Supplementary Information – Exposure profiles

METHODS AND MATERIALS

To assess the risk of chlorothalonil on relevant fish species, fish population modeling was conducted using annual chemographs of daily exposure. Since daily monitoring data rarely exists for pesticides, available monitoring data from the National Water Quality Monitoring Council's Water Quality Portal (WQP) was utilized by the SEAWAVE-QEX model [1] to generate the exposure profile necessary for population modeling. The WQP is the premiere source of discrete water quality data in the United States, created by combining publicly accessible water quality data, on a national scale, from the United States Environmental Protection Agency's (USEPA) Storage and Retrieval Data Warehouse (STORET), the United States Geological Society's (USGS) National Water Information System (NWIS), and over 400 state, federal, tribal, and local agencies [2]. SEAWAVE-QEX is a statistical model developed, and released in 2018, by the USGS, that simulates daily pesticide concentrations in surface water, from less-than-daily monitoring datasets, using streamflow and other covariates specific to a monitoring site [1]. SEAWAVE-QEX incorporates measured pesticide concentrations, seasonality, streamflow variability, and long-term trends in its regression and simulations. In 2019, the USEPA presented SEAWAVE-QEX as a tool to quantitively assess water monitoring data for pesticide risk assessment in a white paper it published, entitled "Approaches for Quantitative Use of Surface Water Monitoring Data in Pesticide Drinking Water Assessments" [3]. To utilize monitoring data with SEAWAVE-QEX, the associated monitoring dataset must meet the following minimum data requirements described in [1]:

- at least 3 individual years with 6 or more observations, 30 percent or more of which are uncensored
- at least 30 observations for all years combined
- at least 10 uncensored observations for all years combined

All available monitoring data for chlorothalonil was downloaded from the WQP and queried for sites meeting these minimum data requirements. Of the resulting 3,751 monitoring sites in the WQP with monitoring data for chlorothalonil, none of these sites met the minimum requirement of having at least 10 uncensored observations for all years combined. To account for the lack of chlorothalonil monitoring sites meeting the minimum data requirements for SEAWAVE-QEX, all available monitoring data for 4-Hydroxychlorothalonil, a metabolite of chlorothalonil, was downloaded from the WQP and queried for suitable sites to be used as a surrogate. Of the resulting 854 monitoring sites in the WQP with monitoring data for 4-Hydroxychlorothalonil, 5 of the sites met all minimum data requirements. These 5 sites, all USGS monitoring stations, were in Georgia, Michigan, North Carolina, Oregon, and Texas, respectively (Figure S1). The USGS monitoring site in TX, USGS-08057200, was ultimately selected for use with the SEAWAVE-QEX model, due to its relatively higher exposure values for 4-Hydroxychlorothalonil, which provides a more conservative exposure profile for population modeling. The USGS-08057200 monitoring site is in North-Central Texas, near the city of Dallas, and has a watershed area of approximately 67 square miles, with a land use that is 95% urban, 2% agriculture, 2% grassland, and 1% forest, based on the United States Department of Agriculture's (USDA) National Agricultural Statistics Survey's (NASS) Cropland Data Layer (CDL) [4] for 2020 (Figure S2). The monitoring site's watershed intersects both Dallas and Collin County, which have an average annual chlorothalonil use of 132 kilograms and 167 kilograms, respectively, from 2012-2018, based on values from the National Water-Quality Assessment Program's (NAWQA) Pesticide National Synthesis Project (PNSP), which generates annual county-level agricultural pesticide use estimates for the conterminous U.S. [5]. 4-Hydroxychlorothalonil monitoring data was available from USGS-08057200 for 9 years (2012-2020) and had 171 observations, 128 (75%) of which were uncensored, across that period. Observed concentration values for 4-Hydroxychlorothalonil ranged from 0.02 ppb to 7.1 ppb, with a mean concentration of 0.33 ppb (Table S1).

