Heterogeneity in biological assemblages and exposure in chemical risk assessment: exploring capabilities and challenges in methodology with two landscape-scale case studies

Supplemental Information

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1. Methods

1.1. Study area

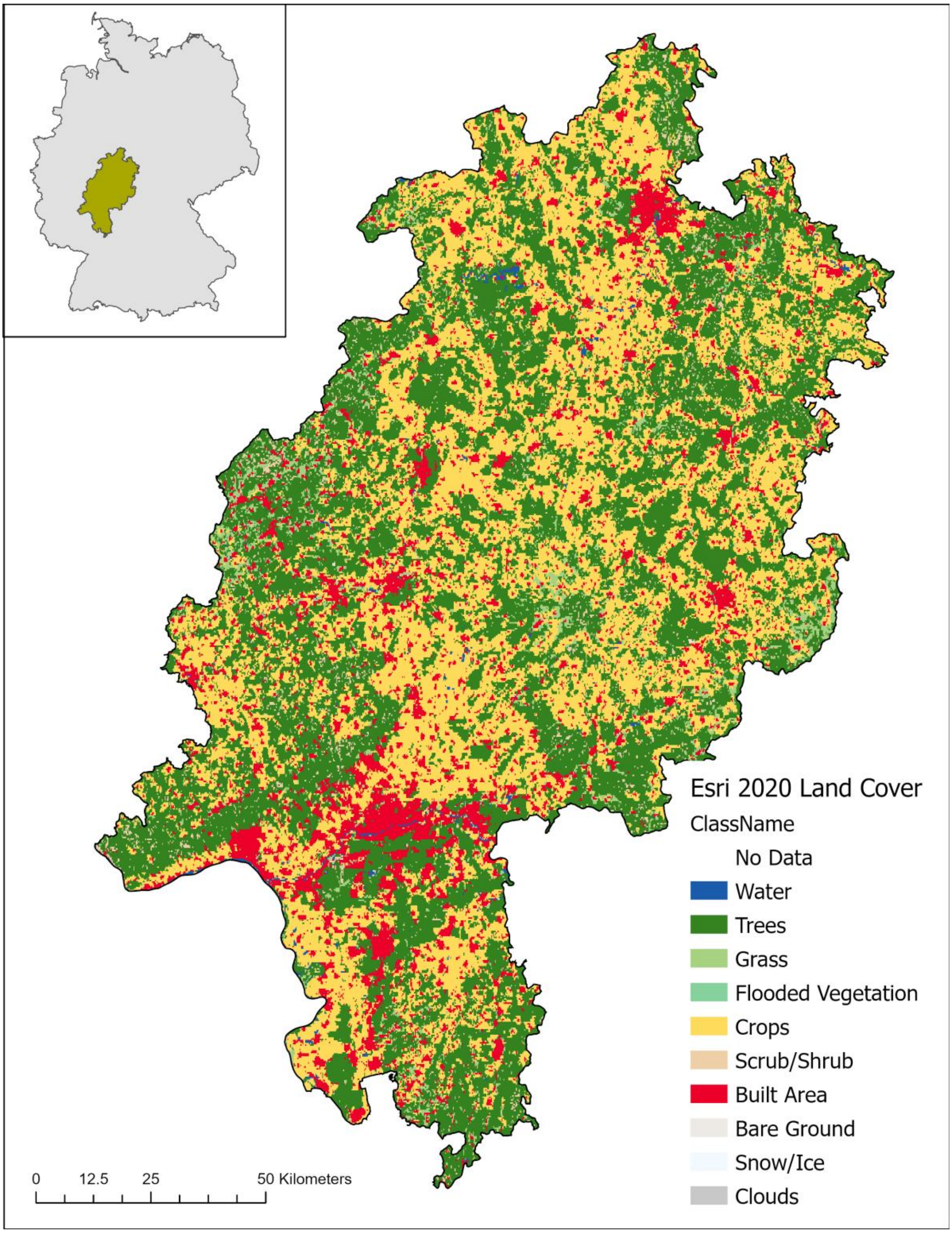
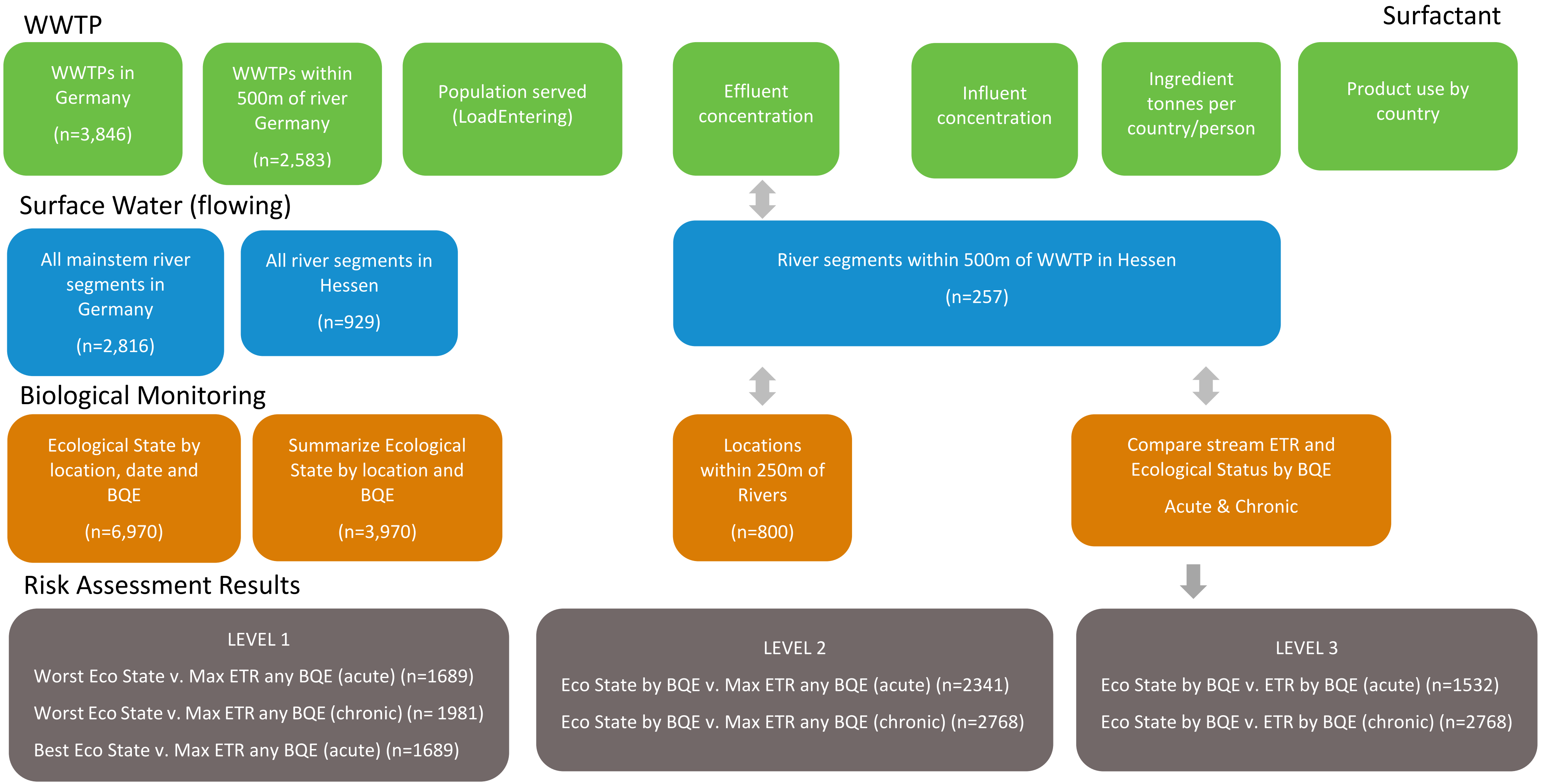


Figure S1. Land cover in study area using 2020 Environmental Systems Research Inc. (ESRI) land cover for Hessen, Germany

1.2. Down-the-drain chemicals

The methodology implemented is summarised in Figure S2, including source of surfactant (green), aquatic habitat (blue), biological monitoring data (orange) and resulting risk assessment results (grey).



WWTP = Wastewater Treatment Plant, BQE = Biological Quality Element, ETR = Exposure Toxicity Ratio

Figure S2. Overview of down-the-drain case study analysis

1.2.1. <u>Estimation of anionic surfactant exposure concentrations in surface waters in Hessen</u>

The following steps were performed to estimate the surfactant usage for Germany:

1. 2017 tonnage was obtained for the EU plus Switzerland for product types that contain surfactants (primarily laundry and household care). (Euromonitor 2018, accessed March 2018)
2. Population projections were downloaded from Wikipedia (March 2018).
3. EU-wide surfactant usage (3 grams per capita per day or 1095 grams per capita per annum) (HERA 2013) was distributed across the different product types proportionally based on volume sales of each product type.
4. For each of the 12 product types, the volume calculated in step 3 was distributed across the 30 countries proportionally by product volume per country.
5. The surfactant volume for each product type was summed across each country giving a distribution around the mean 3 grams ranging from 6.7 to 1.3 g/cap/day for Spain and Slovenia respectively.
6. Assumptions:
    a. There was the same amount of surfactant in each formulation independent of brand or product type.
    b. Only the 12 product types contribute to the total surfactant mass used
    c. 2017 volume data is representative across other years.

Table S1. Country-specific surfactant usage per person in 2017 (source) [cap = capita]

Geography	Total (g/cap/annum)	Total (g/cap/day)
Spain	2454	6.724
Italy	1826	5.003
United Kingdom	1545	4.234
Germany	**1463**	**4.009**
Croatia	1437	3.938
Netherlands	1437	3.936
Portugal	1368	3.747
Cyprus	1323	3.625
Belgium	1304	3.572
Malta	1281	3.510
France	1281	3.508
Luxembourg	1204	3.299
Switzerland	1185	3.246
Austria	1068	2.926
Bulgaria	1048	2.870
Finland	999	2.737
Czech Republic	957	2.621
Denmark	936	2.564
Greece	873	2.391
Slovakia	868	2.379
Poland	821	2.250
Hungary	821	2.248
Ireland	798	2.188

Geography	Total (g/cap/annum)	Total (g/cap/day)
Romania	795	2.178
Sweden	754	2.066
Norway	711	1.947
Estonia	621	1.703
Latvia	614	1.683
Lithuania	603	1.653
Slovenia	454	1.245

