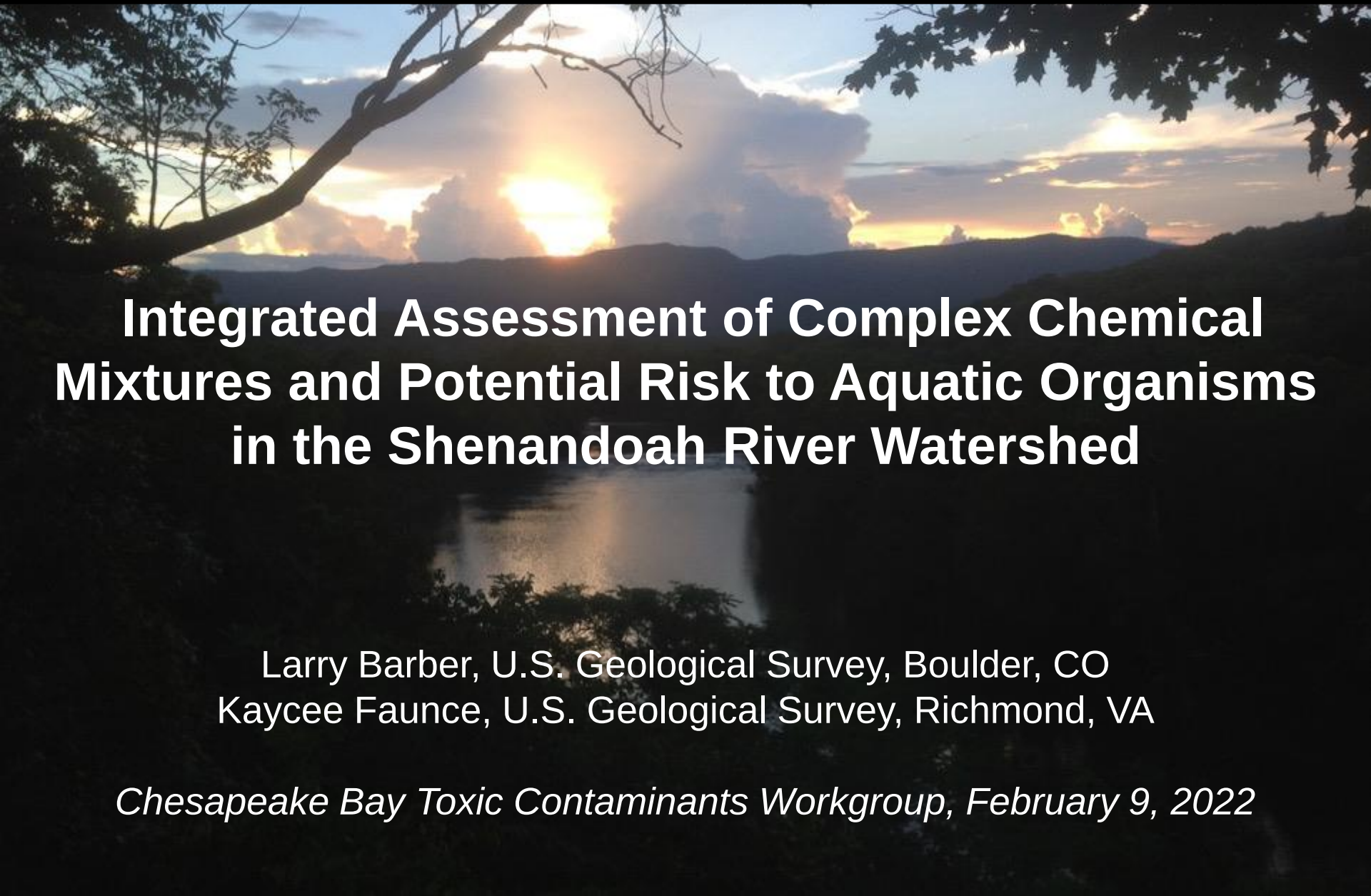


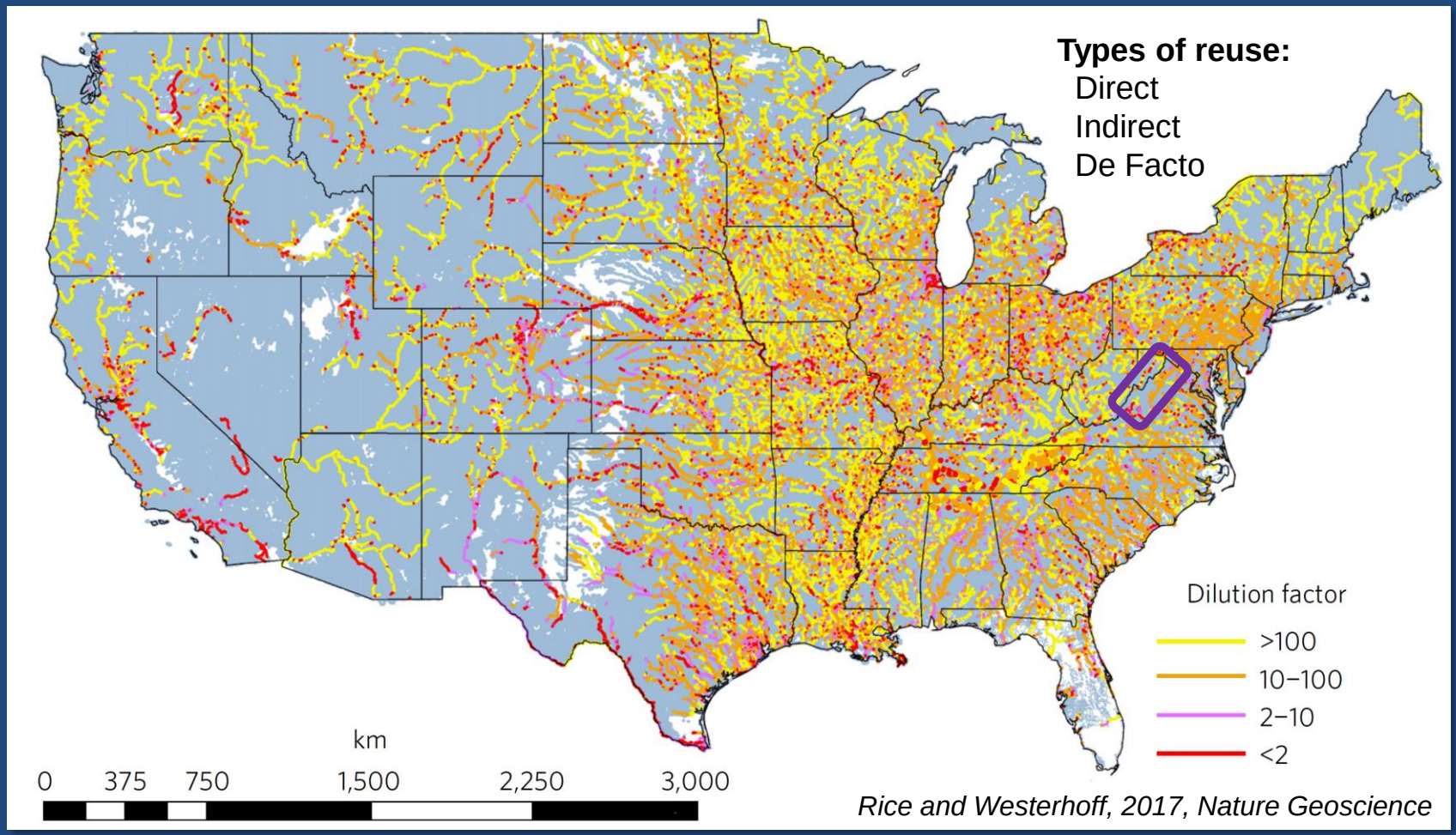
Integrated Assessment of Complex Chemical Mixtures and Potential Risk to Aquatic Organisms in the Shenandoah River Watershed

Larry Barber, U.S. Geological Survey, Boulder, CO
Kaycee Faunce, U.S. Geological Survey, Richmond, VA

Chesapeake Bay Toxic Contaminants Workgroup, February 9, 2022

Wastewater Reuse is Critical Water Resource

- Municipal and industrial wastewater treatment plants (WWTPs)
- Maintain in-stream flows and water supplies
- Source of chemical loading



Rice and Westerhoff, 2017, Nature Geoscience

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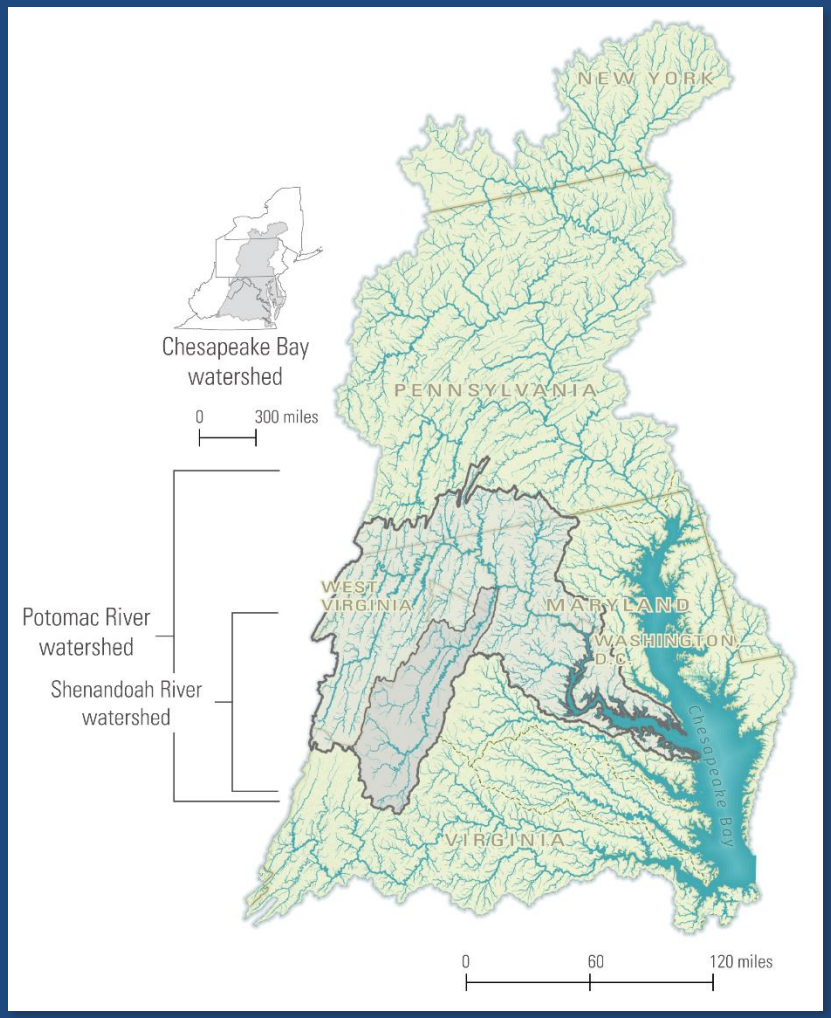
Scaling of Hydrological/Contaminant Information