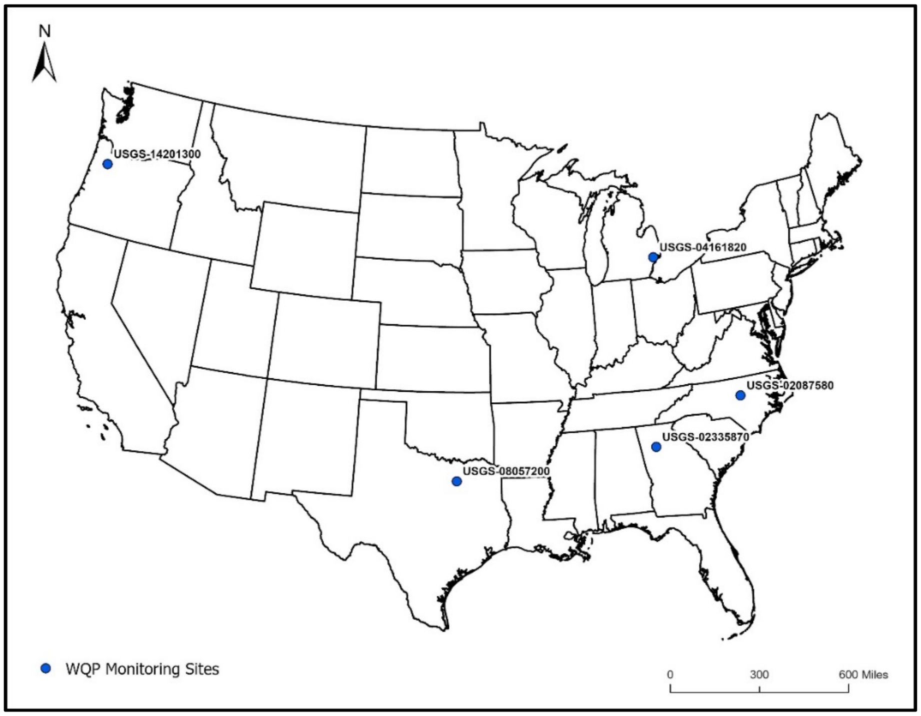

Figure S1. Location of monitoring sites in the WQP for 4-Hydroxychlorothalonil that meet minimum data requirements for SEAWAVE-QEX.

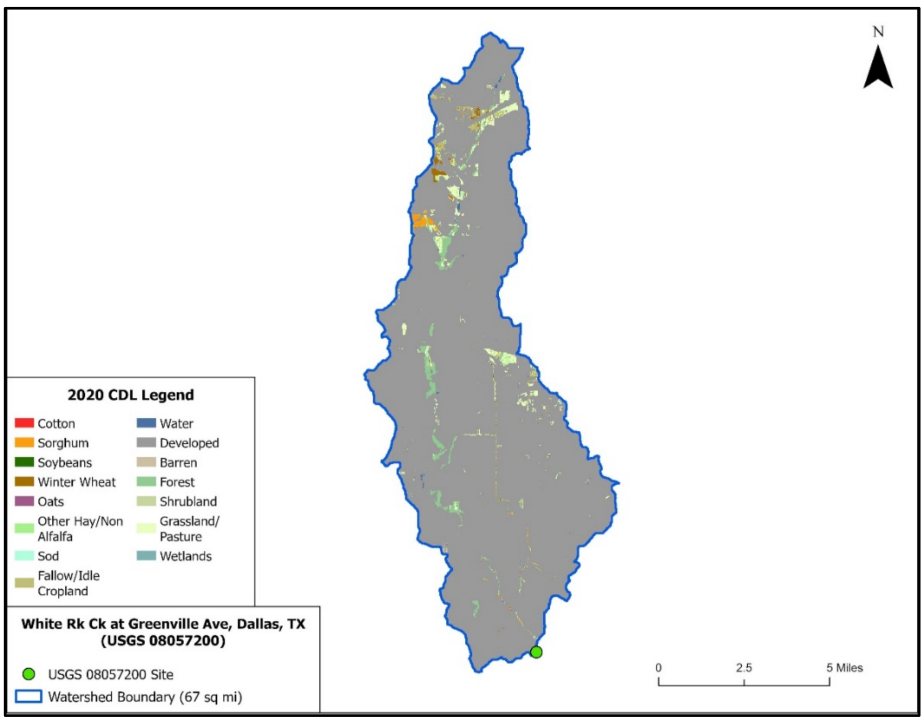

Figure S2. USGS-08057200 Watershed with 2020 Land Use.