1.2.2. River flow and dilution factor

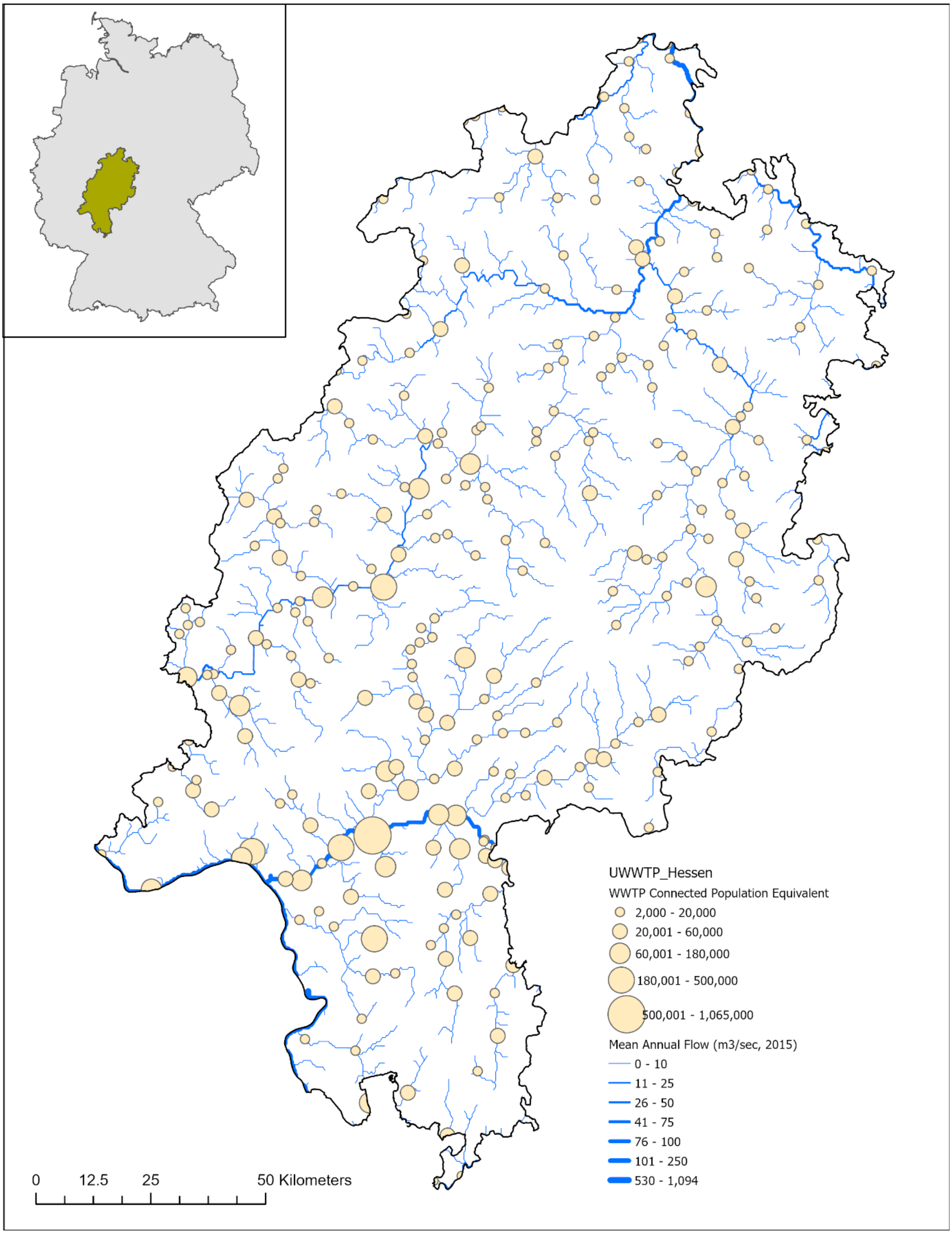
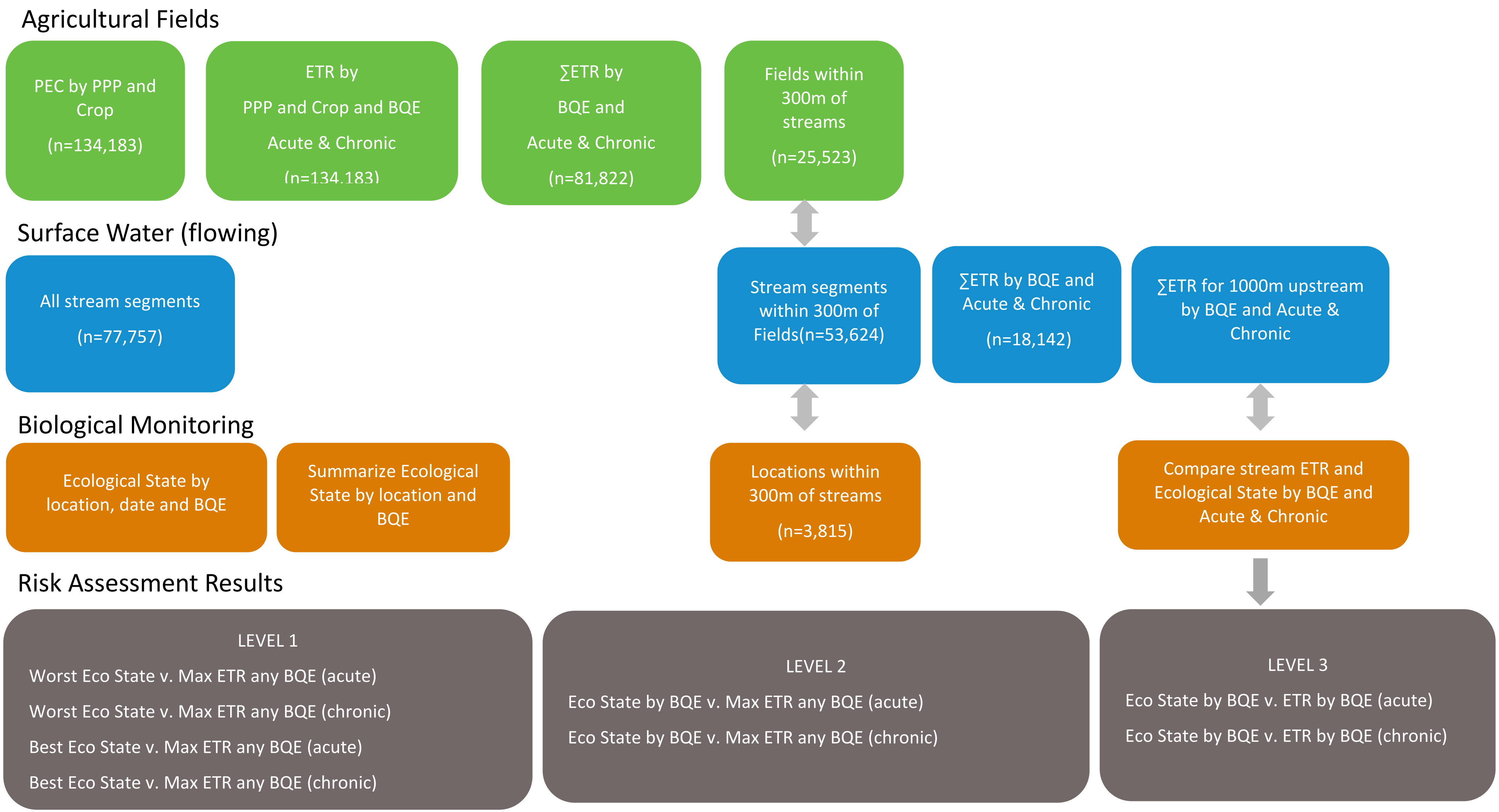


Figure S3. 2015 mean annual flow from FLO1K (Barbarossa et al 2018) assigned to HydroRIVERS in Hessen (n=929), with WWTP Population Equivalent connected [UWWTP = urban waste water treatment plant; WWTP = waste water treatment plant]

1.3. Estimation of PPP exposure concentrations in surface waters

The methodology implemented is summarised in Figure S4, including source of PPPs (green), aquatic habitat (blue), biological monitoring data (orange) and resulting risk assessment results (grey).



PEC = Predicted Environmental Concentration, PPP = Plant Protection Product, BQE = Biological Quality Element, ETR = Exposure Toxicity Ratio

Figure S4. Overview of PPP case study analysis

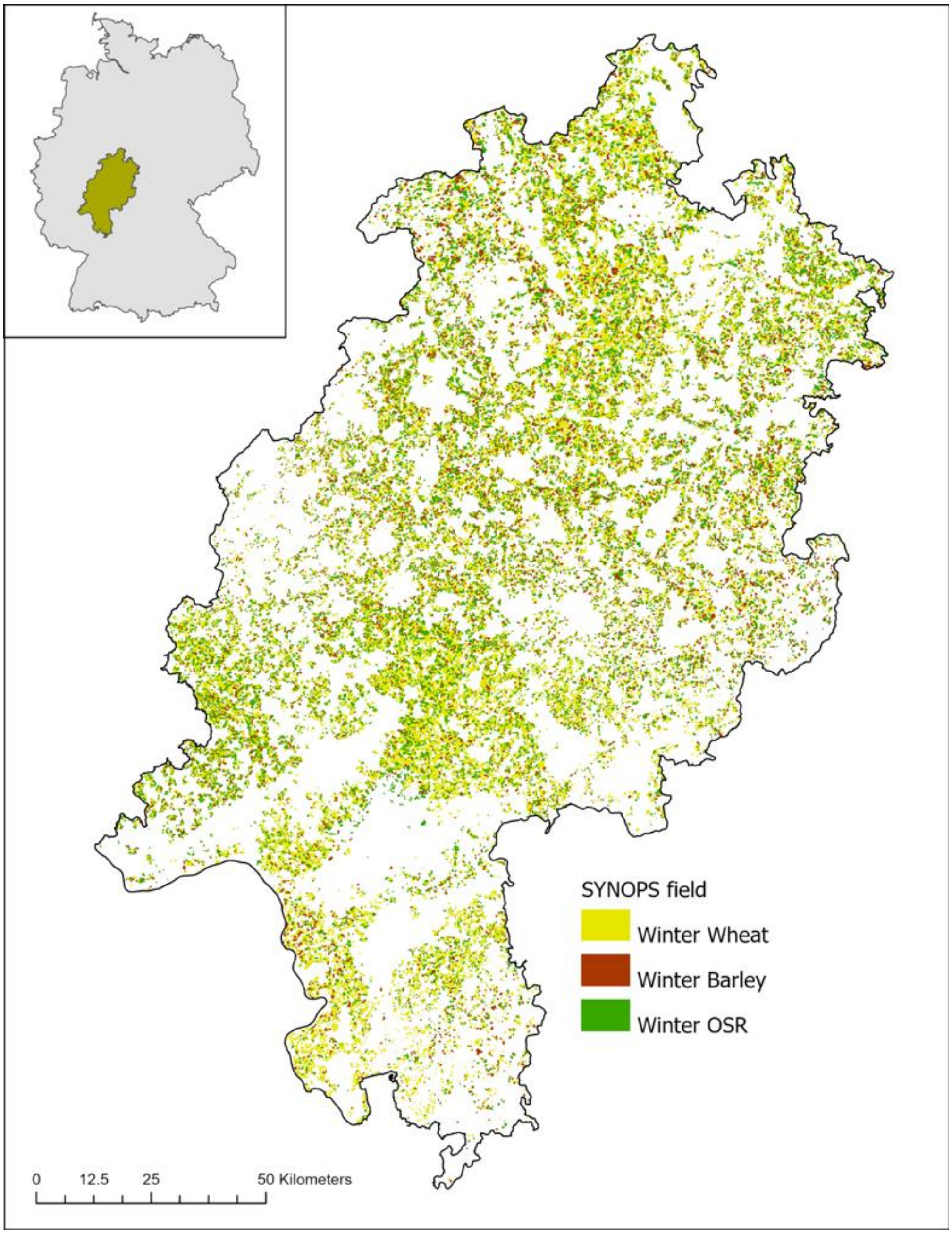


Figure S5. Spatial extent and distribution of 81,822 SYNOPS fields containing the three crops selected for modelling and analysis [OSR = Oil seed rape]

Table S2. Details of Plant Protection Product (PPP) applications modelled for the case study

Number of PPPs per field	Number of fields	% of fields	
Three	4,855	5.9%	
Two	42,651	52.1%	
One	34,316	41.9%	
Total	81,822		
Fields with PPP and crop	**Number of PPP / crop combinations**	**% of fields for each PPP**	**Crop**
Herbicide	19,781	100%	Winter oilseed rape
Insecticide	32,625	63%	Winter wheat
	10,725	21%	Winter barley
	8,815	17%	Winter oilseed rape
Fungicide	40,836	66%	Winter wheat
	3,419	5%	Winter barley
	17,982	29%	Winter oilseed rape
Total	134,183		
Number of applications per field by PPP	**Number of fields**	**% of fields for each PPP**	**Number of applications**
Herbicide	18,131	92%	1 application
	1,650	8%	2 applications
Insecticide	42,946	82%	1 application
	8,201	16%	2 applications
	1,018	2%	3 applications
Fungicide	34,620	56%	1 application
	21,448	34%	2 applications
	3,542	6%	3 applications
	2,137	3%	4 applications
	490	1%	5 applications
Total	134,183		

Table S3. Number and type of Plant Protection Product (PPP) applications per field

Number of PPPs	Herbicide	Insecticide	Fungicide	Number of Fields	% of Fields
3	X	X	X	4,855	6%
2	X	X		1,480	52%
	X		X	10,663	
		X	X	30,508	
1	X			2,783	42%
		X		15,322	
			X	16,211	
				81,822	

1.3.3. Detailed stream hydrology

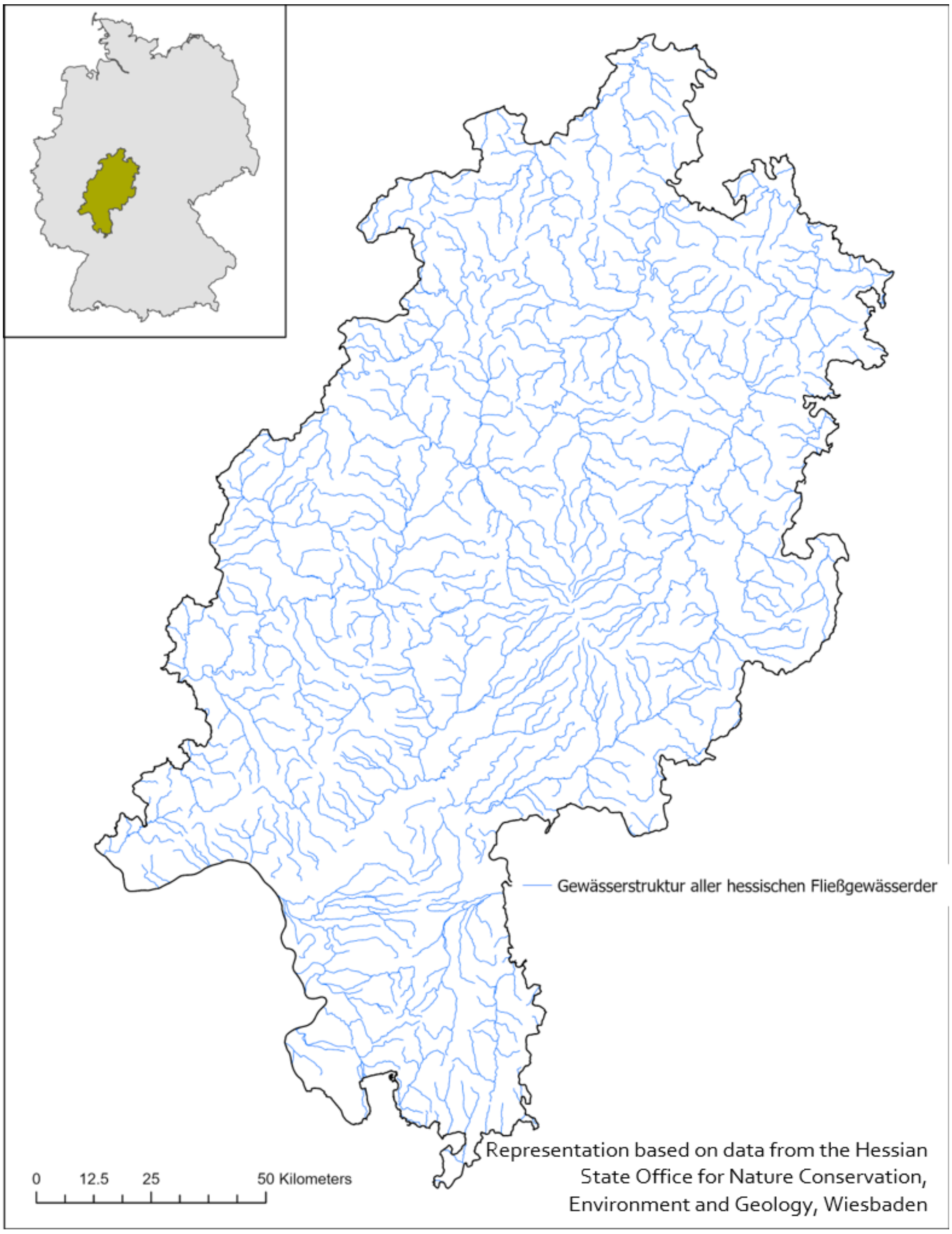


Figure S6. Detailed hydrology for Hessen (Gewässerstruktur aller hessischen Fließgewässerder) (representation based on data from the Hessian State Office for Nature Conservation, Environment and Geology, Wiesbaden)

