

The background of the slide is a photograph of a sunset over a river. The sun is low on the horizon, partially obscured by clouds, creating a warm orange and yellow glow. The river reflects the light from the sun. Silhouettes of trees and hills are visible in the foreground and background.

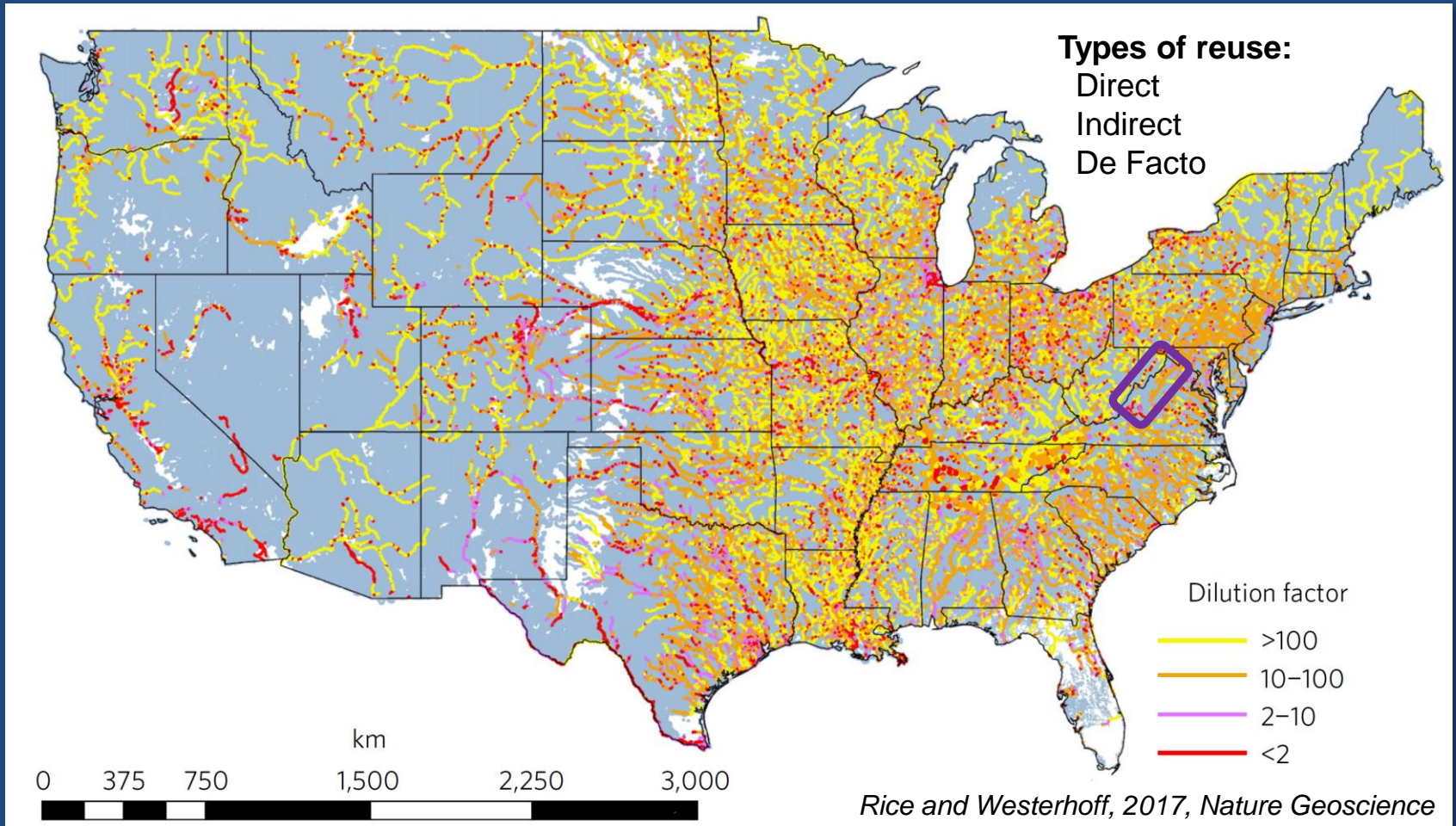
Integrated Assessment of Complex Chemical Mixtures and Potential Risk to Aquatic Organisms in the Shenandoah River Watershed