Watershed

River reach

Reach chemistry

Exposed population

Organism effect

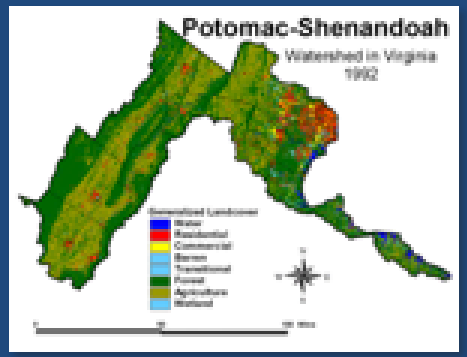
Molecular

Scaling

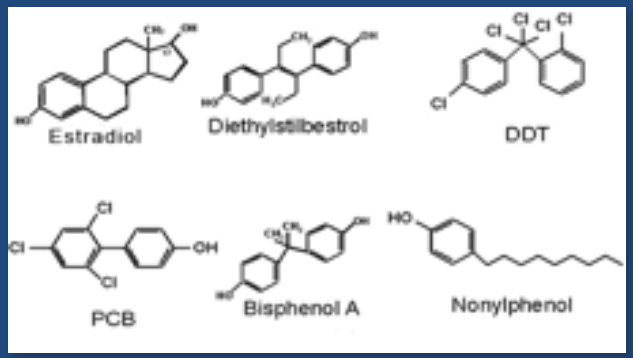
Transdisciplinary Science

USGS

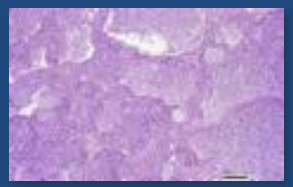
Research Hypotheses



Landscape *predicts* Chemistry



Chemistry *predicts* Biology



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Shenandoah River Watershed 2013-2022

- Kandel et al., 2017, Shenandoah River Accumulated Wastewater Ratio. U.S. Geological Survey Data Release. [https://doi.org/10.5066/F7RF5S8X]
- Kandel, et al., 2017, Shenandoah River accumulated wastewater ratio mapper: [https://va.water.usgs.gov/webmap/shenmap/]
- Barber et al., 2019, Integrated assessment of wastewater reuse, exposure risk, and fish endocrine disruption in the Shenandoah River Watershed. Environ. Sci. Technol., v. 53, p. 3429-3440. [https://doi.org/10.1021/acs.est.8b05655]
- Barber et al., 2019, Assessment of endocrine disruption in the Shenandoah River Watershed – Chemical and biological data from mobile laboratory fish exposures and other experiments conducted during 2014, 2015, and 2016. U.S. Geological Survey Data Release. [https://doi.org/10.5066/F7QF8S22]
- Weisman et al., 2019, De facto reuse and disinfection by-products in drinking water systems in the Shenandoah River watershed. Environ. Sci.: Water Res. Technol., v. 5, p. 1699-1708. [https://doi.org/10.1039/C9EW00326F]
- Weisman et al., 2021, Temporal variations of de facto wastewater reuse and disinfection by-products in public water systems in the Shenandoah River watershed, USA. Water Pract. Technol., v. 16, p. 1434-1445. [https://doi.org/10.2166/wpt/2021.076]
- Barber et al., 2022, Watershed-scale risk to aquatic organisms from complex chemical mixtures in the Shenandoah River. Environ. Sci. Technol., v. 56, p. 845-861. [https://doi.org/10.1021/acs.est.1c04045]

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Article

Watershed-Scale Risk to Aquatic Organisms from Complex Chemical Mixtures in the Shenandoah River

Larry B. Barber,* Kaycee E. Faunce, David W. Bertolatus, Michelle L. Hladik, Jeramy R. Jasmann, Steffanie H. Keefe, Dana W. Kolpin, Michael T. Meyer, Jennifer L. Rapp, David A. Roth, and Alan M. Vajda

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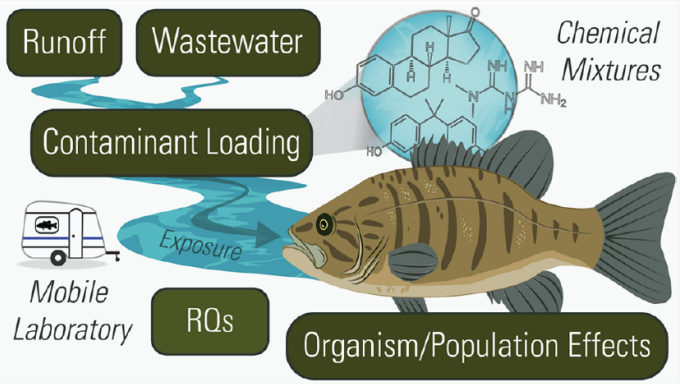
ABSTRACT: River waters contain complex chemical mixtures derived from natural and anthropogenic sources. Aquatic organisms are exposed to the entire chemical composition of the water, resulting in potential effects at the organismal through ecosystem level. This study applied a holistic approach to assess landscape, hydrological, chemical, and biological variables. On-site mobile laboratory experiments were conducted to evaluate biological effects of exposure to chemical mixtures in the Shenandoah River Watershed. A suite of 534 inorganic and organic constituents were analyzed, of which 273 were detected. A watershed-scale accumulated wastewater model was developed to predict environmental concentrations of chemicals derived from wastewater treatment plants (WWTPs) to assess potential aquatic organism exposure for all stream reaches in the watershed. Measured and modeled concentrations generally were within a factor of 2. Ecotoxicological effects from exposure to individual components of the chemical mixture were evaluated using risk quotients (RQs) based on measured or predicted environmental concentrations and no effect concentrations or chronic toxicity threshold values. Seventy-two percent of the compounds had RQ values <0.1, indicating limited risk from individual chemicals. However, when individual RQs were aggregated into a risk index, most stream reaches receiving WWTP effluent posed potential risk to aquatic organisms from exposure to complex chemical mixtures.



KEYWORDS: *Shenandoah River, wastewater reuse, water quality, inorganic chemicals, organic chemicals, complex chemical mixtures, aquatic toxicity, risk quotient, risk index*

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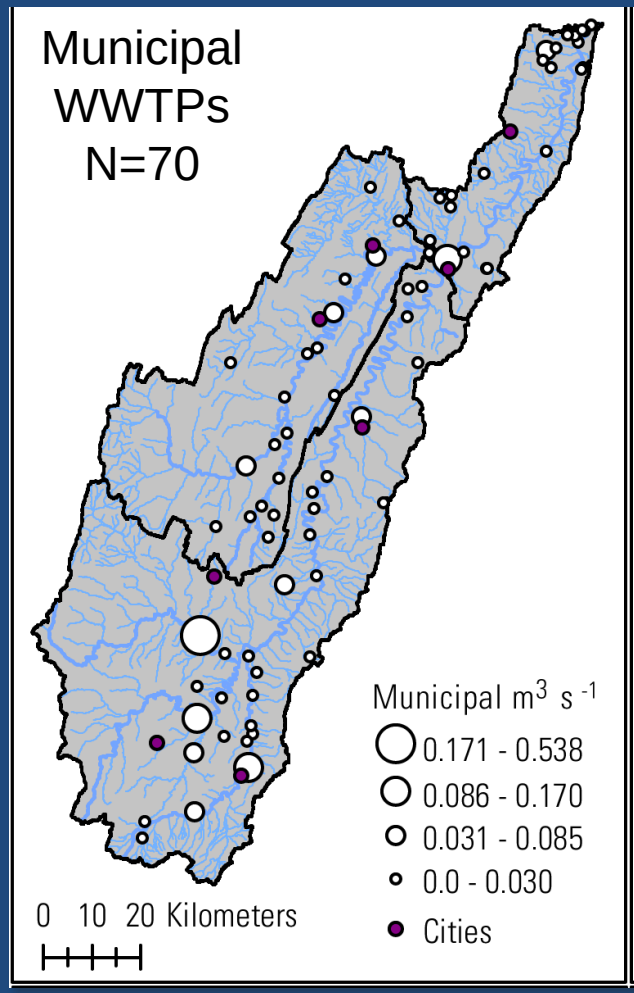
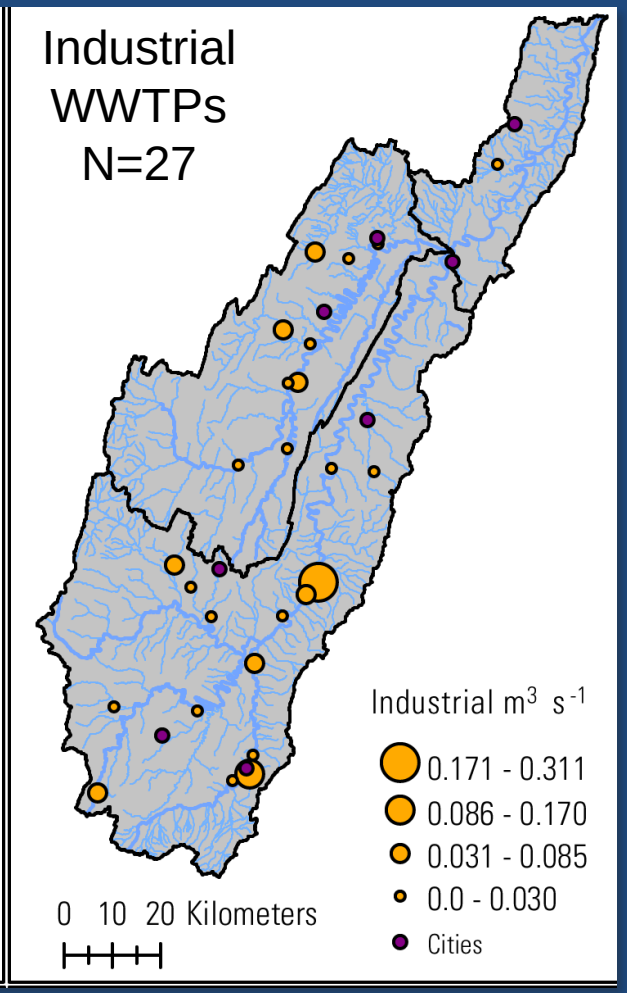
Municipal and Industrial Wastewater Reuse