Table S1. Monitoring data statistics for 4-Hydroxychlorothalonil at USGS-08057200

Concentration Statistic	Mean	Median	90th percentile	Minimum	Maximum
Daily (ppb)	0.33	0.13	0.74	0.02	7.10

After the USGS-08057200 monitoring dataset was selected to be utilized with the SEAWAVE-QEX model to generate the necessary chemographs for fish population modeling, SEAWAVE-QEX was setup following the methodology outlined by the USEPA in their SEAWAVE-QEX standard operating procedure (SOP) [6]. The first step in the setup process was to prepare the 4-Hydroxychlorothalonil concentration dataset for input into the SEAWAVE-QEX model, which included updating the input file format and setting the dataset's associated limit of detection (LOD). Using the concentration dataset's corresponding metadata, the dataset's LOD value was set to 0.098 ppb, which was utilized by the SEAWAVE-QEX model as its censoring limit for all censored observations. Next, since SEAWAVE-QEX was developed for use with streamflow as a covariate, daily flow data was programmatically downloaded for USGS-08057200 from the USGS Daily Values Site Web Service (https://waterservices.usgs.gov/rest/DV-Service.html) and prepared for input into the model. Once the concentration and streamflow data were prepared for model input, SEAWAVE-QEX was run for years 2012-2020, using the model's default input values (Table S2). However, due to missing streamflow data for USGS-08057200 from 2/13/2017 to 3/14/2017, the model was not simulated for this period. Concentrations were set equal to the maximum of the two values simulated just before and just after the gap, i.e., to the value simulated for 2/12/2017. Once run, model results and diagnostic plots were evaluated, following the USEPA's SEAWAVE-QEX SOP [6], to ensure a proper model fit.

RESULTS AND DISCUSSION

Monitoring data was utilized by the SEAWAVE-QEX model to generate the daily exposure profile that was necessary for fish population modeling. SEAWAVE-QEX was run for years 2012-2020, using 4-Hydroxychlorothalonil monitoring data from USGS-08057200. Utilizing default input values, the SEAWAVE-QEX model developed a regression and then fit 100 conditional simulations. Model results and diagnostic plots were evaluated to ensure a proper model fit. The daily mean concentration of the 100 conditional simulations was utilized to create a single exposure profile for population modeling (Figure 2 in the manuscript). The 4-Hydroxychlorothalonil concentration values from this exposure profile ranged from 0.02 ppb to 8.07 ppb, with a mean concentration of 0.30 ppb (Table S3). The maximum annual 4-day rolling average concentration, representing an acute exposure duration, of the simulated exposure profile was 4.59 ppb, while the maximum annual 60-day rolling average concentration, representing a chronic exposure duration, was 1.21 ppb (Table S3).

Table S2. SEAWAVE-QEX input parameters

Variable	Description	Value
minss	Minimum number of days between samples	3
ncs	Number of conditional simulations	100
samcov	Length of sampling season	full
istrans	Transformation of pesticide data	1 (log transformation)

Table S3. 4-Hydroxychlorothalonil exposure profile statistics generated by SEAWAVE-QEX for USGS-08057200

Concentration Statistic	Mean	Median	90^{th} percentile	Minimum	Maximum
Daily (ppb)	0.30	0.18	0.56	0.02	8.07
Maximum Annual 4-day Rolling Average (ppb)	2.56	1.84	4.58	0.80	4.59
Maximum Annual 60-day Rolling Average (ppb)	0.66	0.63	1.04	0.36	1.21

References

[1] Vecchia, A.V., Model Methodology for Estimating Pesticide Concentration Extremes Based on Sparse Monitoring Data. U.S. Geological Survey Scientific Investigations Report 2017-5159. **(2018)** 47p. https://doi.org/10.3133/sir20175159.