1.3.4. Upstream Exposure:Toxicity Ratio (ETR) allocation

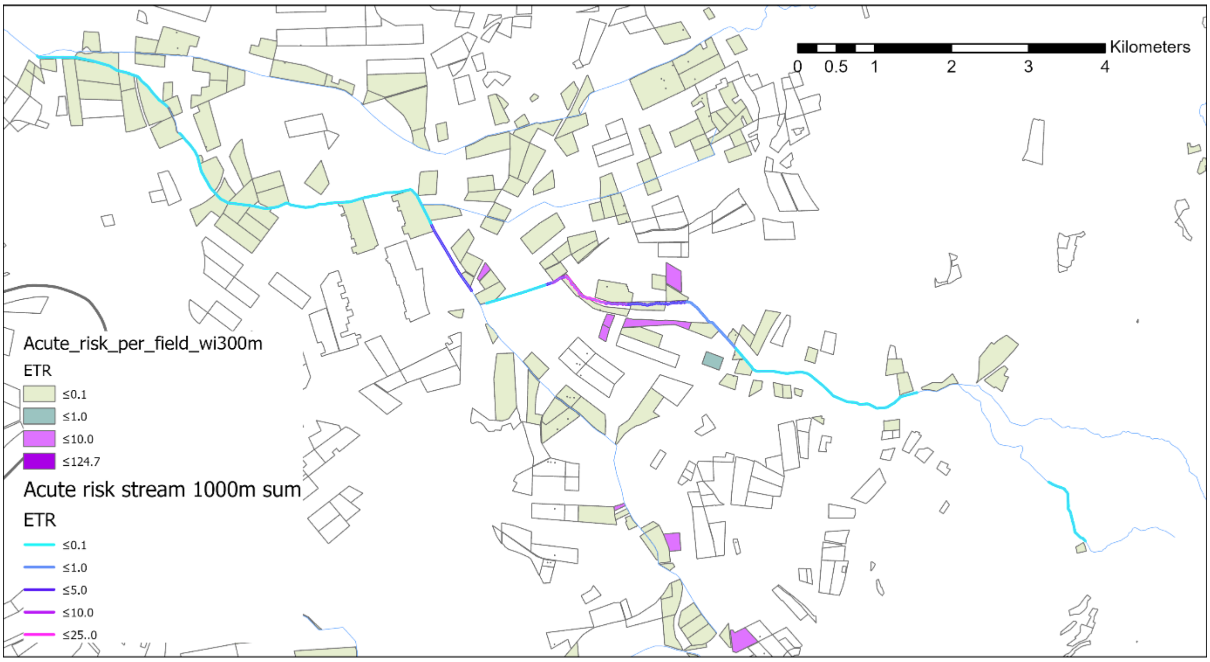


Figure S7. Example of 1000m upstream aggregation of field-level Exposure:Toxicity Ratio (ETR) contributions to detailed stream segments (representation based on data from the Hessian State Office for Nature Conservation, Environment and Geology, Wiesbaden)

2. Results

2.1. Down-the-drain chemical

2.1.1. Predicted Environmental Concentrations (PECs)

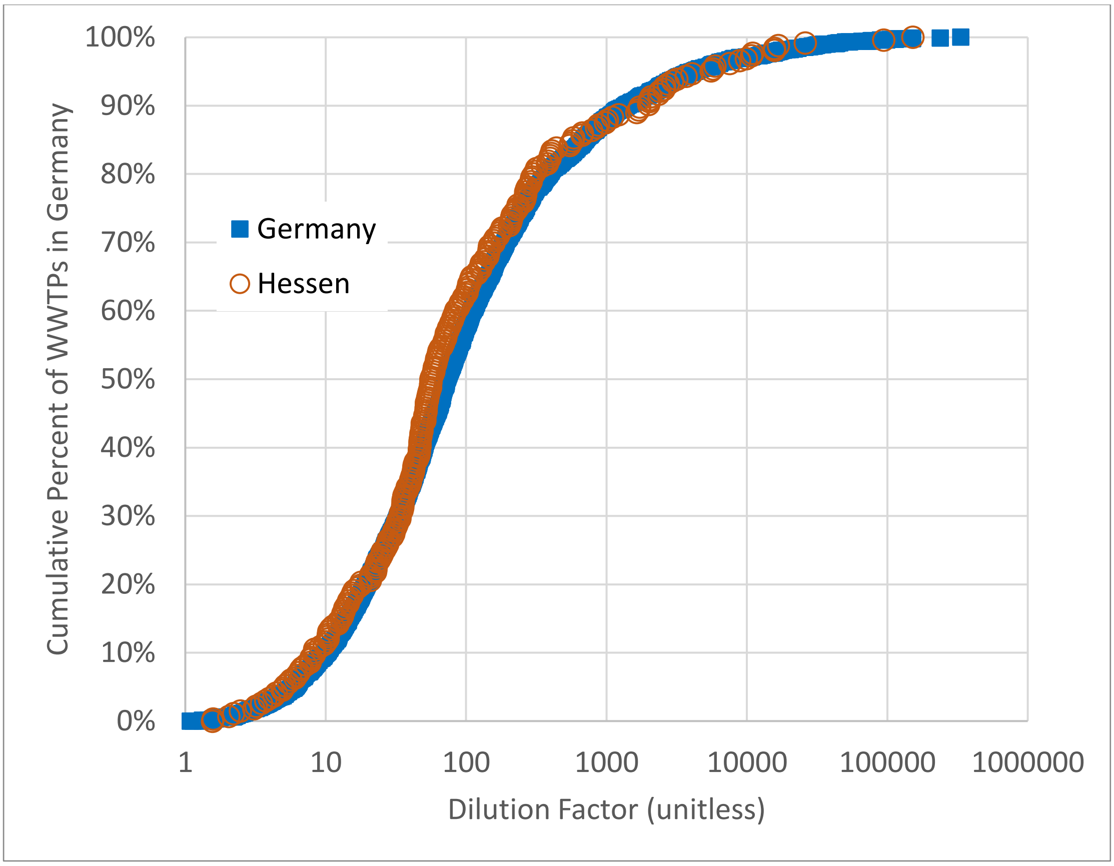


Figure S8. Distribution of Dilution Factor values for WWTPs in Germany (blue, n=2583) and Hessen (orange, n=257) utilising Population Equivalents (EEA 2017) and a single per capita water domestic use of 46.3 m^3 yr-1 per person (Eurostat 2017) [WWTP = waste water treatment plant]

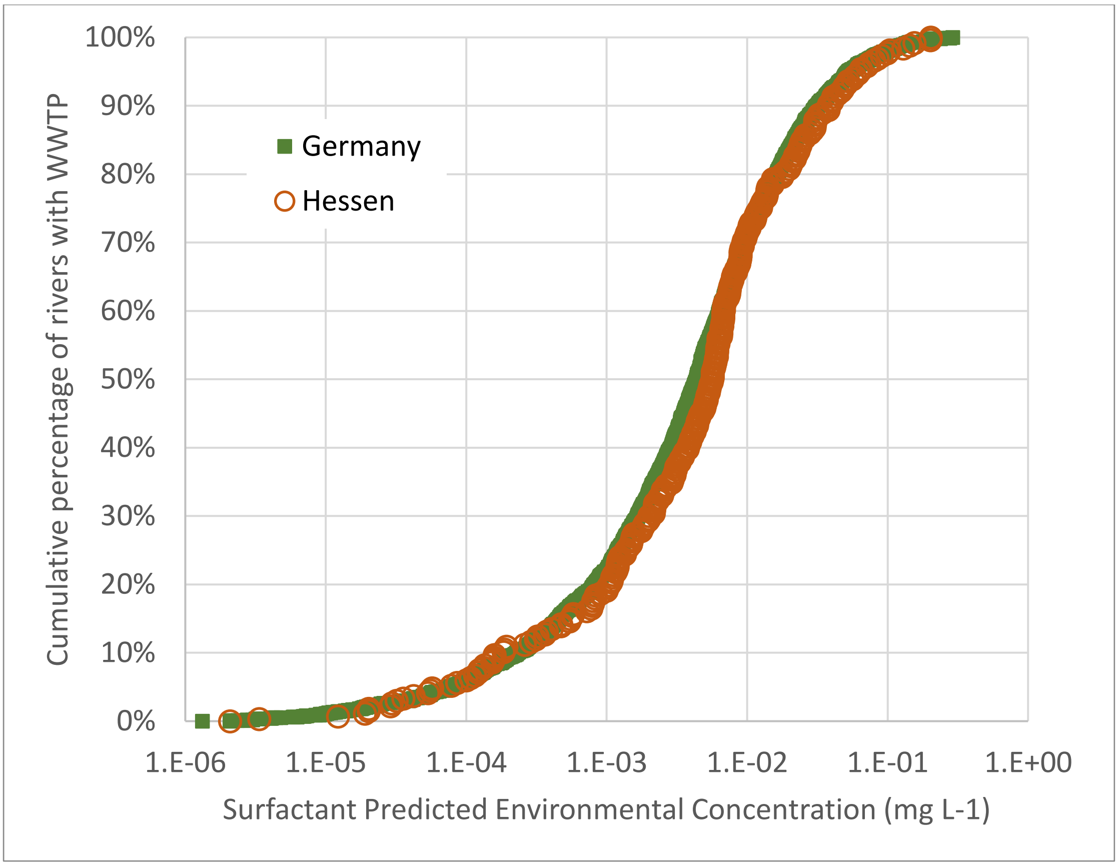


Figure S9. Distribution of Predicted Environment Concentrations (PECs) for river segments with a WWTP in Germany (green, n=2583) and Hessen (orange, n=267). [WWTP = waste water treatment plant]

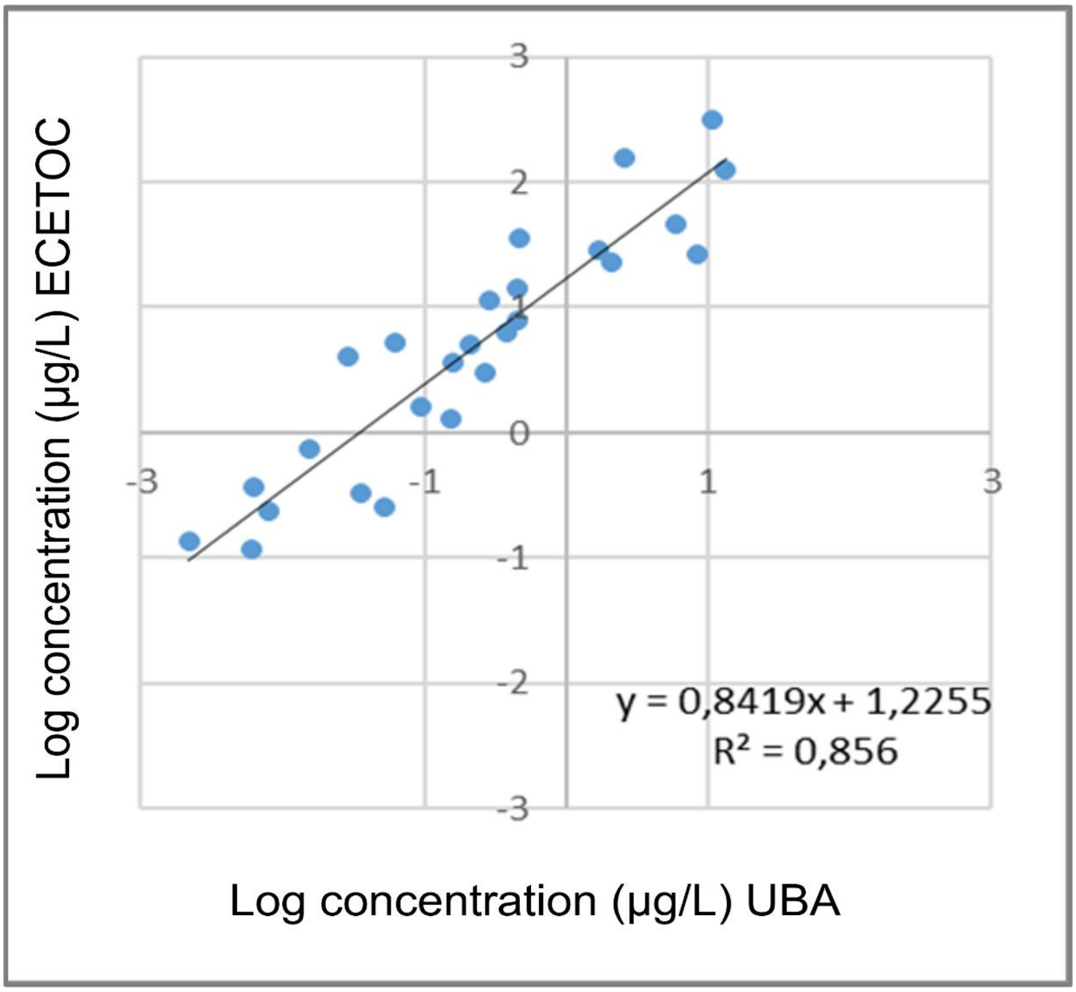


Figure S10. Comparison of Predicted Environment Concentrations (PECs) with PECs derived from surfactant monitoring data (Freeling et al 2019)