	Municipal (cfs)	Industrial (cfs)
Capacity flow	109	66
2015 Average flow	51	28

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Accumulated Wastewater Ratio (ACCWW%)

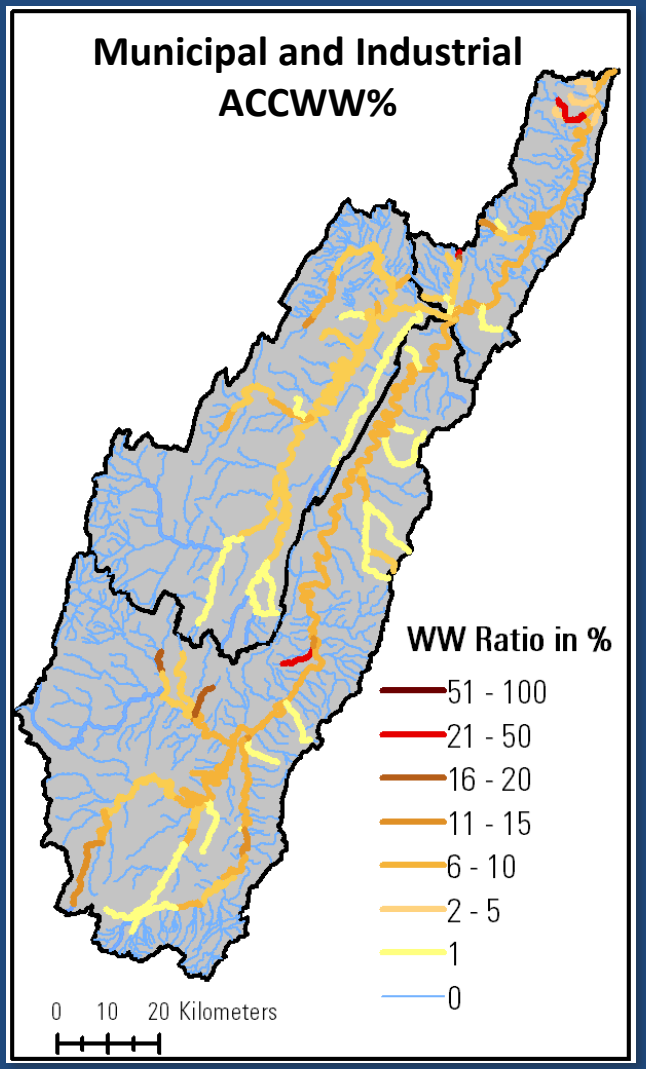
Combine NHDPlus V2 streamflow and ECHO WWTP discharge

420 of 1,754 stream segments have WWTP influence

Incoming + upstream WWTP discharge

ACCWW% for each stream COMID

August flow conditions



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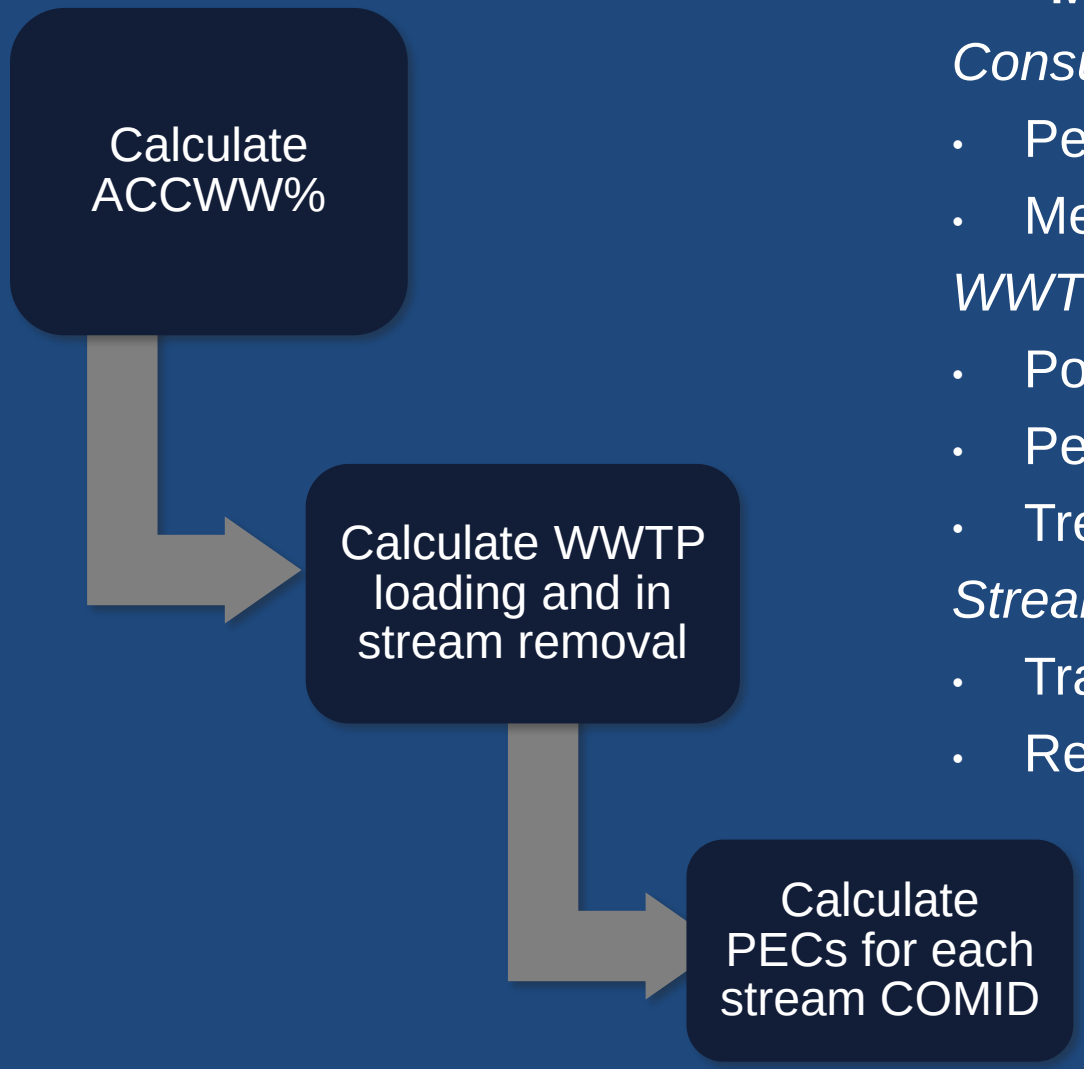
Predicted Environmental Concentrations (PECs)



Municipal WWTP Loading

Consumer Product Chemical Input

- Per capita consumption
- Metabolism

WWTP Input Parameters

- Population served
- Per capita water use
- Treatment type

Stream Input Parameters

- Travel times
- Removal rates

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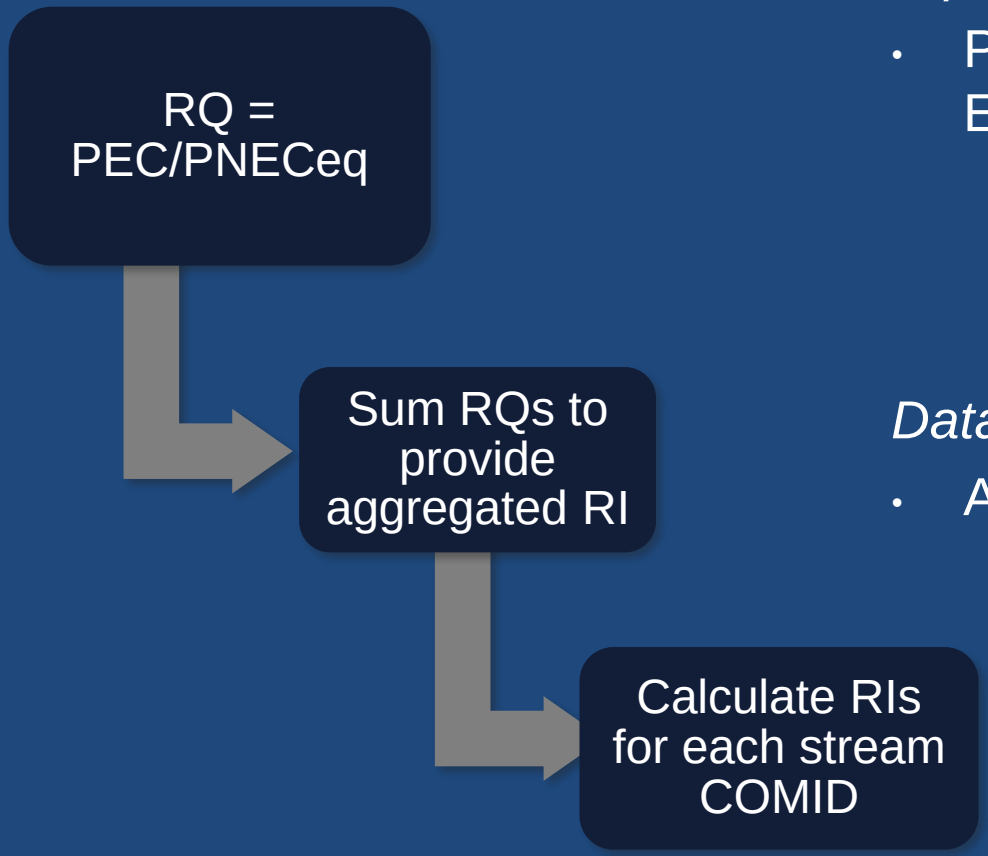
Biological Risk Quotient (RQ) and Risk Index (RI)