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

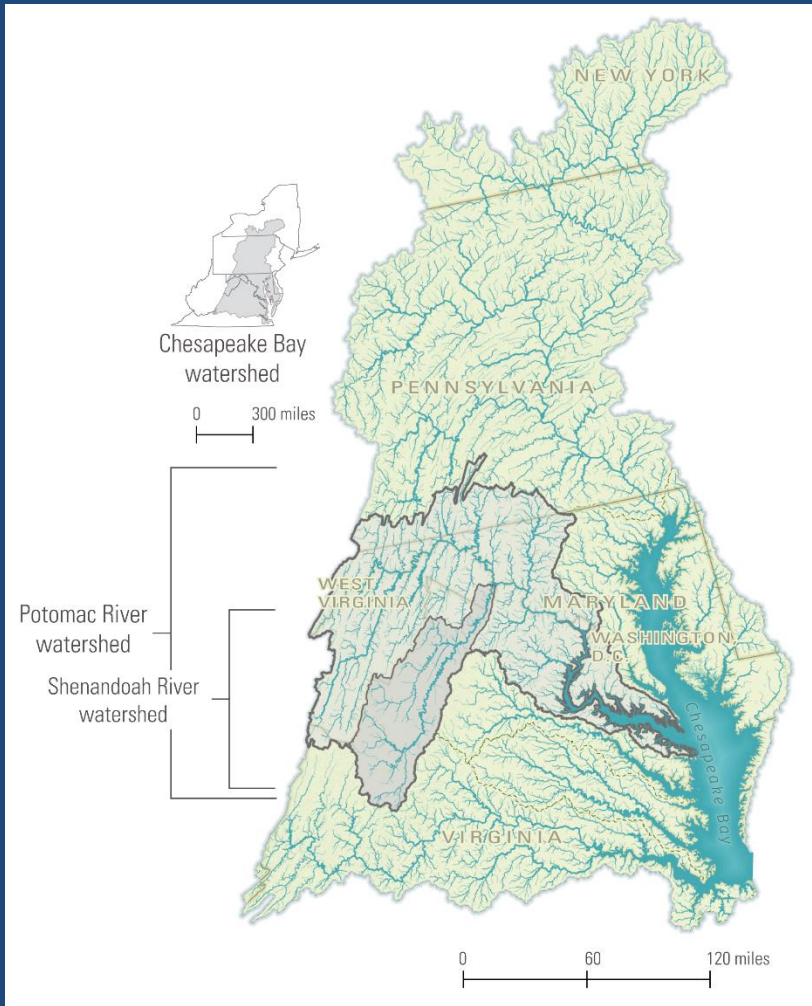
Chesapeake Bay Toxic Contaminants Workgroup, February 9, 2022