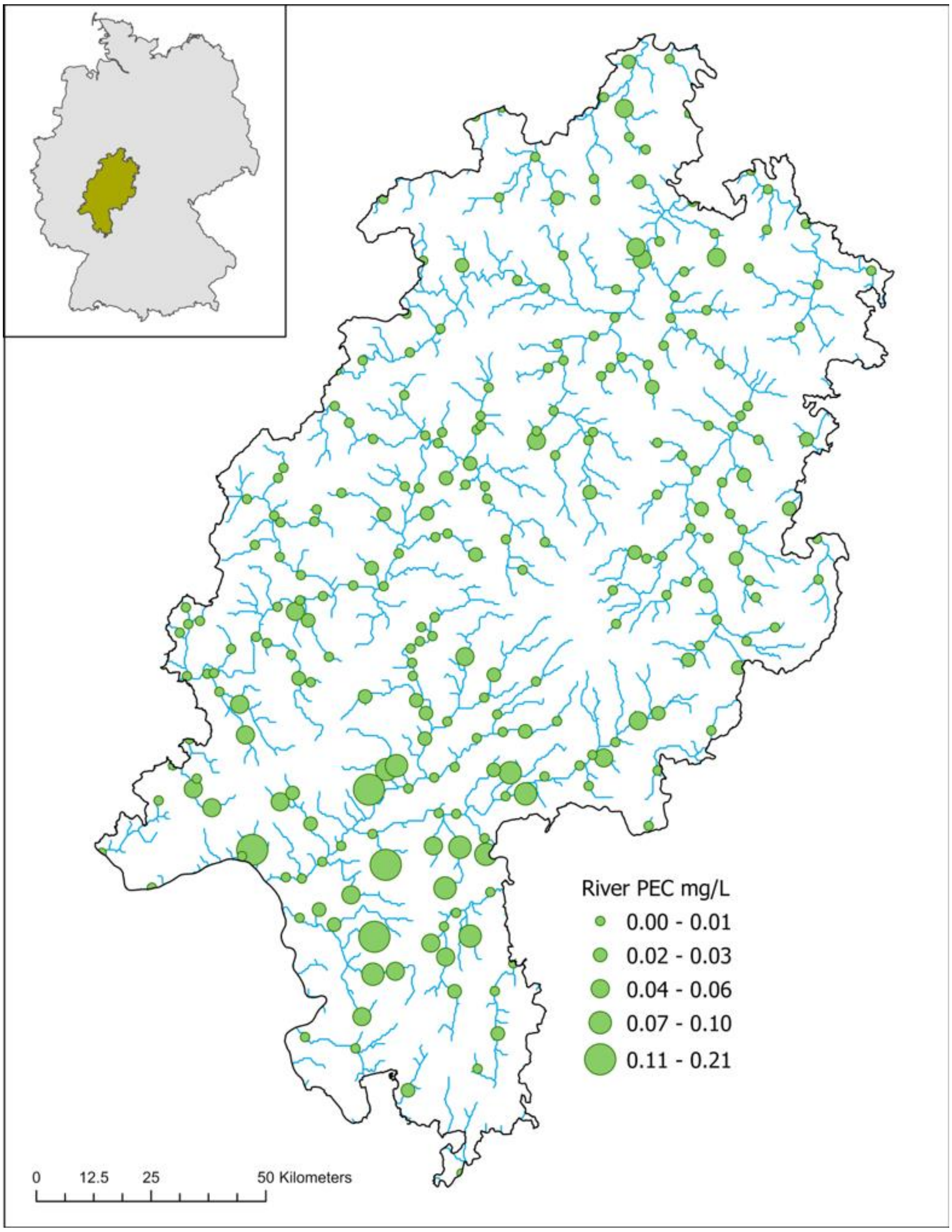


Figure S11. Spatial distribution of surfactant Predicted Environment Concentrations (PECs) in Hessen

2.1.2. Surface water Exposure:Toxicity Ratio (ETR) (risk)

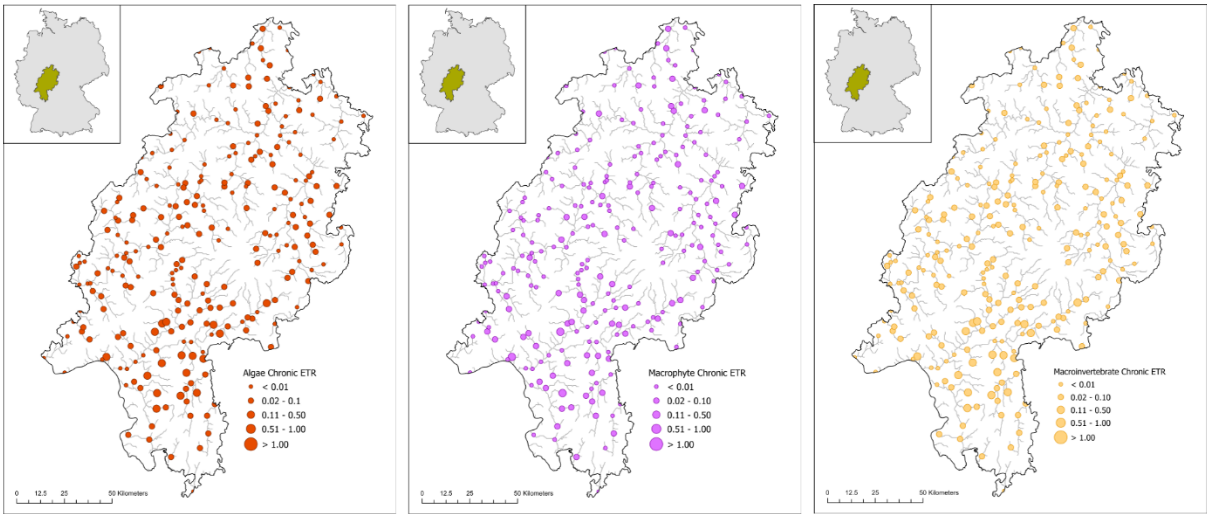


Figure S12. Maps of surfactant risk (chronic) for algae, macrophytes and macroinvertebrates [ETR = Exposure:Toxicity Ratio]

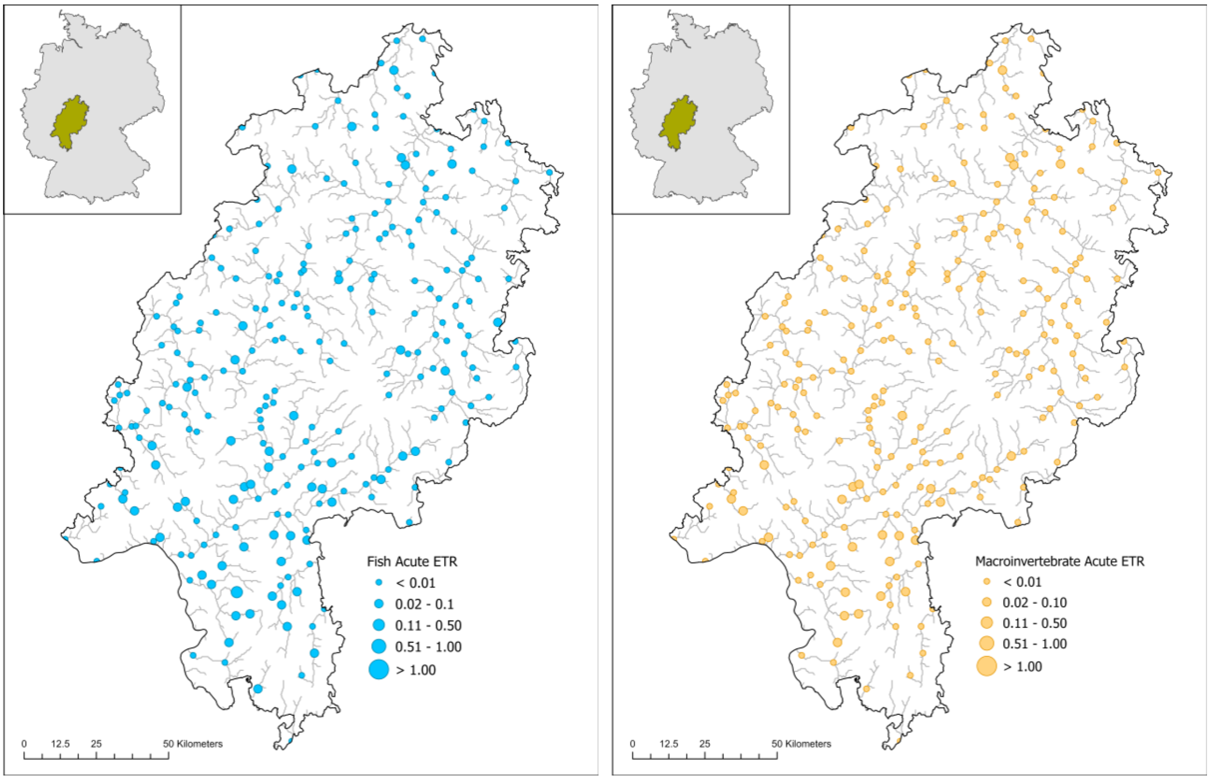


Figure S**13**. Maps of surfactant risk (acute) for fish and macroinvertebrates [ETR = Exposure:Toxicity Ratio]

2.1.3. <u>Comparison of Exposure:Toxicity Ratios (ETRs) and Ecological Status</u>

For a single location, more than one BQE could be reported, each of which has a BQE-specific ecological status. We develop an analysis which addressed three "levels" of ecological resolution for our assessment.

Level 1 - "Best" ecological status BQE per site compared to ETR of highest risk across all BQEs (chronic & acute separately). The comparison includes all BQE types in one chart/table.

Level 2 - Each BQE and ecological status per site compared to ETR of highest risk across all BQEs (chronic & acute separately). The comparison includes separate charts/tables for each BQE type.

Level 3 - Each BQE and ecological status per site compared to most relevant ETR (chronic & acute separately). The comparison includes separate charts/tables for each BQE type.

Figure S through Figure S present the surfactant ETR data grouped by BQE and sorted by ecological status for examination of risk distributions and charting. Three levels of association were performed for both acute and chronic ETRs.

With minor differences, Level 1 and 2 analyses indicate similar ETR values whereas level 3 analyses tend to indicate lower ETR values than comparable Level 1 and 2 values. Nevertheless, all Levels indicate similar trends across the range of ecological status classes.

Level 1

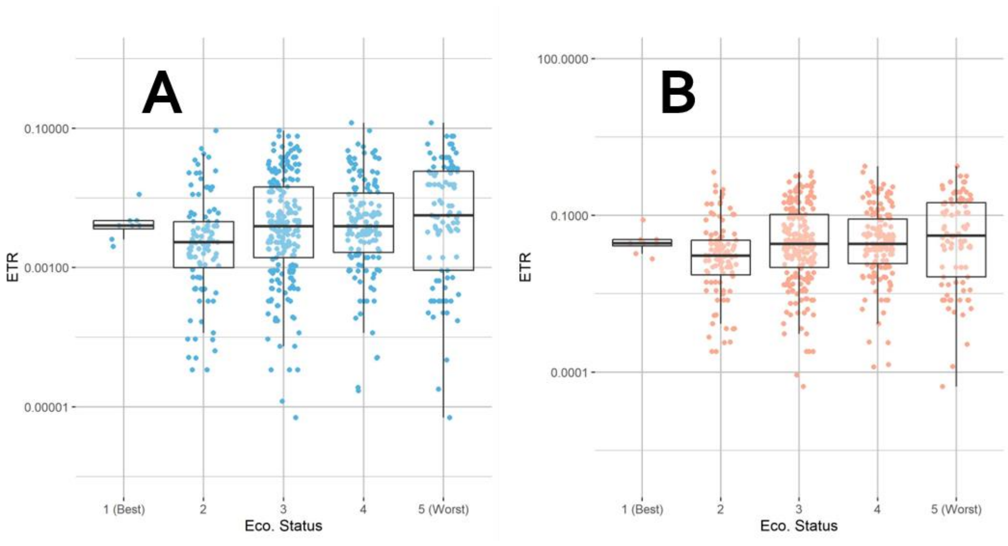


Figure S14. Exposure:Toxicity Ratio (ETR) v ecological status comparing "Best" ecological status Biological Quality Element (BQE) per site compared to ETR of highest risk across all BQEs (i.e., Level 1) for acute (A) and chronic (B)

Level 2

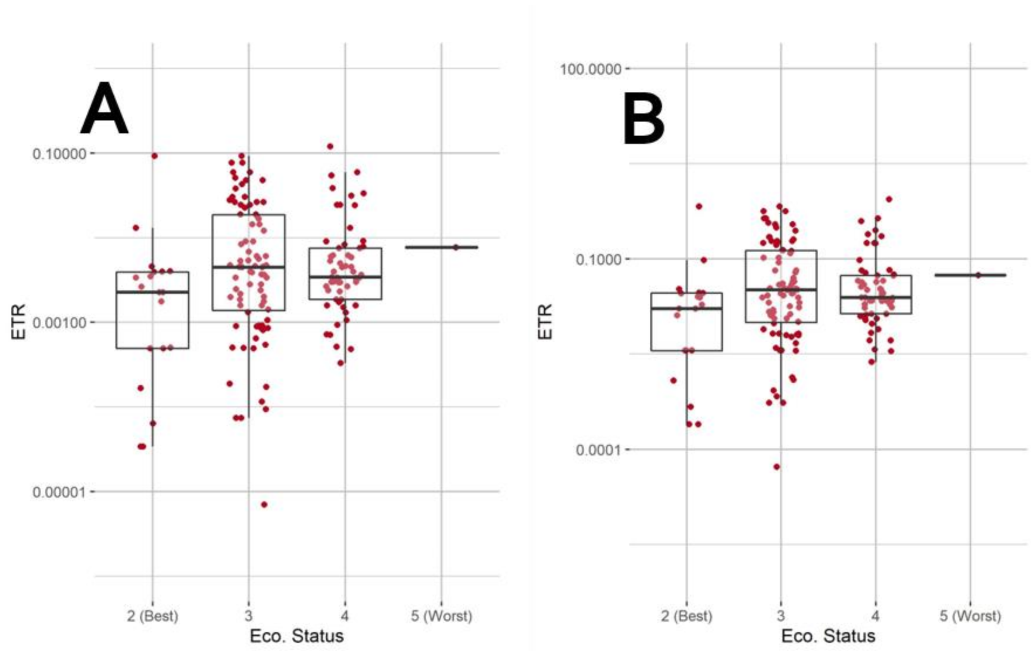


Figure S15. Algae acute (A) and chronic (B) Exposure:Toxicity Ratio (ETR) v ecological status comparing compared to ETR of highest risk across all Biological Quality Elements (BQEs) (i.e., Level 2)