Aquatic Toxicity

- Predicted No Effect Concentration Equivalent ($PNEC_{eq}$)
  - Empirical literature endpoints
  - Multiple species
  - Multiple biomarkers

Data Harmonization and Normalization

- Adjustment Factors
  - Ranged from 1 to 1,000

Challenges

- Complex chemical mixtures
- Diversity of effects and modes of action
- Lack of data for many unregulated compounds

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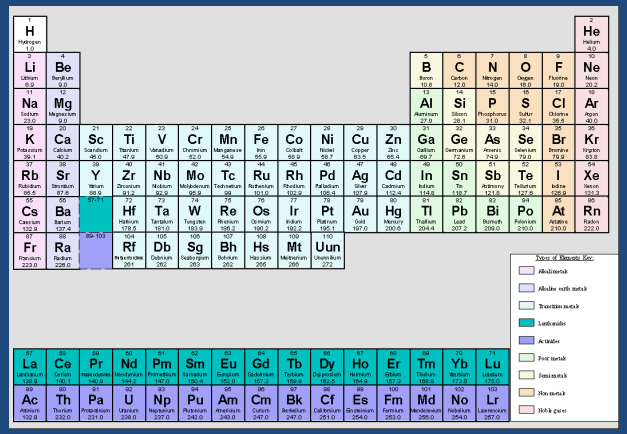
Integrated Chemical and Biological Assessment

Chemical Profiling



Comprehensive
Contemporaneous

Mobile Laboratory Exposures

Fathead minnow (*Pimephales promelas*)

- Photoperiod
- Aeration
- Temperature
- Diet

- 21-d exposure
- Continuous flow
- Weekly water/fish sampling
- Multiple biological endpoints

Wild Fish Assessment

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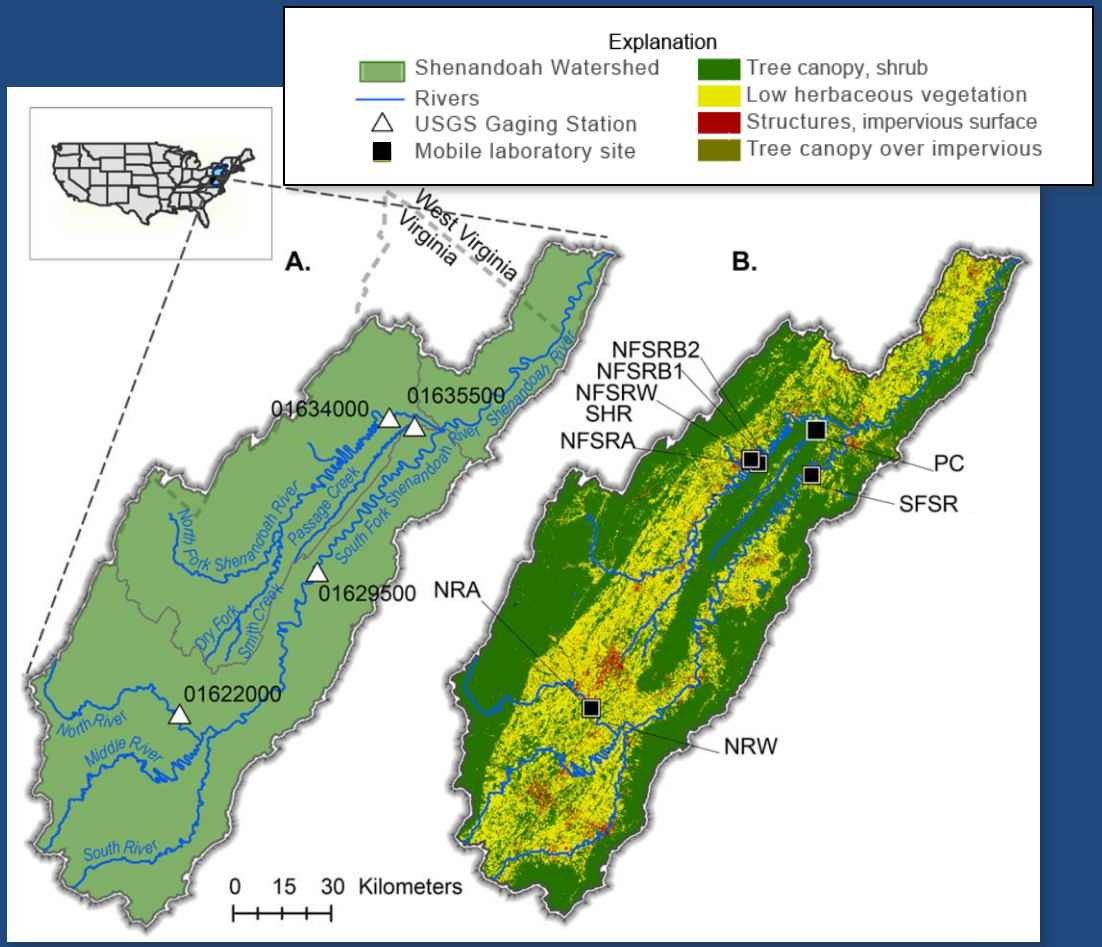
Shenandoah River Watershed Research

Mobile Lab Fish Exposures
2014: 4 Sites
2015: 3 Sites
2016: 5 Sites

Landscape Sampling
2016: 17 Sites

Wild Fish Sampling
2016: 2 sites

ScienceBase data release:
https://doi.org/10.5066/F7QF8S22



SHR - Spring Hollow Run
PC - Passage Creek
NRA - North River above WWTP
NRW - North River WWTP
NFSRA -North Fork Shenandoah River above WWTP
NFSRW - North Fork Shenandoah River WWTP
NFSRW - North Fork Shenandoah below WWTP
SFSR - South Fork Shenandoah River

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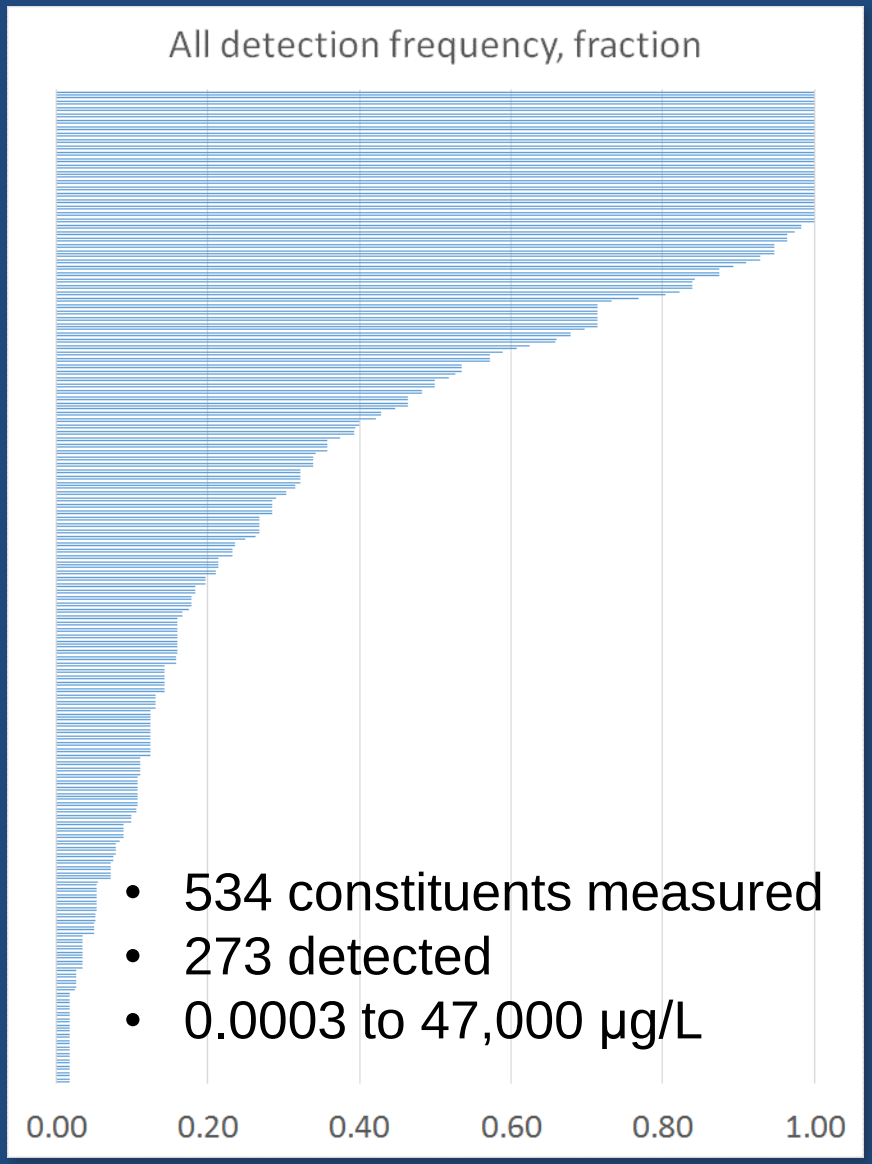
Complex Chemical Mixtures

20 Methods in 6 laboratories

- Field constituents
- Nutrients
- Major ions
- Trace elements
- Pesticides
- Pharmaceuticals
- Personal care products
- Hormones
- Phytoestrogens
- Perfluoroalkyl substances
- Disinfection byproducts

Biological Effects

- Chemical structure
- Concentration
- Mode of action
- Exposure pathways
- Target organism



