2005). Juvenile Chinook Salmon exposed to bifenthrin through their diet (chironomids) had significantly decreased swimming performance and increased biomarkers for liver injury (Magnuson et al. 2022). Delta Smelt exposed to permethrin showed elevated expression of genes associated with protein degradation and apoptosis, and decreased expression of immune function genes (Jeffries et al. 2015). Exposure of Longfin Smelt embryos and larvae to bifenthrin resulted in smaller hatchlings, reduced yolk sac volume, and changes in behavior (Mauduit et al. 2023). Fong et al. (2016) also found negative relationships between application rates of pyrethroid insecticides and annual abundance indices for Longfin Smelt, Delta Smelt, Sacramento Splittail, American Shad, and Striped Bass.

Several management strategies intended to conserve fish (e.g., rice-field and floodplain rearing of fish, flow-augmentation to subsidize the food web, and restoration through increasing Delta outflow or habitat acreage) are being tested to determine efficacy and to better evaluate trade-offs between effects on and benefits to native species. Uncertainties remain about the potential for conservation strategies (such as augmented pulse flows) to have unintended consequences, including increased pesticide exposure in the Delta. This study informs managers of possible negative ecological effects of augmented flows (particularly using agricultural tailwater) that could at least partially negate benefits to fishes; however, our study also demonstrates the complex interplay among drivers of increased pesticide exposure. For example, we have shown that zooplankton, and thus food web contamination, increases with flow modifications (e.g., managed agricultural tailwater or precipitation runoff), which is reflected in both increased pesticide concentrations and pesticide composition. We also showed that pesticide usage and application data are not sufficiently comprehensive to reliably predict exposure. Lastly, we found that the correlation between flow and pesticide effects differ between localized hot-spots (i.e., Yolo Bypass) and regionally integrative bodies of water (i.e., Sacramento River), which is expected, given their different pesticide inputs and different sources of inflow and runoff. Our study demonstrates that management of habitat warrants consideration of multiple pesticide exposure pathways for fish and other organisms in the Delta.

DATA AVAILABILITY

All pesticide concentration data for water and zooplankton samples in the current study can be found in Orlando et al. 2020, <https://doi.org/10.3133/ofr20201076>, Orlando et al. 2021, <https://doi.org/10.5066/P93YBKCR>, and Uychutin et al. 2024, <https://doi.org/10.3133/dr1195>.

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