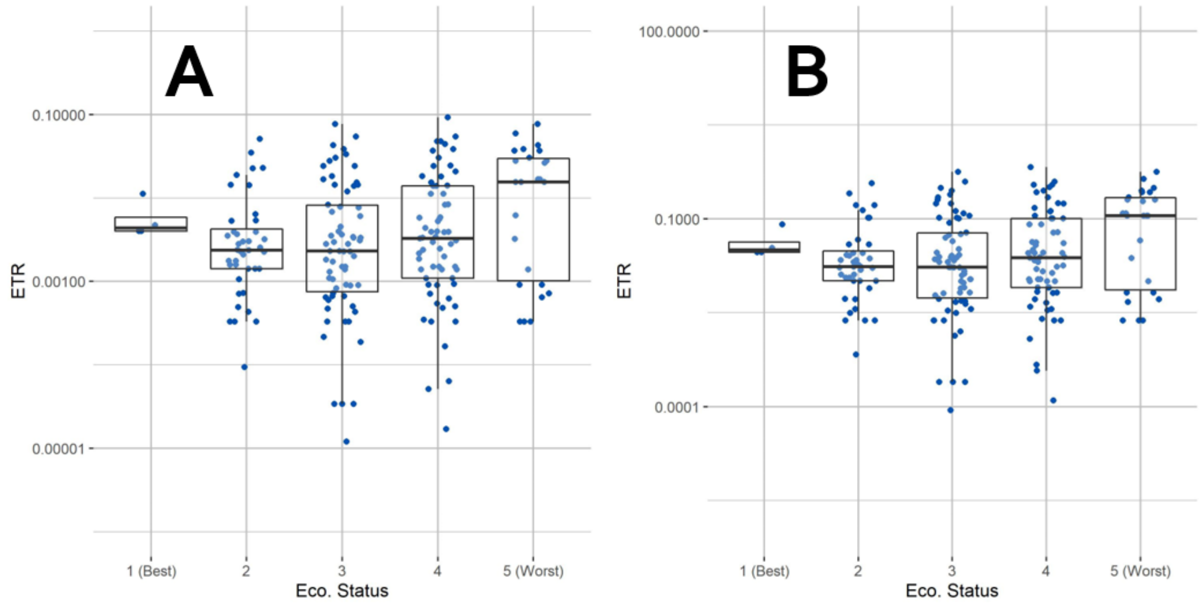


Figure S16. Fish acute (A) and chronic (B) Exposure:Toxicity Ratio (ETR) v ecological status comparing compared to ETR of highest risk across all Biological Quality Elements (BQEs) (i.e., Level 2)

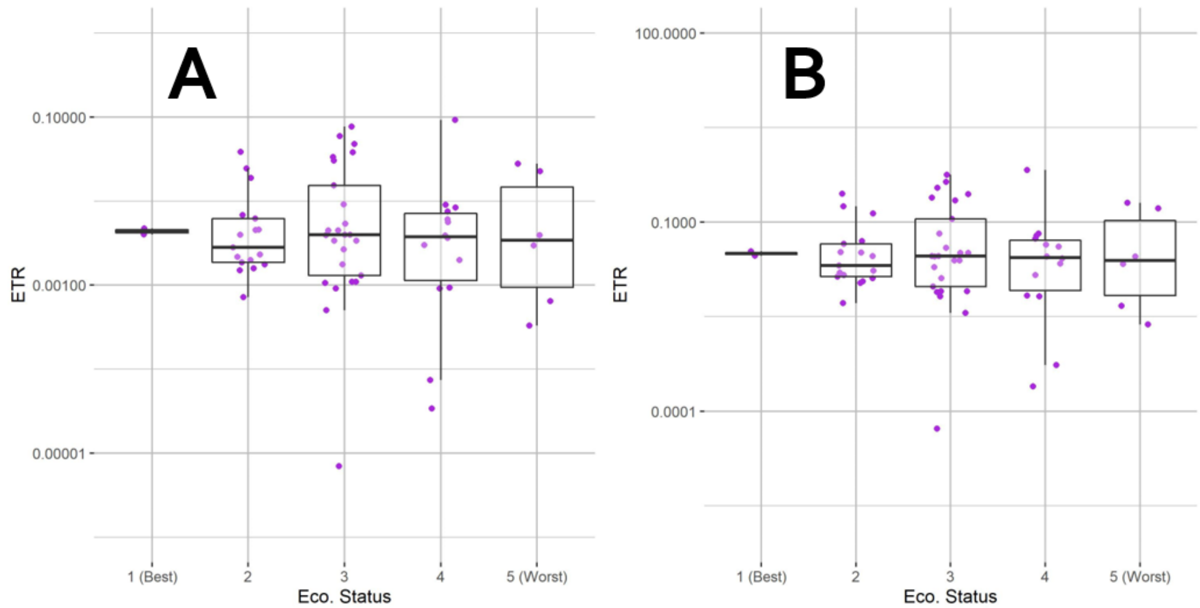


Figure S17. Macrophyte acute (A) and chronic (B) Exposure:Toxicity Ratio (ETR) v ecological status comparing compared to ETR of highest risk across all Biological Quality Elements (BQEs) (i.e., Level 2)

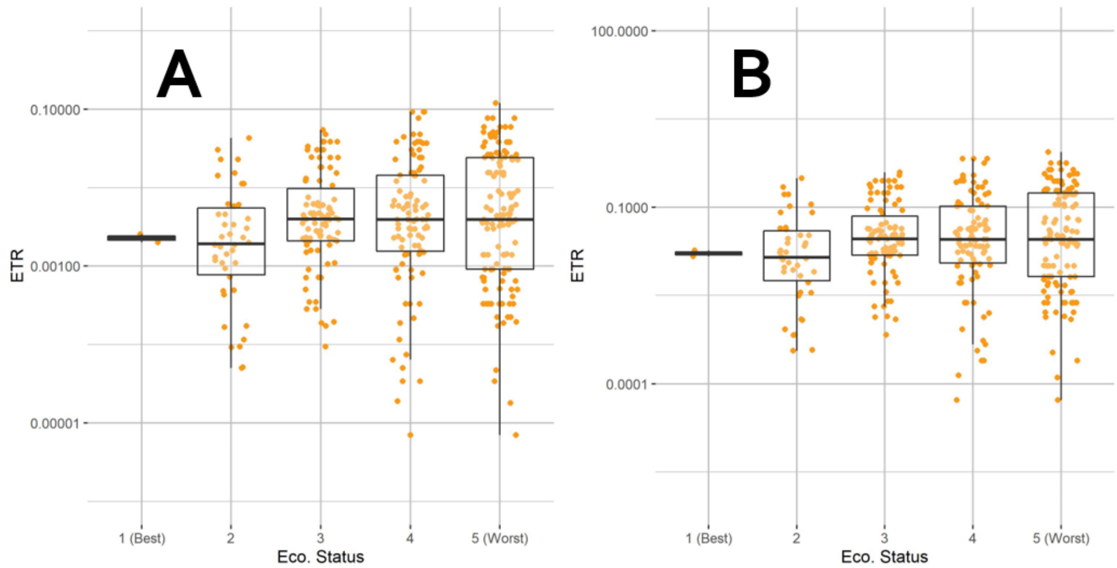


Figure S18. Macroinvertebrate acute (A) and chronic (B) Exposure:Toxicity Ratio (ETR) v ecological status comparing compared to ETR of highest risk across all Biological Quality Elements (BQEs) (i.e., Level 2)

<u>Level 3</u>

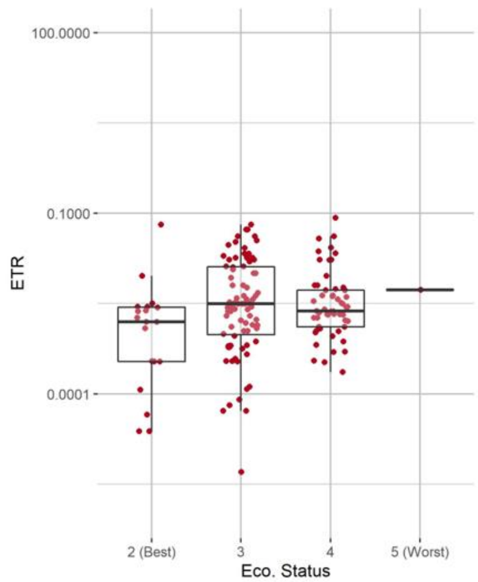


Figure S19. Algae chronic Exposure:Toxicity Ratio (ETR) v ecological status derived from the same taxonomic group (Level 3)

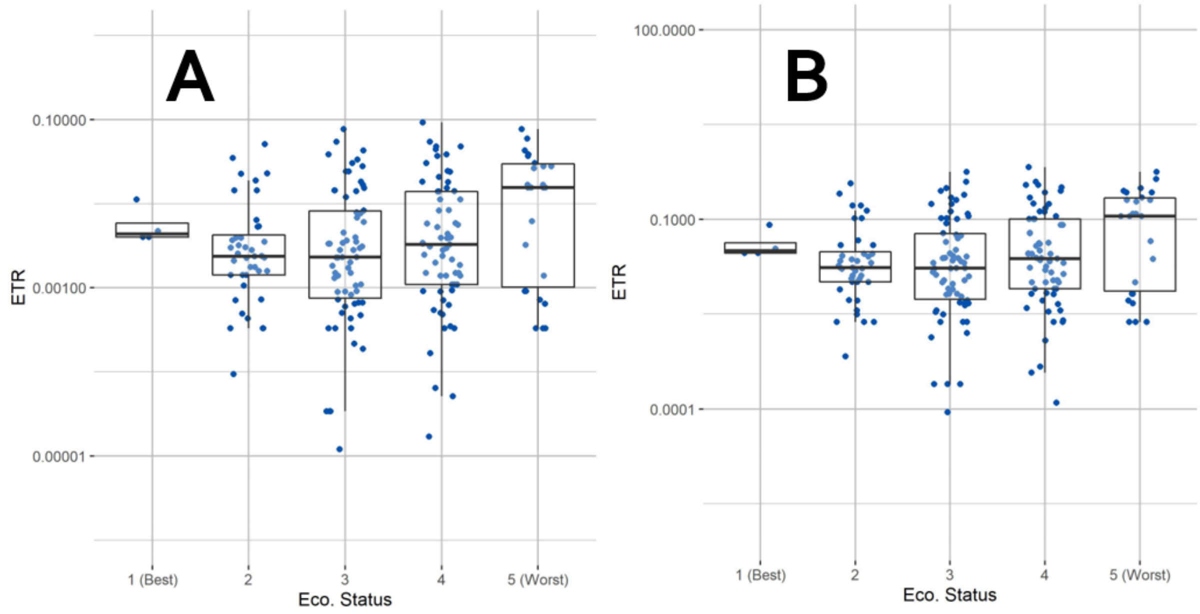


Figure S20. Fish acute (A) and chronic (B) Exposure:Toxicity Ratio (ETR) v ecological status derived from the same taxonomic group (Level 3)

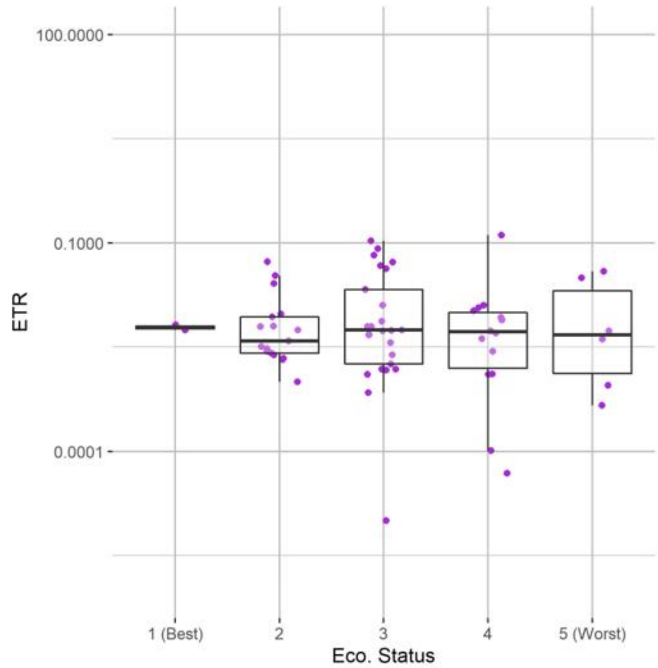


Figure S21. Macrophyte chronic Exposure:Toxicity Ratio (ETR) v ecological status derived from the same taxonomic group (Level 3)