- 534 constituents measured
- 273 detected
- 0.0003 to 47,000 µg/L

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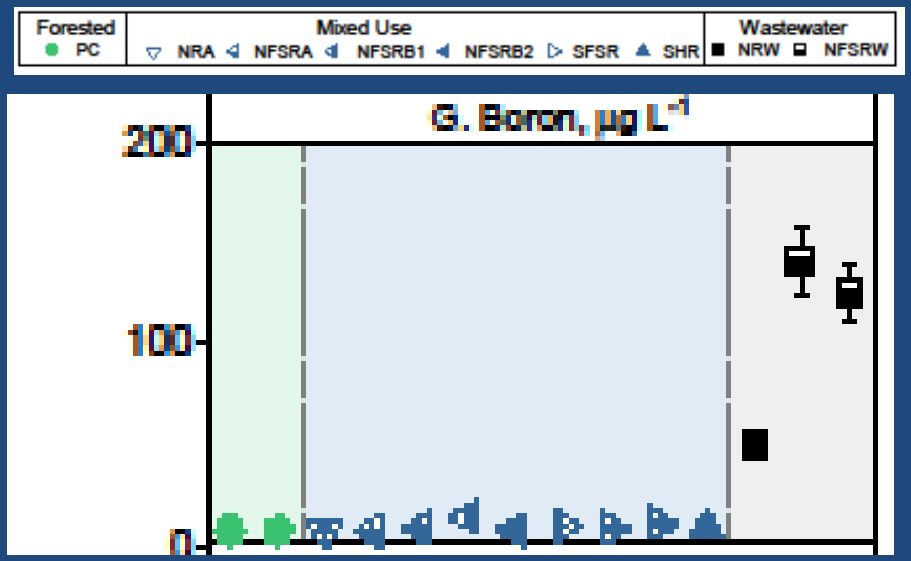
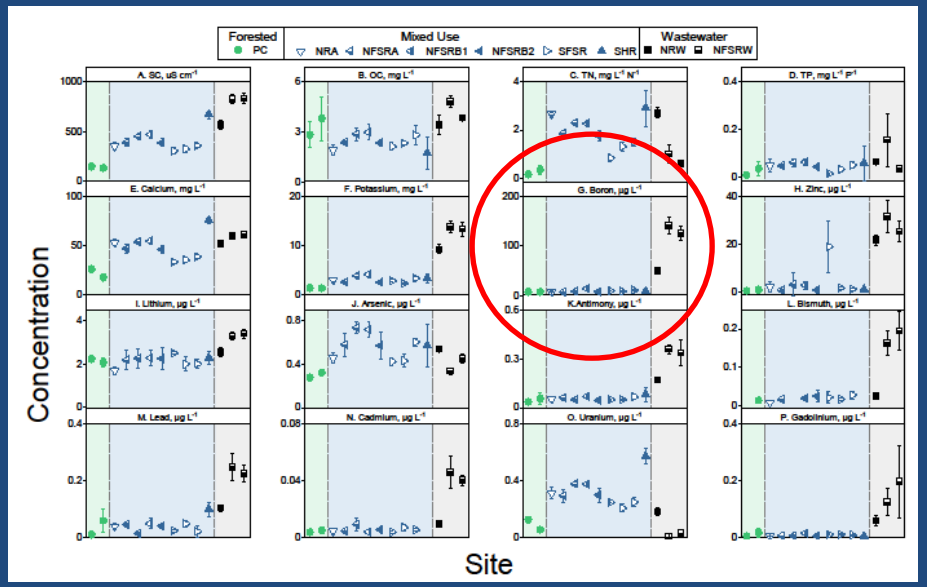
Inorganic Contaminants

- >60 Nutrients and Elements
- Range of sources and behaviors
- Range of biological effects





- Boron is geochemically conservative
- Low freshwater background concentrations
- Enriched in wastewater from use in cleaning products

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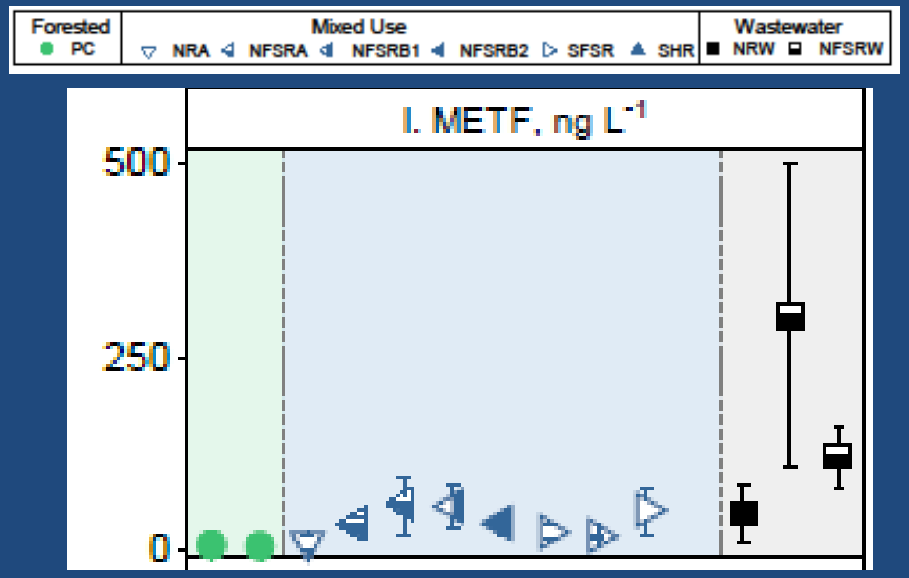
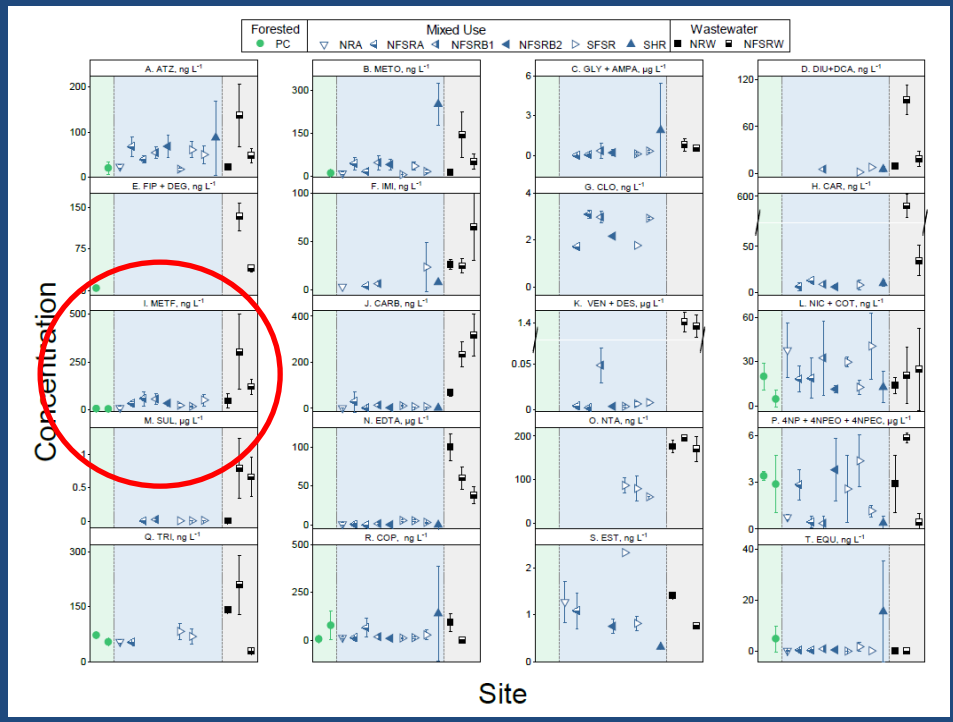
Organic Contaminants

- >250 Synthetic and biogenic compounds
- Range of sources and behaviors
- Range of biological effects





- Metformin is high use anti-diabetic pharmaceutical
- Low freshwater background concentrations
- Enriched in wastewater

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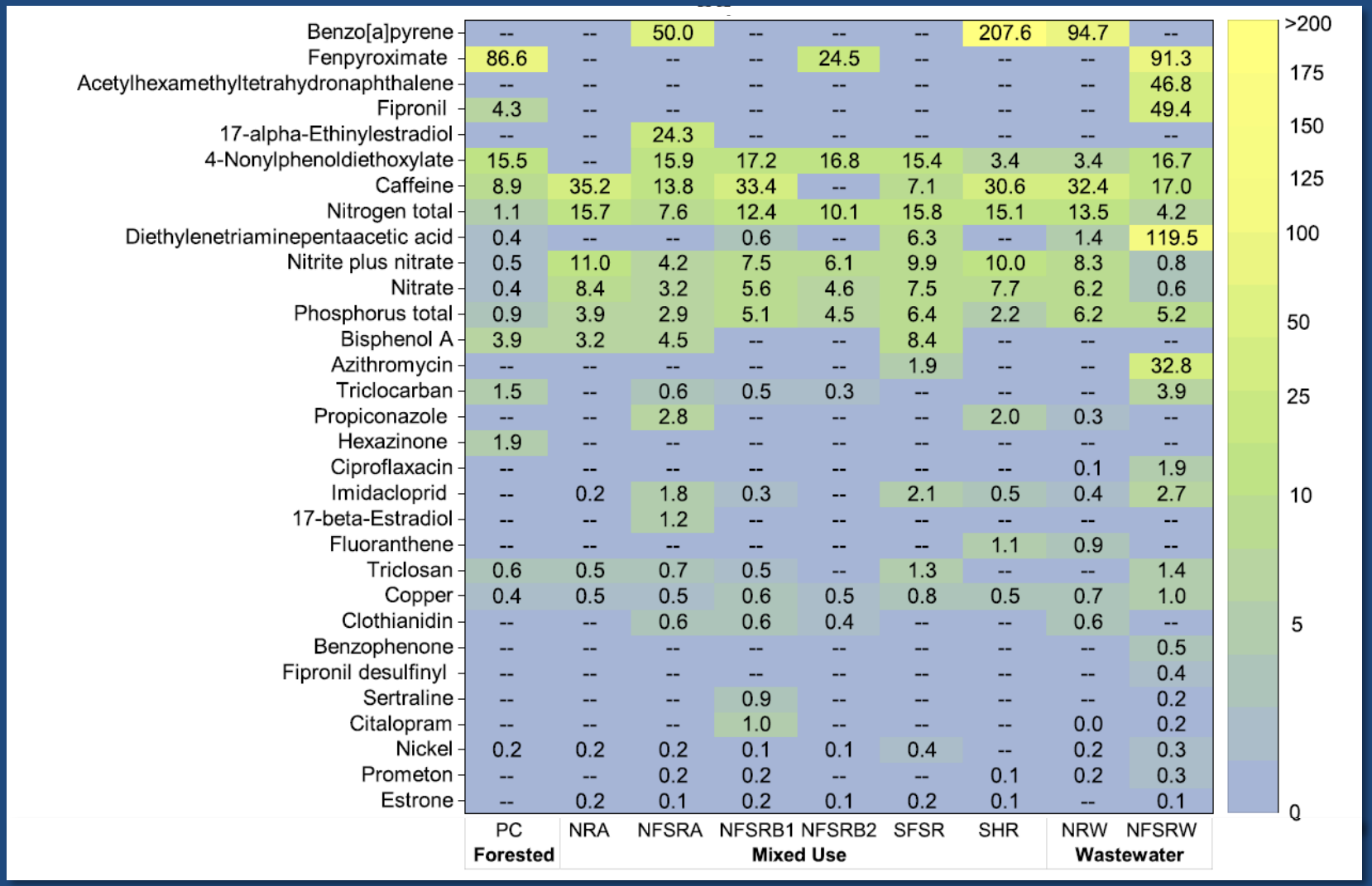
$PNEC_{eq}$ Risk Quotient Ranking