[2] USEPA & USGS, *Water Quality Portal*. **2022**. Available Online: https://www.waterqualitydata.us/ (accessed on 3 February 2022)

[3] USEPA, Approaches for Quantitative Use of Surface Water Monitoring Data in Pesticide Drinking Water Assessments: U.S. Environmental Protection Agency's Office of Pesticide Programs, Docket Number: EAP-HQ-OPP-2019-0417-0003, **2019**, 255p.

[4] USDA-NASS, USDA National Agricultural Statistics Service Cropland Data Layer. **2022**. Published crop-specific data layer. USDA-NASS, Washington, DC. Available online: https://nassgeodata.gmu.edu/CropScape (accessed on 3 February 2022).

[5] USGS-NAWQA, Pesticide National Synthesis Project. National Water-Quality Assessment Program, **2022**. Available online : https://water.usgs.gov/nawqa/pnsp/usage/maps/county-level/ (accessed on 3 February 2022)

[6] USEPA,. Standard Operating Procedure for Using SEAWAVE-QEX to Estimate Pesticide Concentrations: U.S. Environmental Protection Agency's Office of Pesticide Programs, Docket Number: EAP-HQ-OPP-2019-0417-0007, **2019**, 62p.

Supplementary Information – Population dynamics

Effects of stochastic droughts

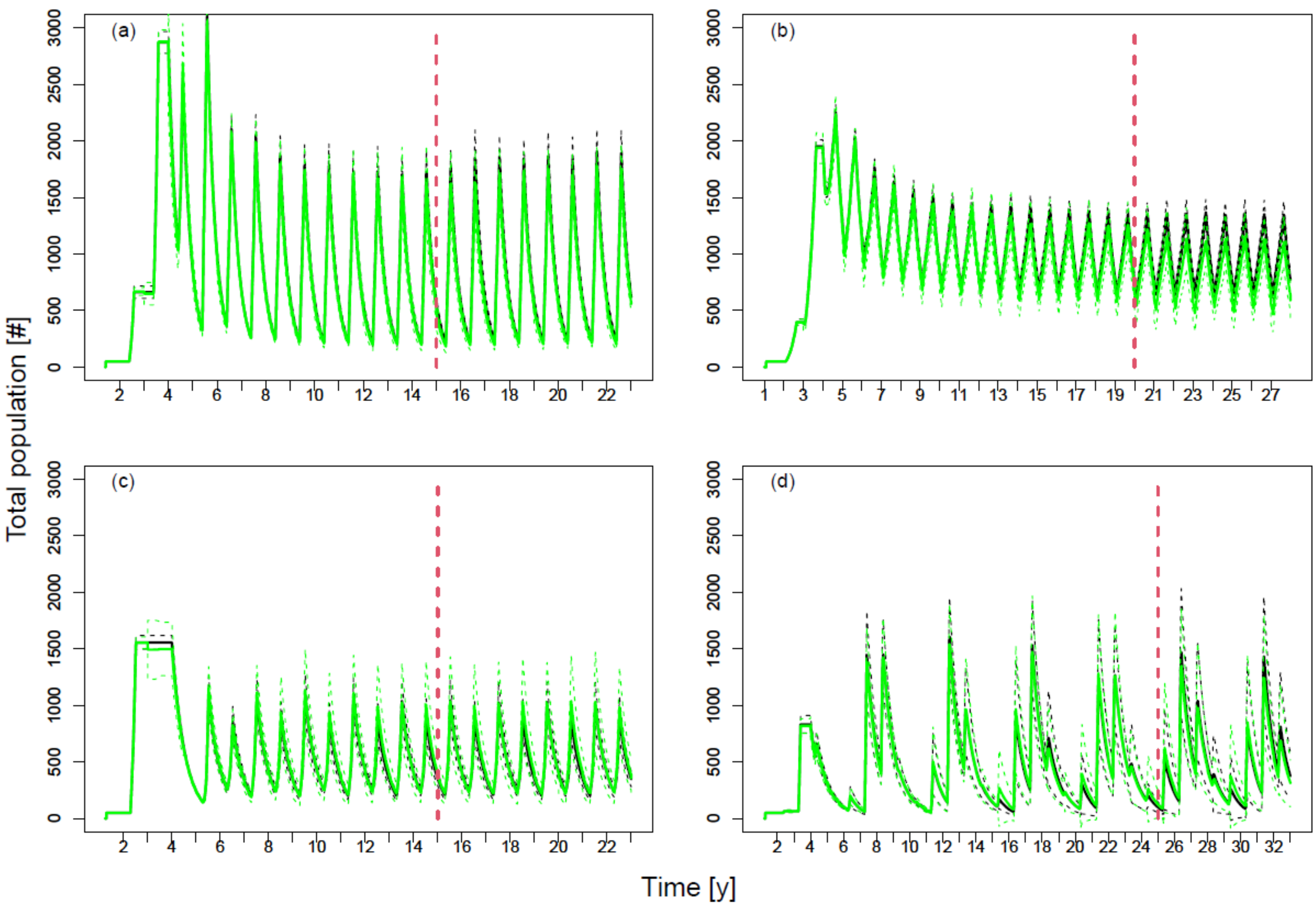

Figure S1: Population dynamics for the four species. Solid lines show the average population abundance over 40 replicates. Dotted lines define the standard deviation. The red dotted line shows when stabilization occurred. Black: population dynamics without stochastic effects due to droughts. Green: population dynamics with added stochastic mortality due to drought events. (a) Topeka shiner; (b) Devils River minnow; (c) Spikedace; (d) Humpback chub.

Effects of density dependence

We show the effect of density dependence on the population dynamics of four species of Cyprinidae (without exposure). Humpback chub is the species with larger biomass. Therefore, density dependence, which scales with the adult biomass, plays a relevant role in shaping the dynamics. The other species show larger oscillations but not completely different dynamics, as with the Humpback chub.

The egg survival had to be adjusted to find new stability and avoid increasing population abundances over time. Because the different species have different mortality rates and fecundity, egg survival adjustments were species-specific.The new and old values are showed in table S1.