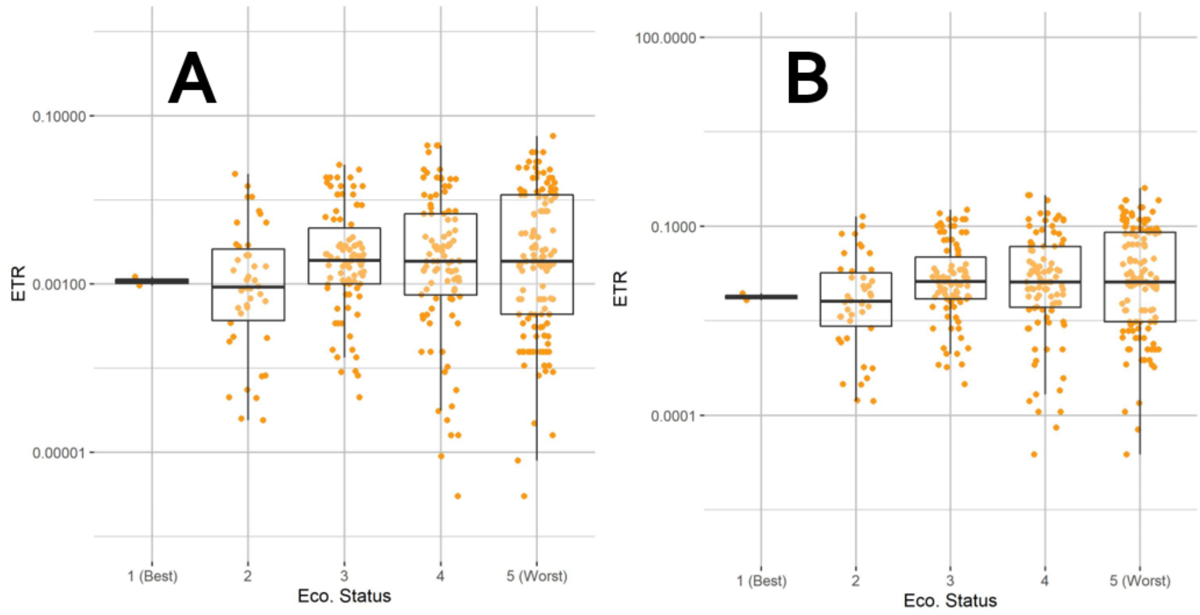
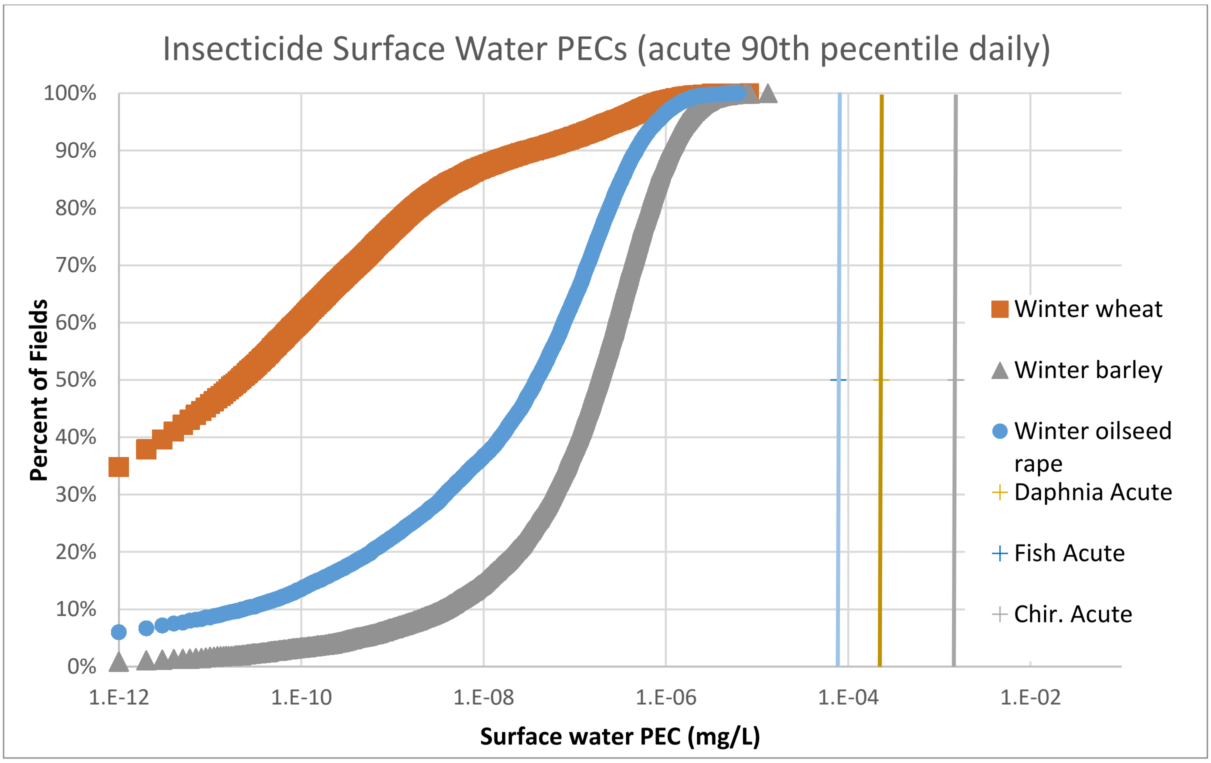


Figure S22. Macroinvertebrate acute (A) and chronic (B) Exposure:Toxicity Ratio (ETR) v ecological status derived from the same taxonomic group (Level 3)

2.2. Plant Protection Products

2.2.4. <u>Predicted Environmental Concentrations (PECs)</u>

For the PPP case study, surface water PECs were generated at the field-level for the herbicide, insecticide and fungicide applied to that crop (i.e., winter wheat, winter barley or winter OSR). Prior to combining into a single field-level risk value, the PPP-specific PECs can be reported based on the crop to which it was applied. The following figures show the distribution of aquatic PECs in relation to the chronic ecotoxicological endpoints (main paper Table 1). Some ecotoxicological endpoints are not charted as they were larger than the x-axis scale.



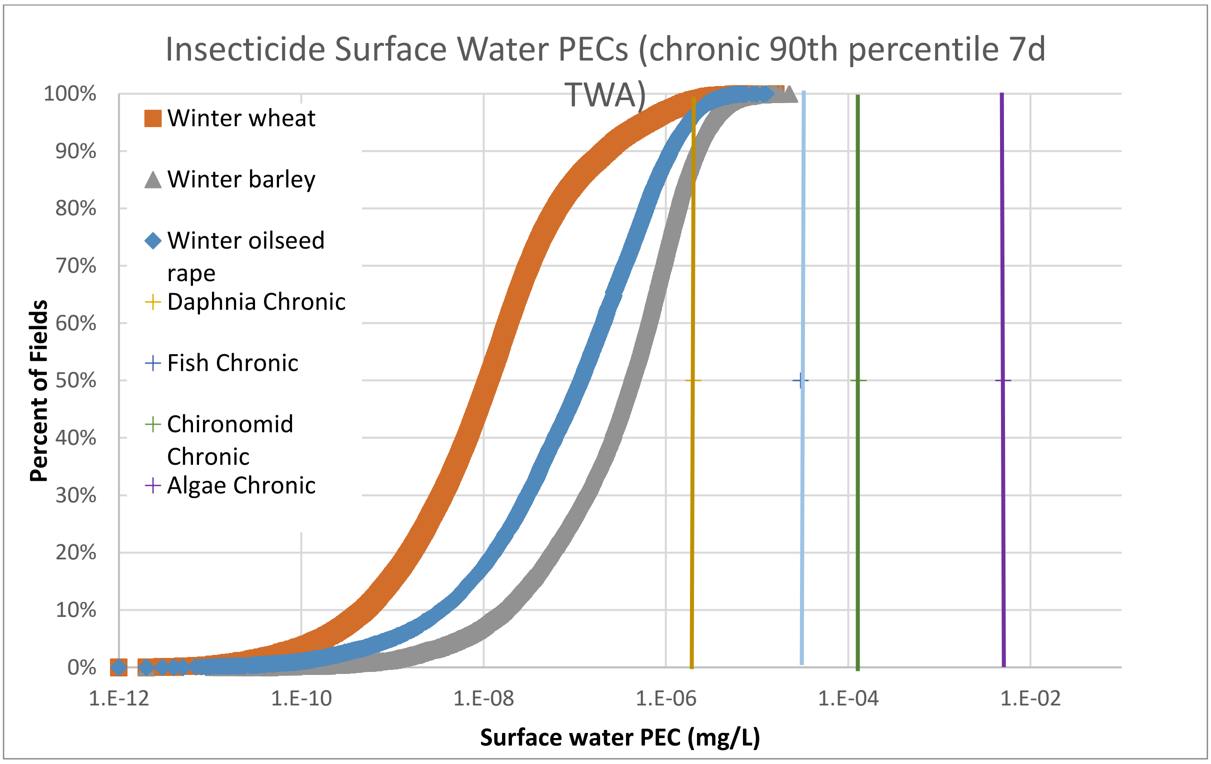
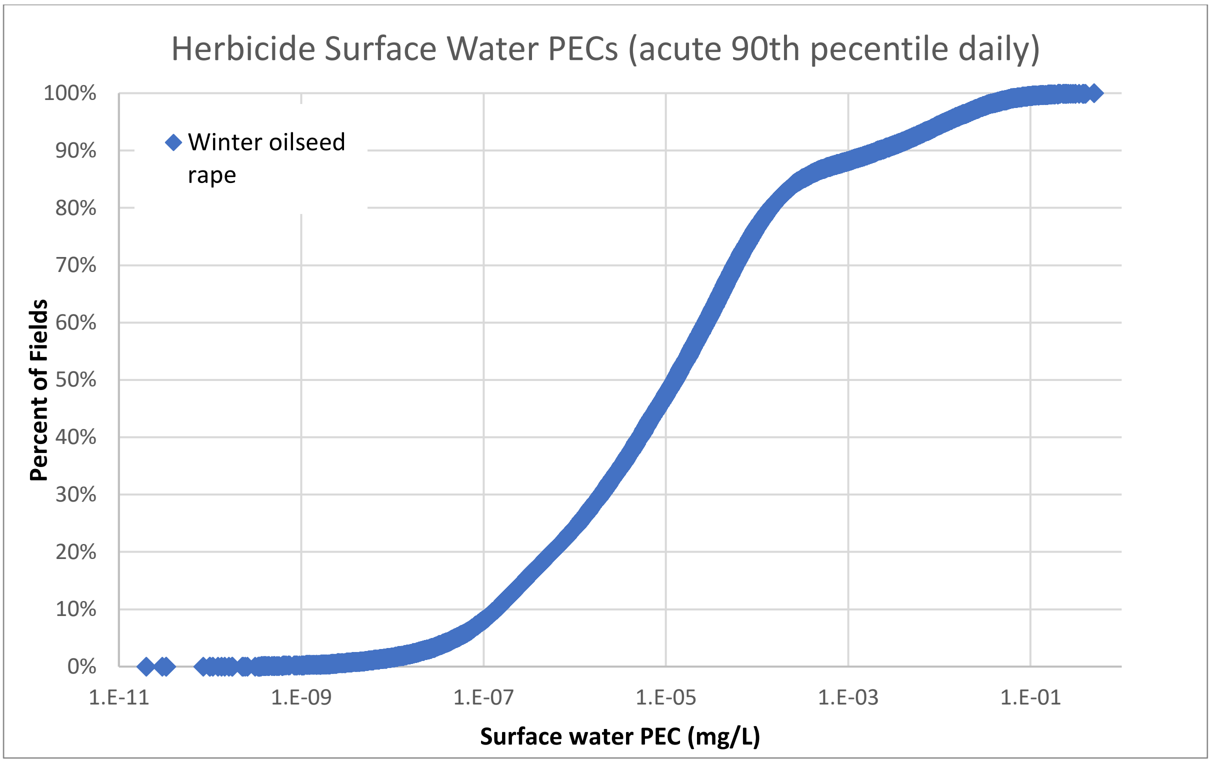


Figure S23. Distribution of insecticide acute (TOP) and chronic (BOTTOM) Predicted Environmental Concentrations (PECs) by crop along with ecotoxicology endpoints for each Biological Quality Element (BQE)



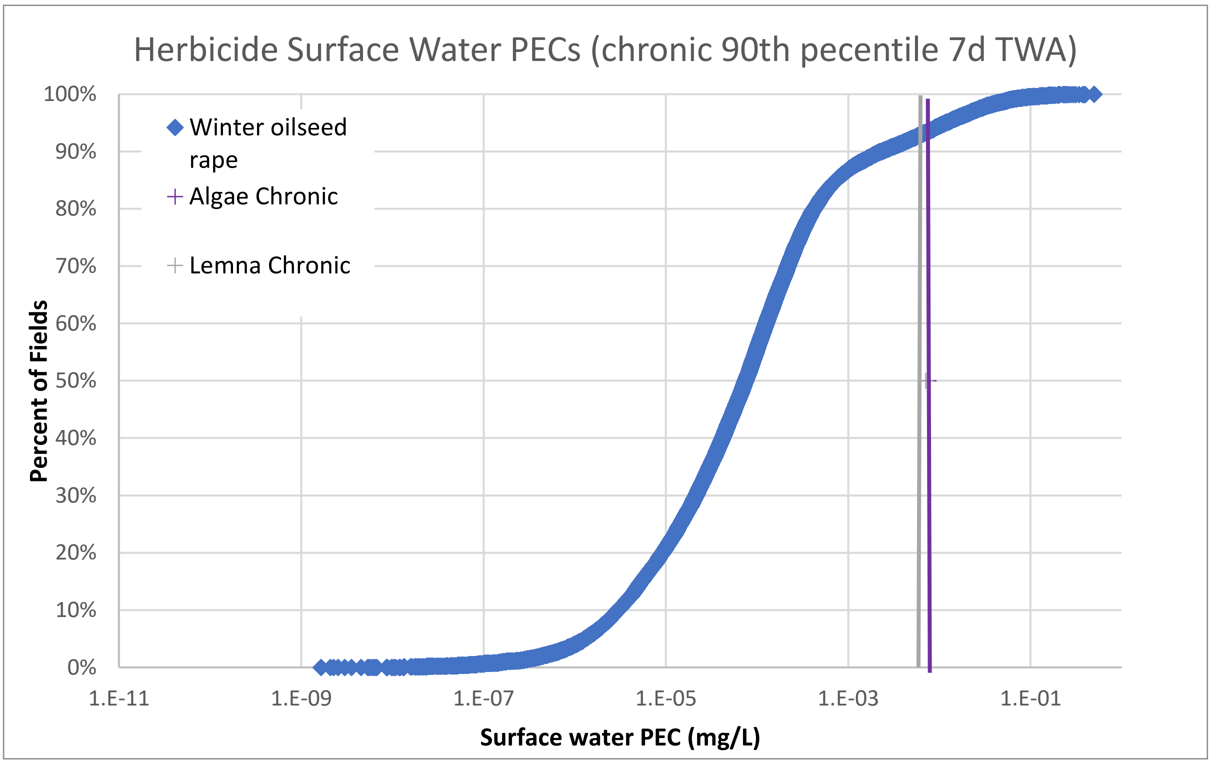
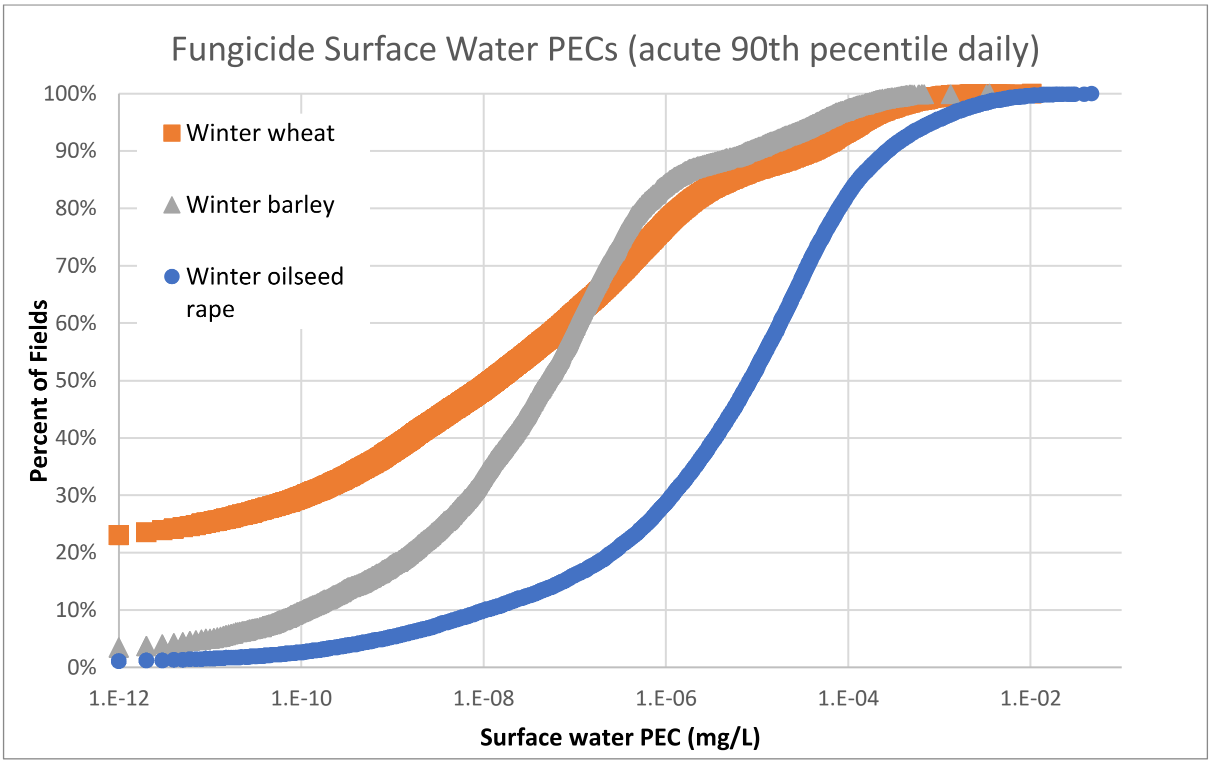