- Top 25th percentile includes nutrients, trace elements, and organic contaminants
- Similar RQ rankings across sites and landscape characteristics

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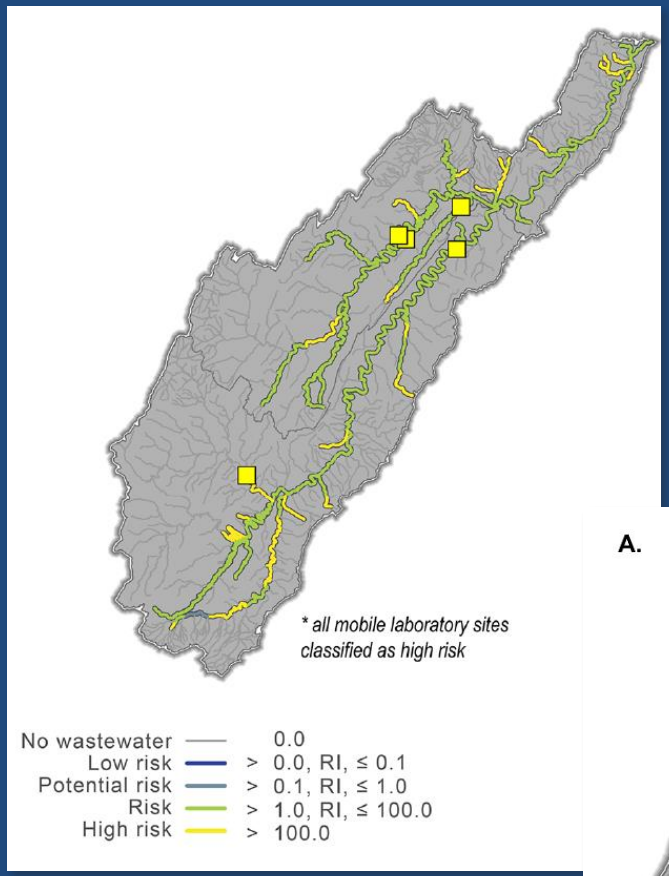
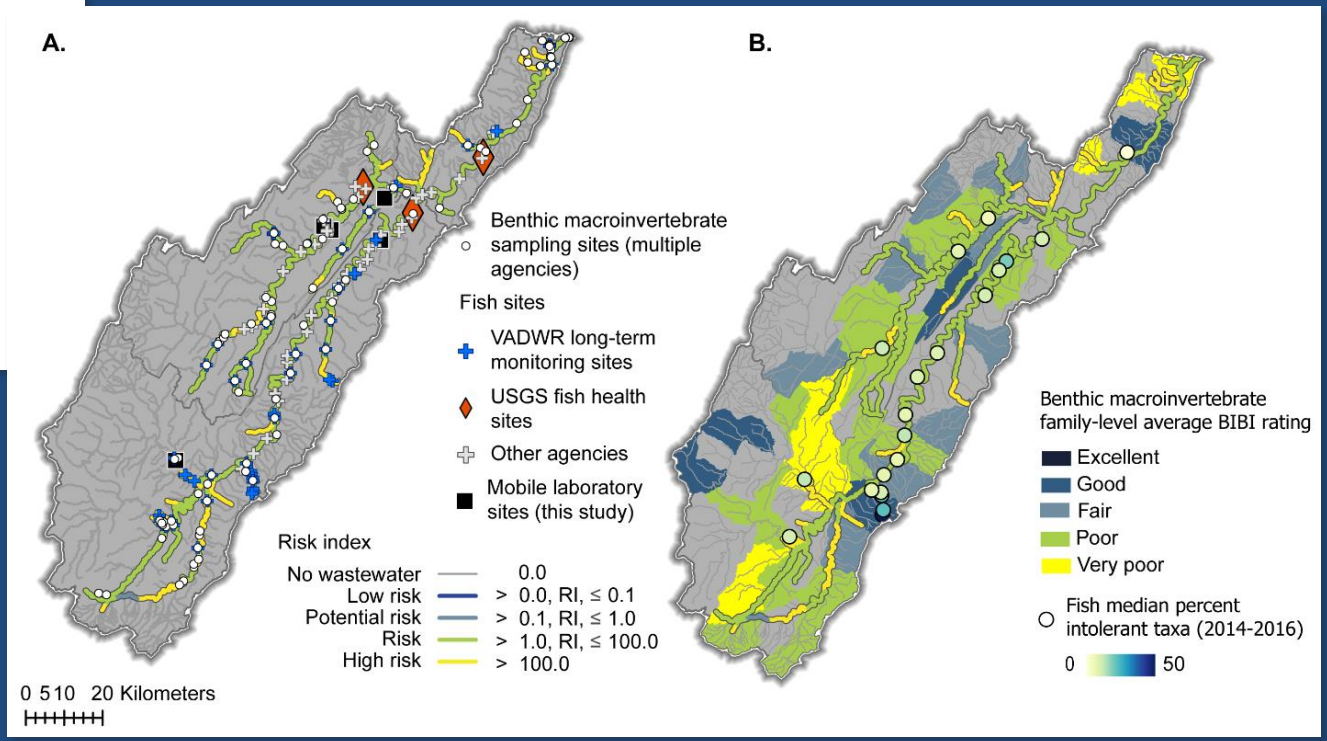
WW Risk Index and Aquatic Community Health



- Higher number of compounds/higher RI
- >90% WW impacted reaches had predicted risk
- Biological indicators indicate degradation



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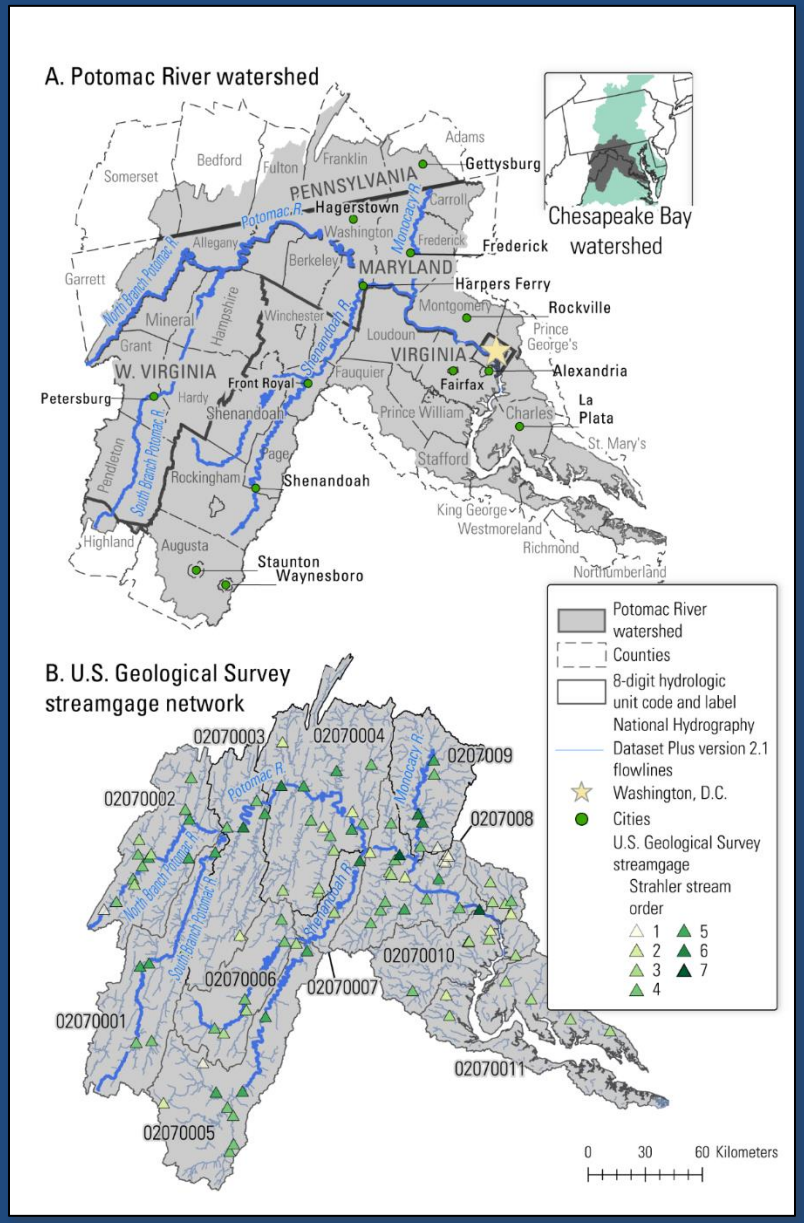
Landscape *predicts* Chemistry *predicts* Biology