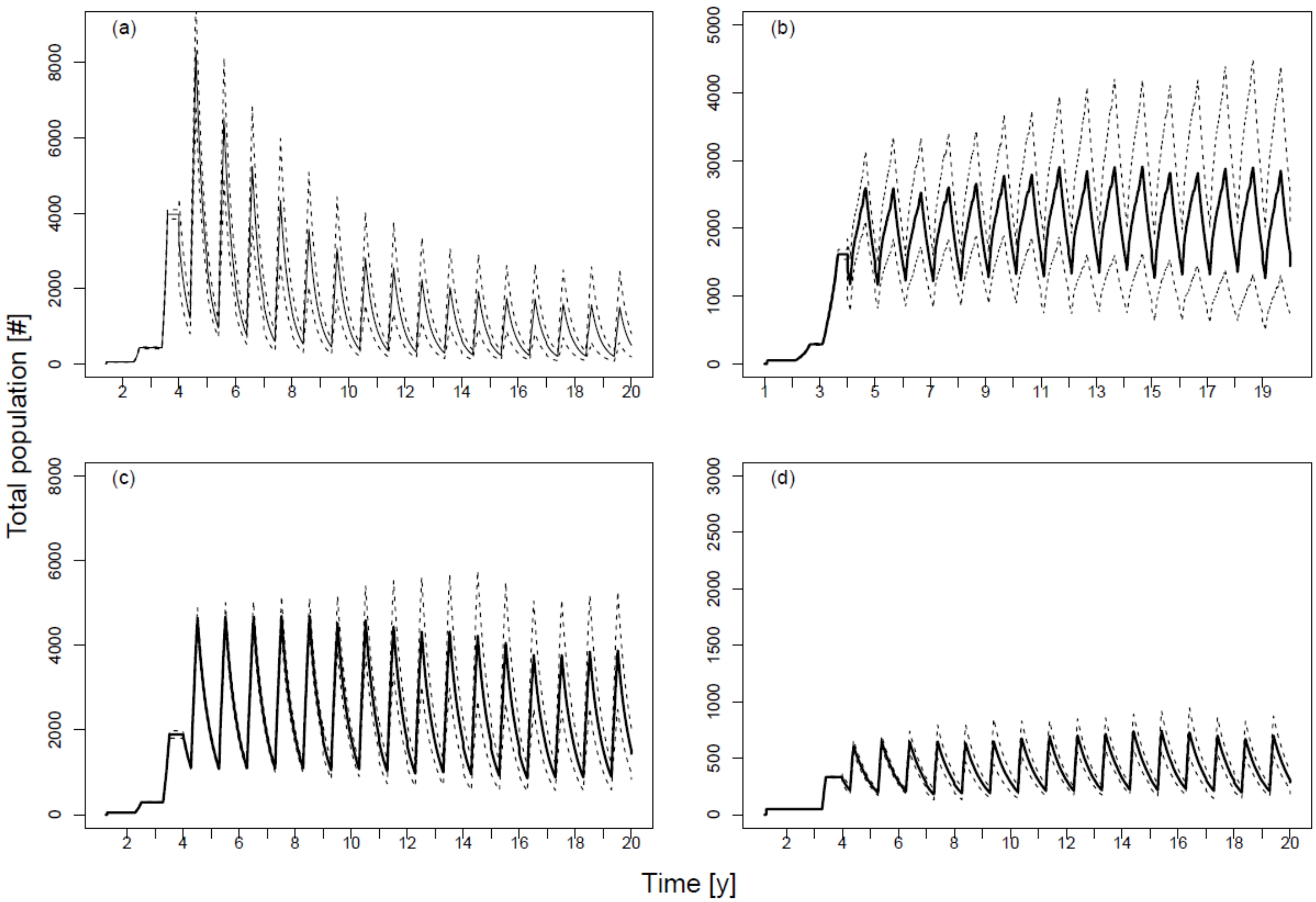

Figure S2: Population dynamics for the four species in the absence of density dependence. Solid lines show the average population abundance over 40 replicates. Dotted lines define the standard deviation. (a) Topeka shiner; (b) Devils River minnow; (c) Spikedace; (d) Humpback chub.