Figure S24. Distribution of herbicide acute (TOP) and chronic (BOTTOM) Predicted Environmental Concentrations (PECs) by crop along with ecotoxicology endpoints for each Biological Quality Element (BQE)



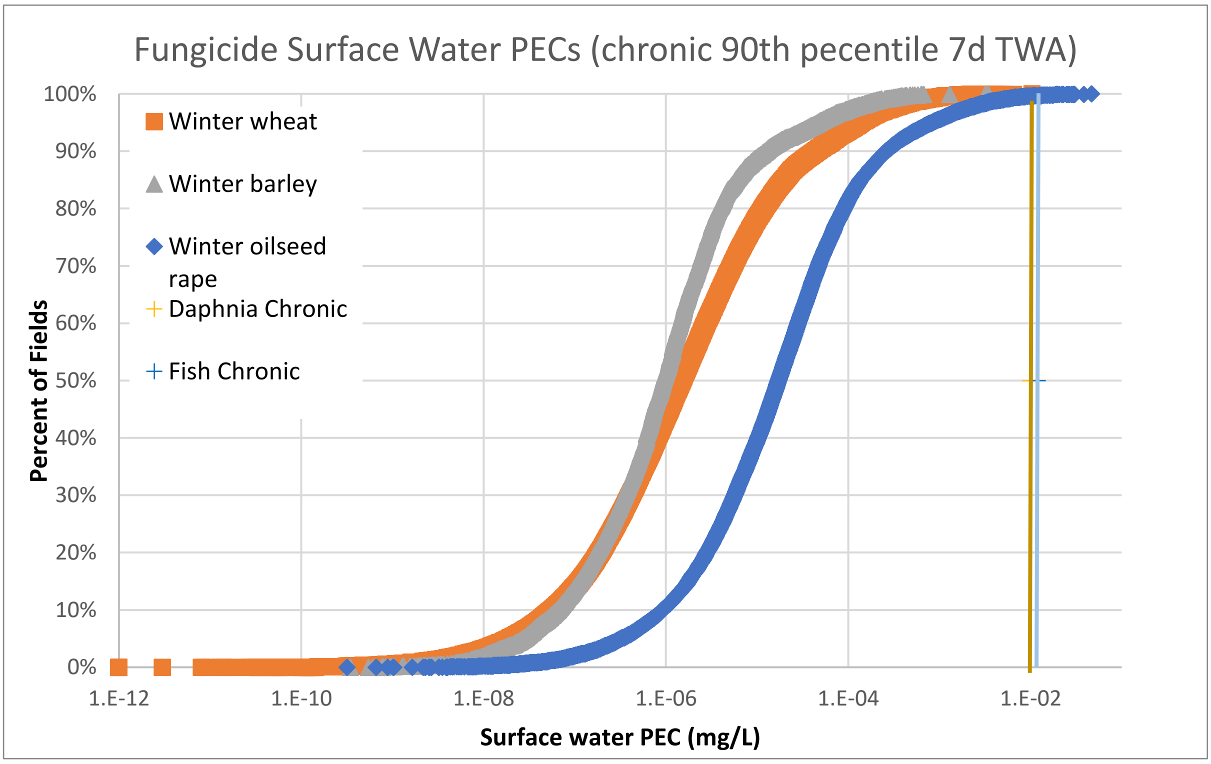


Figure S25. Distribution of fungicide acute (TOP) and chronic (BOTTOM) Predicted Environmental Concentrations (PECs) by crop along with ecotoxicology endpoints for each Biological Quality Element (BQE)

2.2.5. Surface water Exposure:Toxicity Ratio (ETR) (risk)

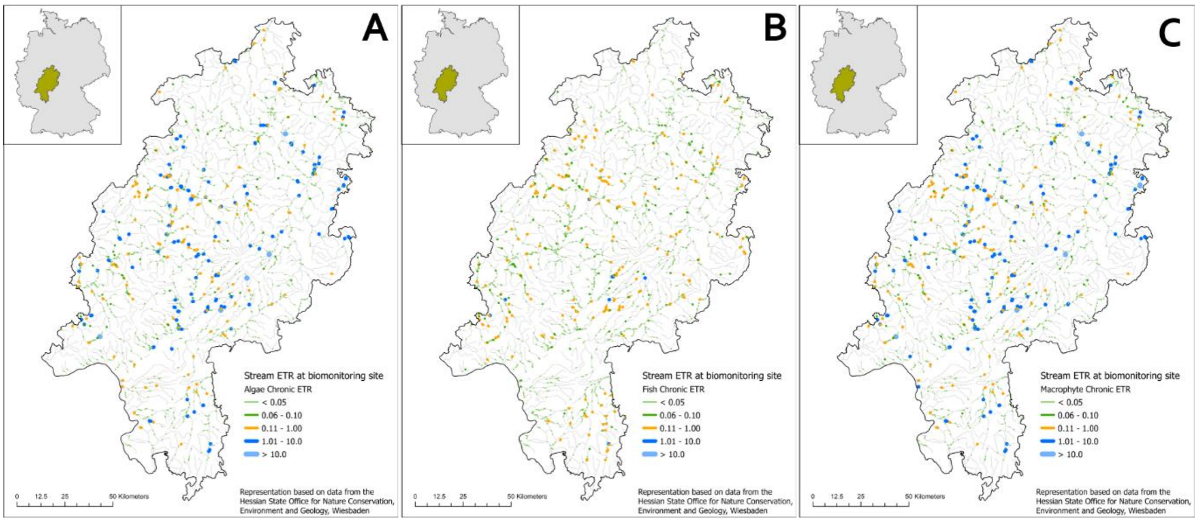


Figure S26. Maps of Plant Protection Product risk (chronic) for algae (A), fish (B) and macrophytes (C) [ETR = Exposure:Toxicity Ratio]

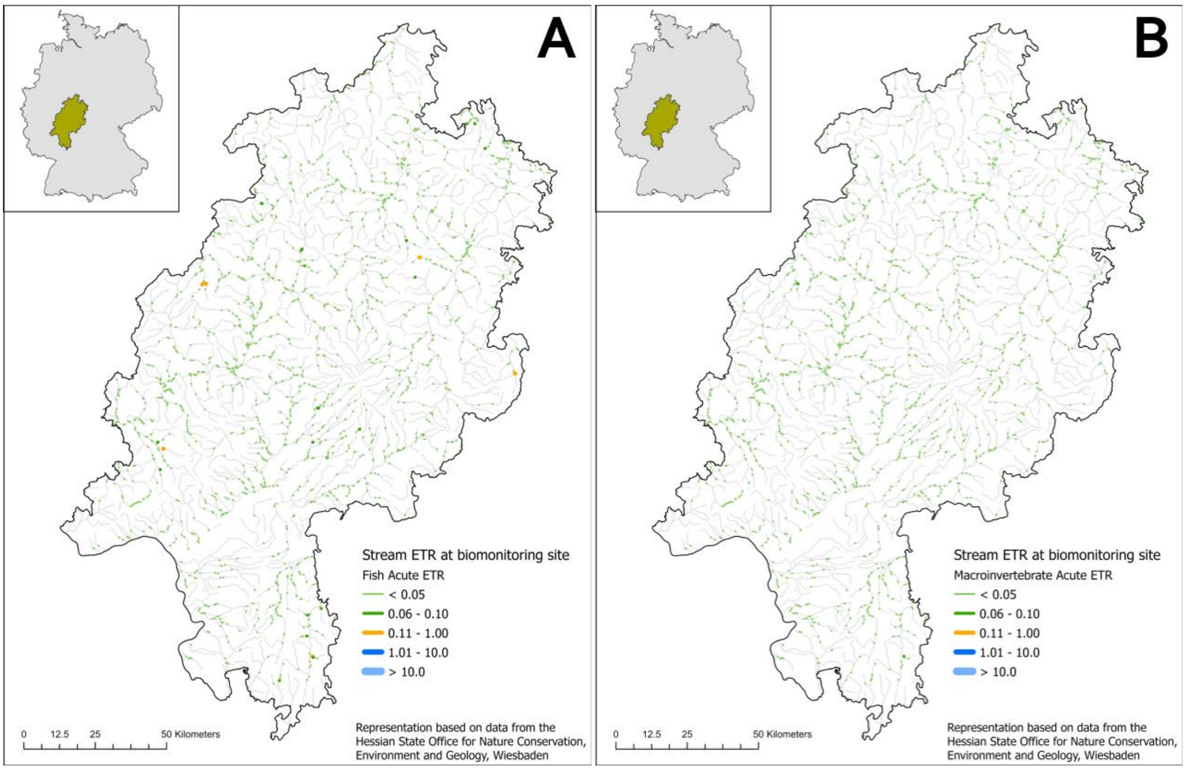


Figure S27. Maps of Plant Protection Product risk (acute) for fish (A) and macroinvertebrates (B) [ETR = Exposure:Toxicity Ratio]

2.2.6. <u>Comparison of Exposure:Toxicity Ratios (ETRs) and Ecological Status</u>

Figure S through Figure S present the PPP ETR data grouped by BQE and sorted by ecological status for examination of risk distributions and charting. Three levels of association were performed for both acute and chronic ETRs.

With minor differences, Level 1 and 2 analyses indicate similar ETR values whereas level 3 analyses tend to indicate lower ETR values than comparable Level 1 and 2 values. Nevertheless, all Levels indicate similar trends across the range of ecological status classes.