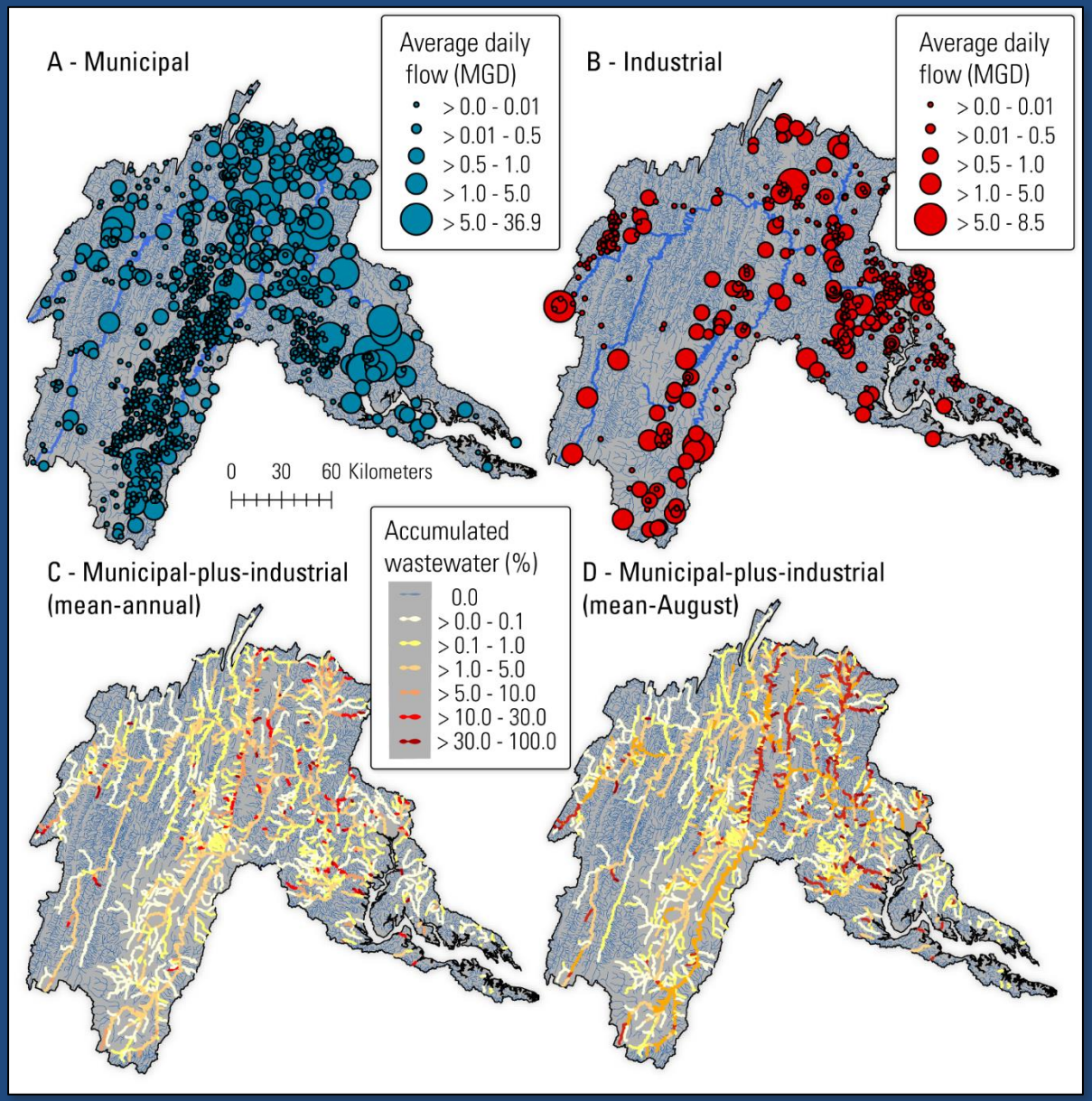
- Widespread occurrence of complex chemical mixtures related to multiple sources and landscape activities
- MECs in WWTP effluents and streams generally below $PNEC_{eq}$
- Fathead minnow exposures indicate physiological, histological, transcriptomic, and metabolomic effects consistent with exposure to low level complex contaminant mixtures
- Relations between MECs and PECs, RIs, model organism effects, and wild organism effects

Expanding Coverage and Capabilities

- Expansion to the Potomac River watershed
  - Faunce et al. In review. Wastewater Reuse and Perceived Ecological Risk Posed by Wastewater Contaminant Mixtures in Streams of the Potomac River Watershed

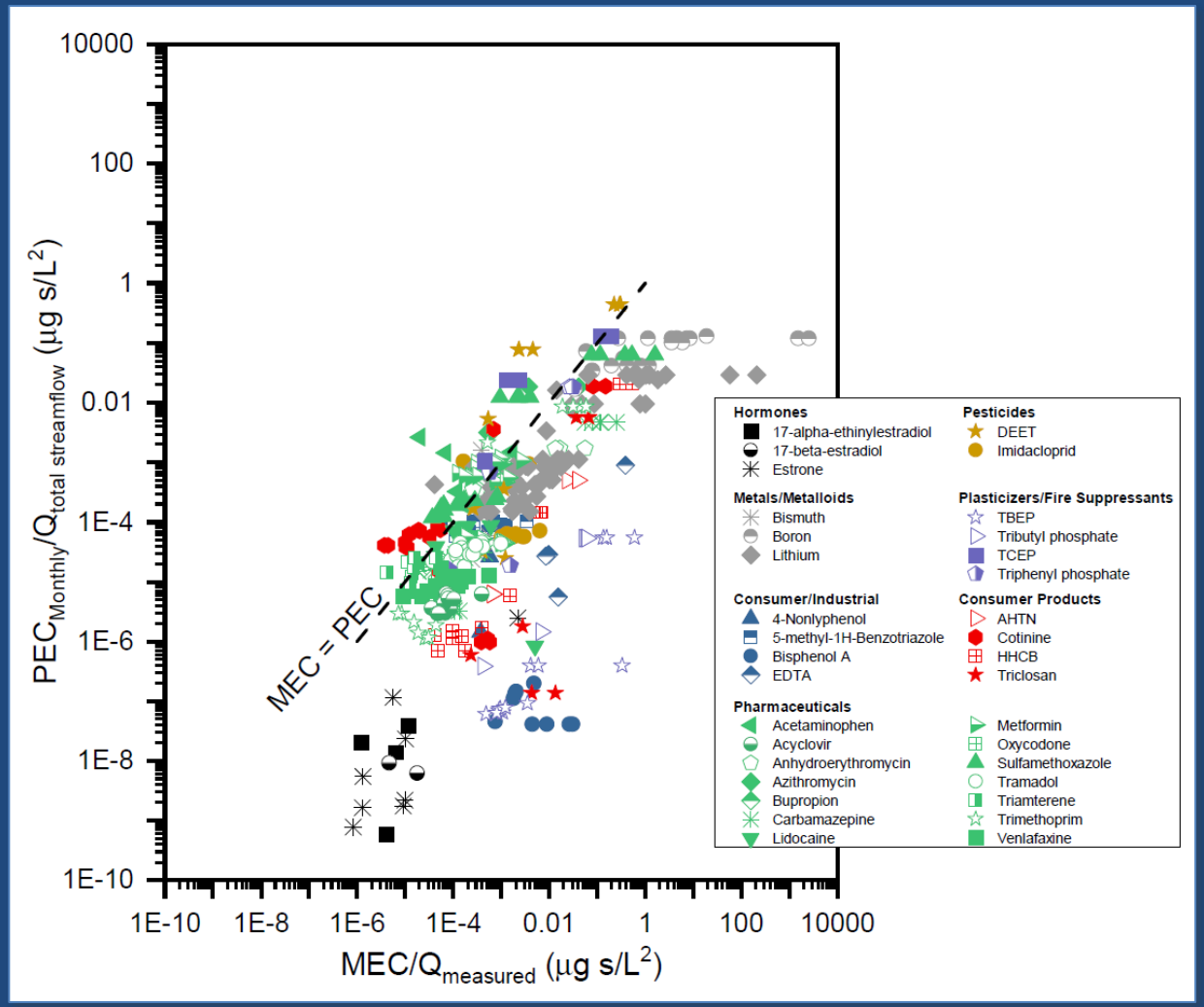


Expanding Coverage and Capabilities

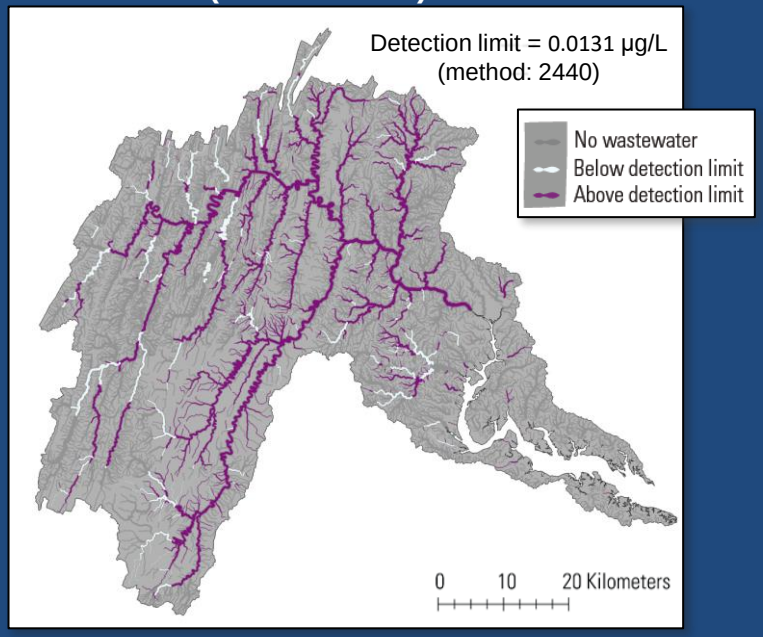


Validation and Verification

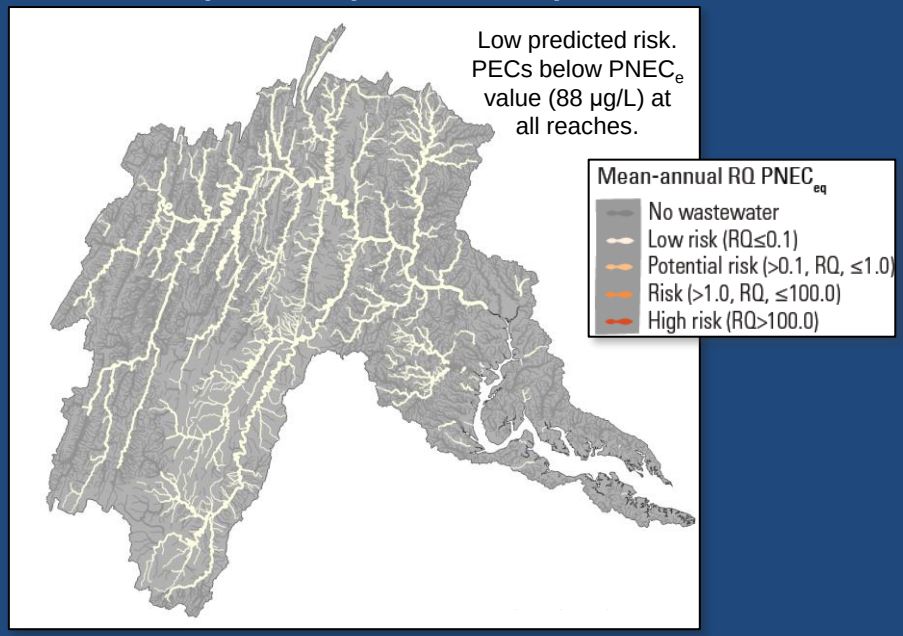
- Stream sampling validation of model predictions planned for summer 2022
- Predictions compared to measured environmental concentrations compiled from the USEPA Water Quality Portal and ScienceBase data releases allow evaluation of general patterns
- Modeling and evaluation of industrial discharged chemicals and landscape inputs would greatly expand predictive capabilities