Exposure effects

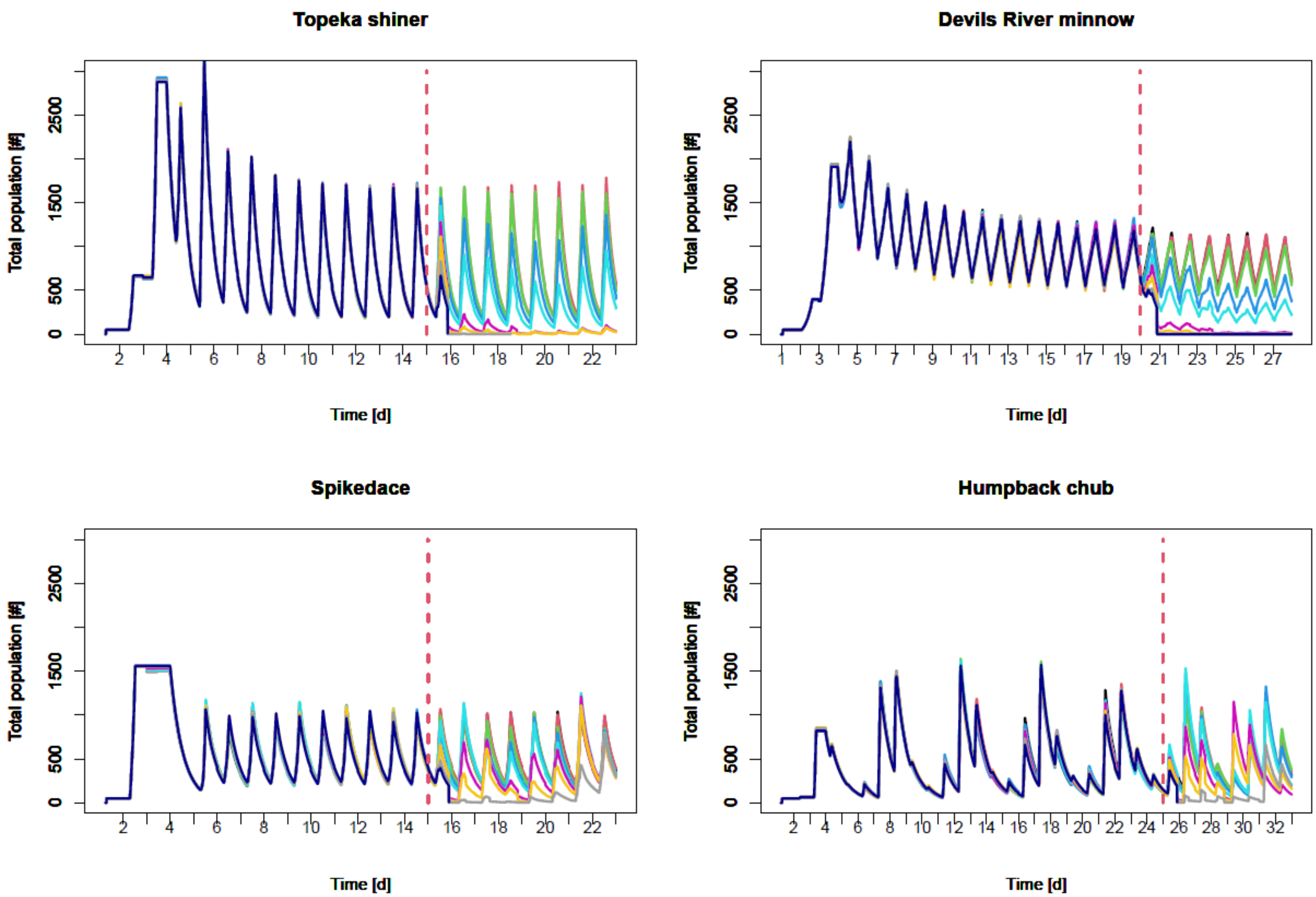

Figure S3: Population dynamics for the four species when applying different exposure magnification factors (EMF). Solid lines show the average population abundance over 40 replicates. Dotted black lines define the standard deviation. The red dotted line shows when stabilization occurred. Different colors define different EMF. Black: no exposure; red: EMF = 1; green: EMF = 2; blue: EMF = 4; cyan: EMF = 5; magenta: EMF = 7; yellow: EMF = 8; grey: EMF = 10; dark blue: EMF = 11. Simulations continue for three years after the end of the exposure, and in some cases, we can see a fast recovery trend.

Table S1. Egg survival for the simulations with and without the effects of density dependence on egg and larva.

Species	Egg survival - Model with density dependence	Egg survival - Model without density dependence
Topeka shiner	0.1	0.056
Devils River minnow	0.5	0.35
Spikedace	0.1	0.0087
Humpback chub	0.1	0.0025

Table S2. Relative population abundances when adding up effect sub-models. Average populations are calculated over exposure time (5 years), the ratios of over-time averages are calculated for each replicate, and then ratios are averaged over 40 replicates.

Species	E1	E1 + E2	E1 + E2 + E3	E1 + E2 + E3 + E4
Topeka shiner	0.7	0.7	0.55	0.55
Devils River minnow	0.72	0.7	0.49	0.48
Spikedace	0.89	0.75	0.57	0.57
Humpback chub	0.8	0.72	0.49	0.54

Table S3. Relative difference in the percentage of population abundance with respect to the previous scenario. Percentages are calculated using equation 6 (main text) from the values in table S1.

Species	E1 + E2	E1 + E2 + E3	E1 + E2 + E3 + E4
Topeka shiner	0.75%	20.59%	1.27%
Devils River minnow	3.64%	29.45%	2.22%
Spikedace	15.3%	24.01%	1.01%
Humpback chub	10.74%	31.24%	-8.83%