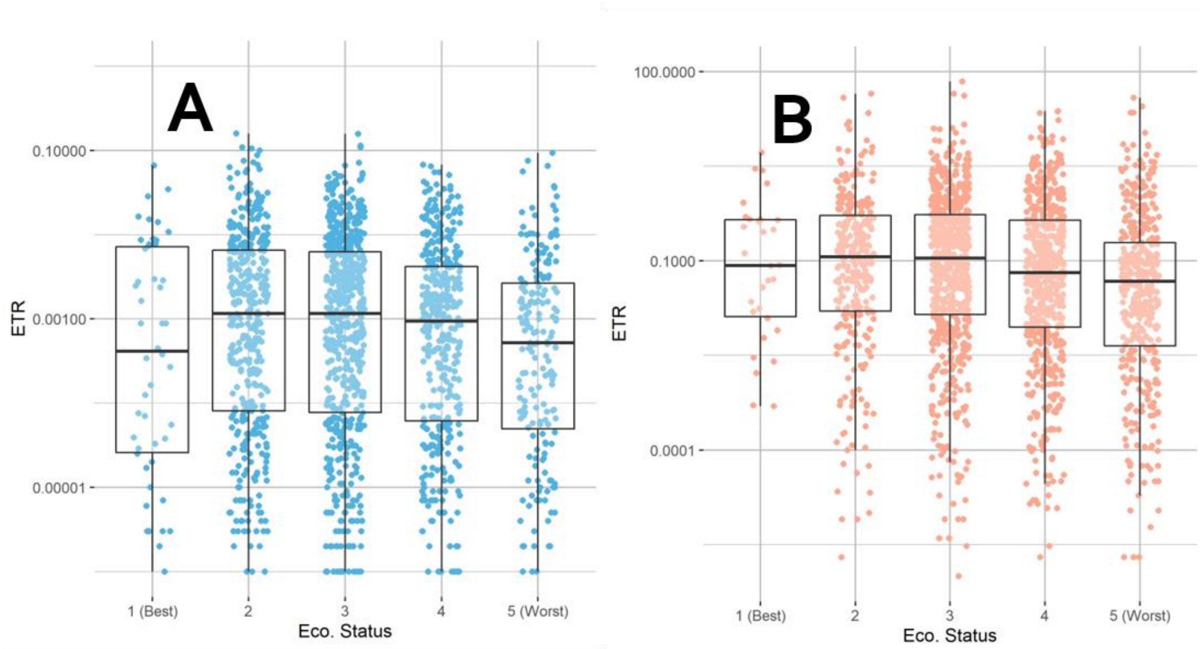


Figure S28. Exposure:Toxicity Ratio (ETR) v ecological status comparing "Best" ecological status Biological Quality Element (BQE) per site compared to ETR of highest risk across all BQEs (i.e., Level 1) for acute (A) and chronic (B)

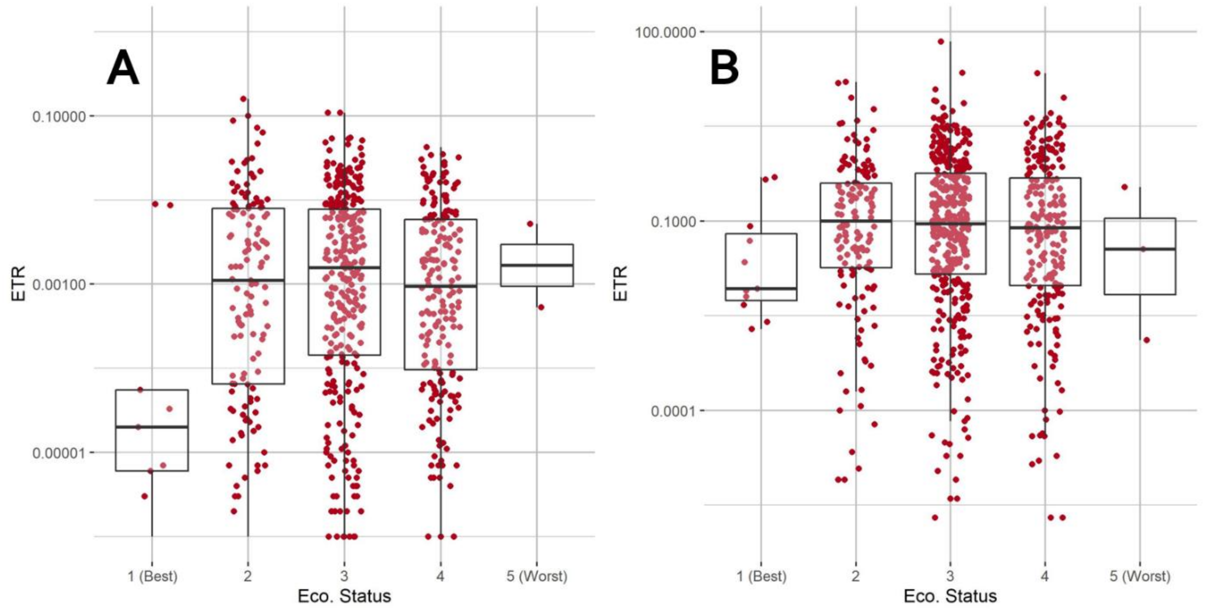


Figure S29. Algae acute (A) and chronic (B) Exposure:Toxicity Ratio (ETR) v ecological status comparing compared to ETR of highest risk across all Biological Quality Elements (BQEs) (i.e., Level 2)

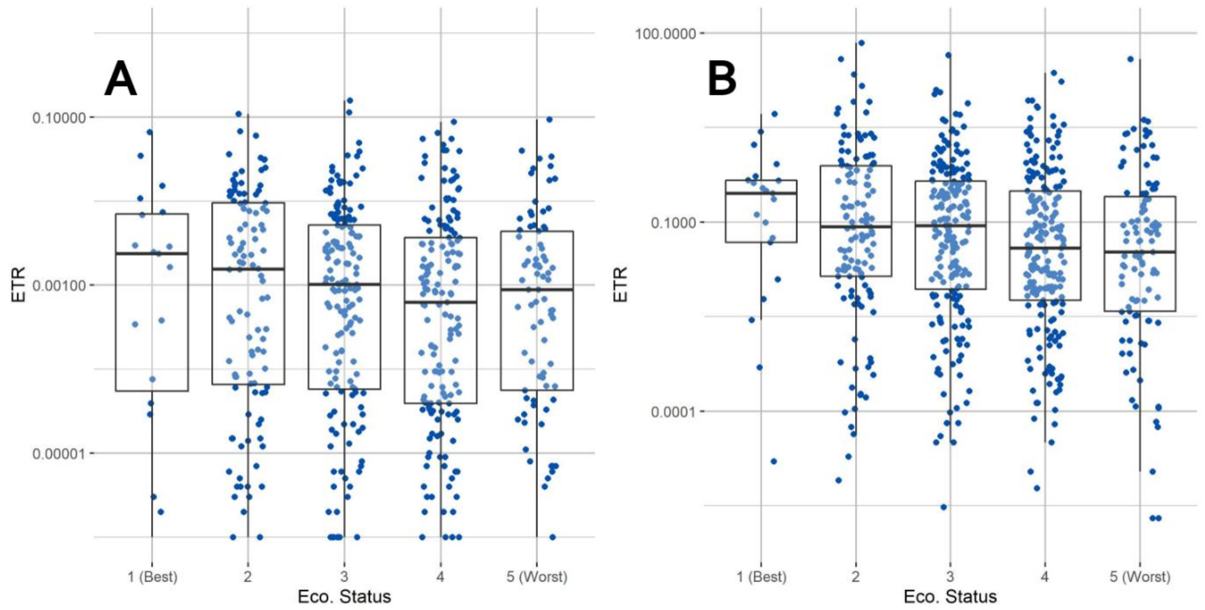


Figure S30. Fish acute (A) and chronic (B) Exposure:Toxicity Ratio (ETR) v ecological status comparing compared to ETR of highest risk across all Biological Quality Elements (BQEs) (i.e., Level 2)

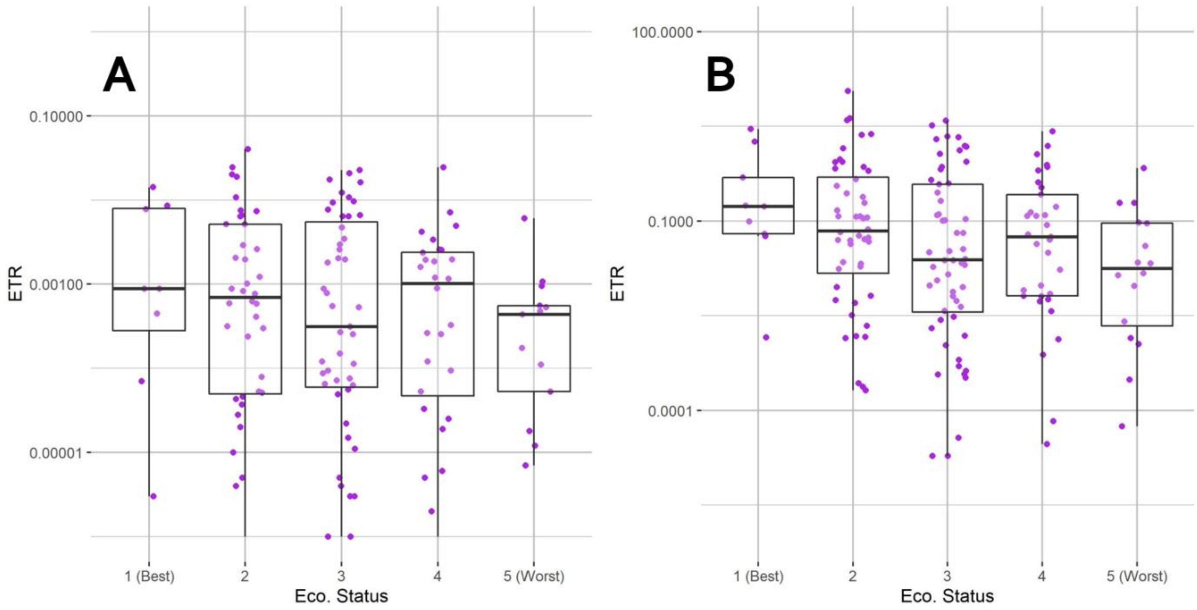


Figure S31. Macrophyte acute (A) and chronic (B) Exposure:Toxicity Ratio (ETR) v ecological status comparing compared to ETR of highest risk across all Biological Quality Elements (BQEs) (i.e., Level 2)

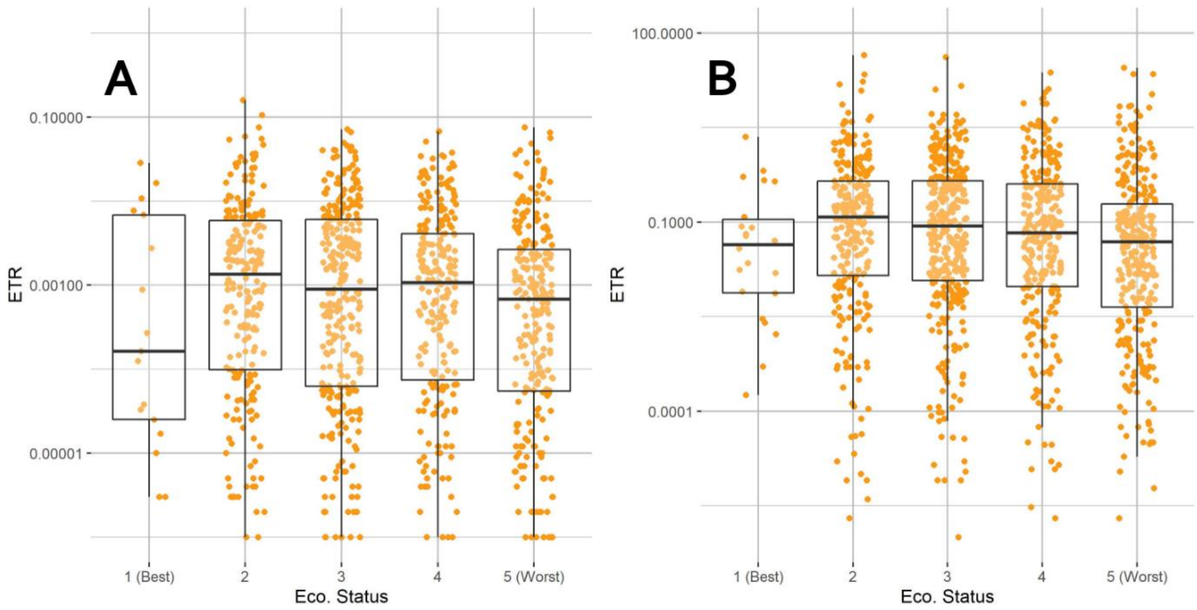


Figure S32. Macroinvertebrate acute (A) and chronic (B) Exposure:Toxicity Ratio (ETR) v ecological status comparing compared to ETR of highest risk across all Biological Quality Elements (BQEs) (i.e., Level 2)

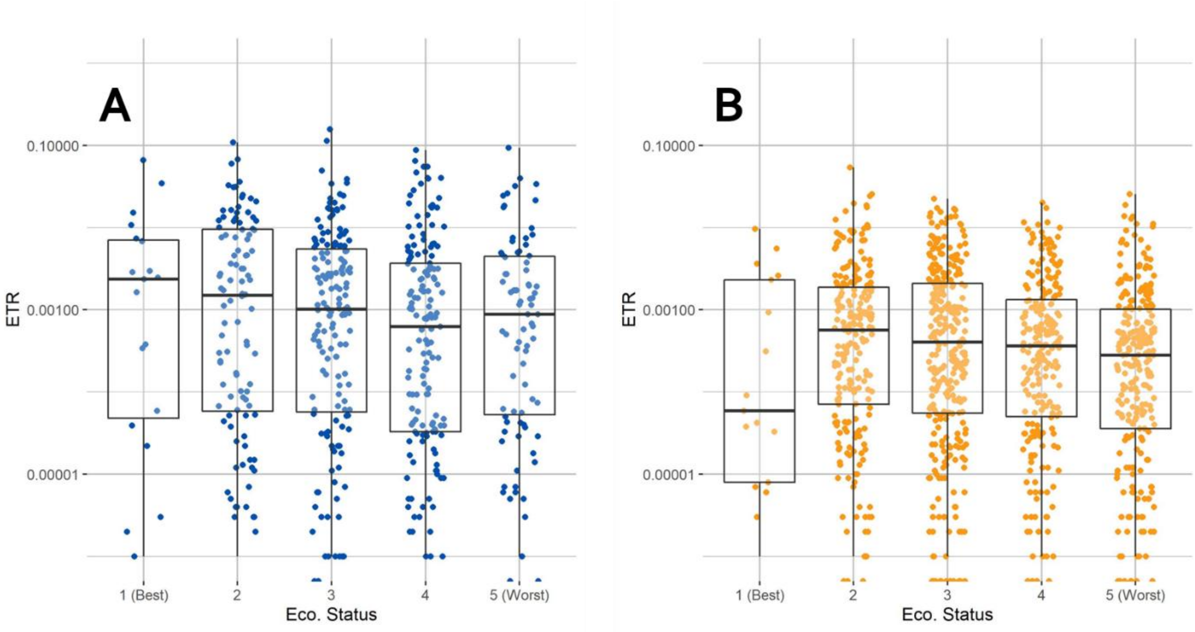


Figure S33. Acute Exposure:Toxicity Ratio (ETR) v ecological status derived from the same taxonomic group (Level 3) for fish (A) and macroinvertebrate (B)

3. References

Barbarossa, V., Huijbregts M. A. J., Beusen, A. H. W., Beck, H. E., King, H., Schipper A. M. 2018. FLO1K, Global Maps of Mean, Maximum and Minimum Annual Streamflow at 1 km Resolution from 1960 through 2015. Scientific Data 5, 180052. DOI - 10.1038/sdata.2018.52.

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