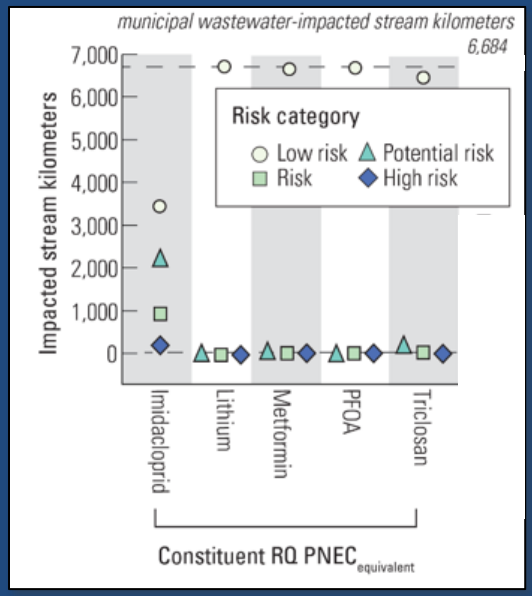
Metformin PECs (mean-annual)



Metformin risk quotients (mean-annual)



Potential risk posed varies by individual contaminant.



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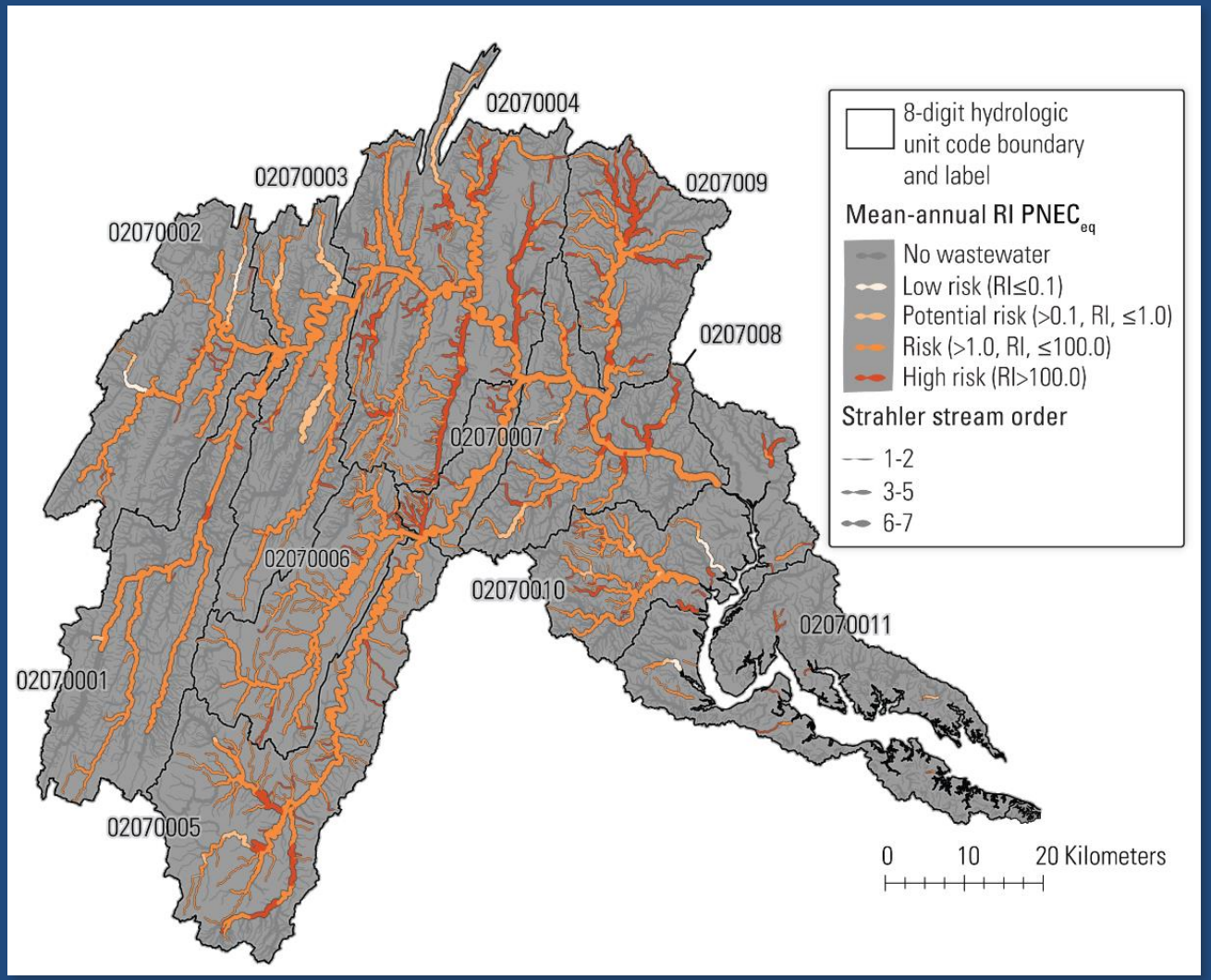
Preliminary information subject to revision. Not for citation or distribution.

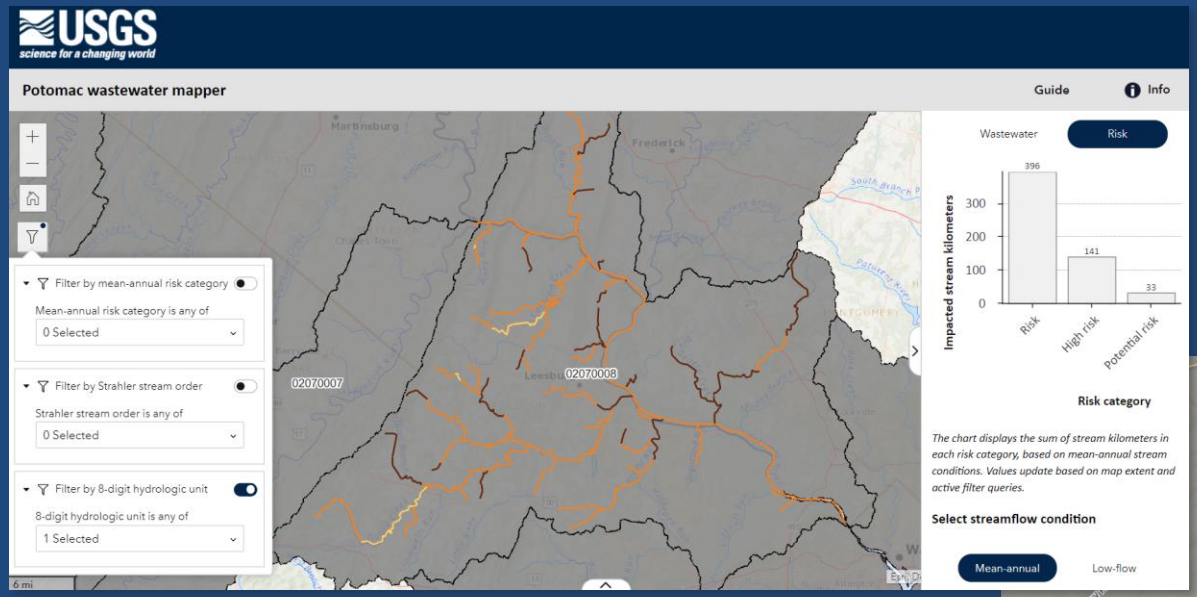
Ecological Risk From Contaminant Mixtures

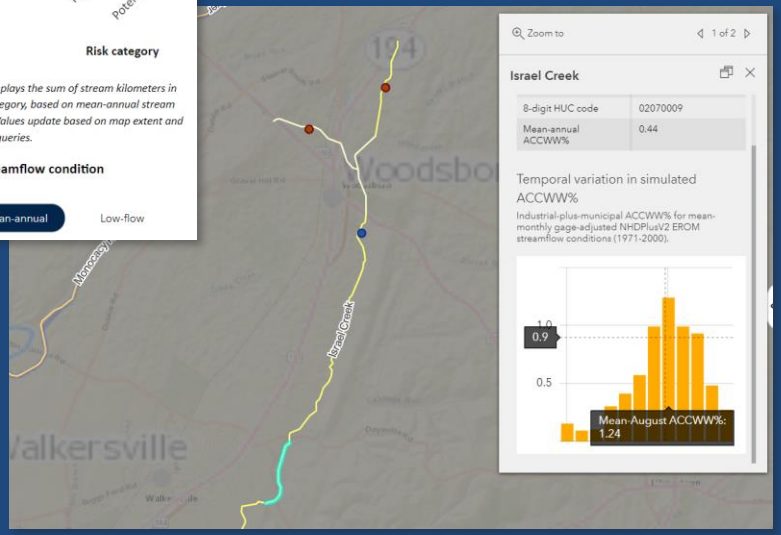
Predicted ecological risk posed by chemical mixtures of up to 51 wastewater-derived contaminants in the Potomac River watershed, based on 2016 average daily municipal wastewater flows and long-term mean-annual streamflow conditions

Chemical mixtures may pose high ecological risk in nearly 1,500 kilometers of watershed streams.



Tools to Help Inform Modeling and Management





Tools to allow users to examine model inputs, predicted risk, and wastewater contributions throughout the watershed are in development.

Thank you

For further information contact:

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- Kaycee Faunce, kfaunce@usgs.gov