Wastewater Reuse is Critical Water Resource

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



Scaling of Hydrological/Contaminant Information



Watershed

River reach

Reach chemistry

Exposed population

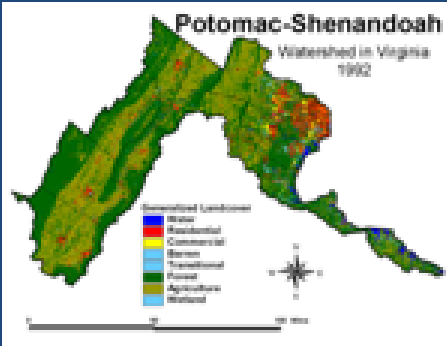
Organism effect

Molecular

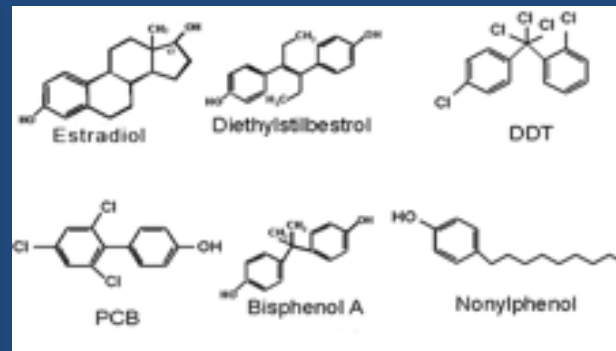
Scaling

Transdisciplinary
Science

Research Hypotheses



Landscape *predicts* Chemistry



Chemistry *predicts* Biology



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>]

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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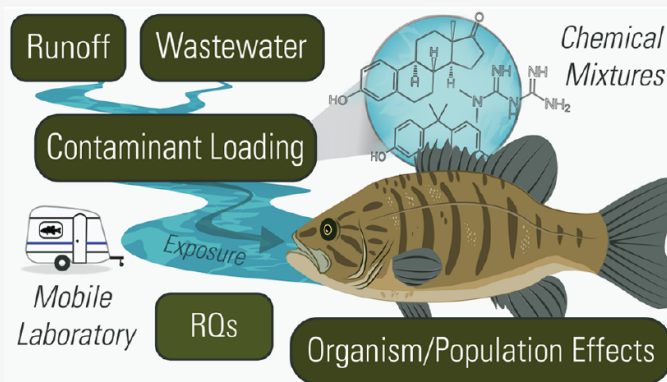


Supporting Information

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 from wastewater treatment plants (WWTPs) to assess potential aquatic organism exposure for all stream reaches in the watershed.

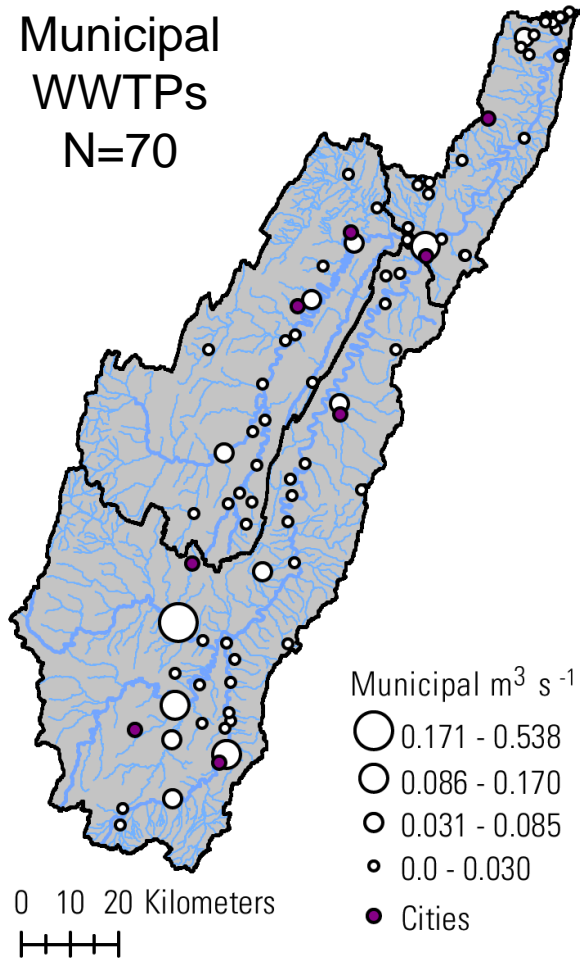
Measured and modeled concentrations generally were within a factor of 2. Ecotoxicological effects from exposure to individual components of the chemical mixture were evaluated using risk quotients (RQs) based on measured or predicted environmental concentrations and no effect concentrations or chronic 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

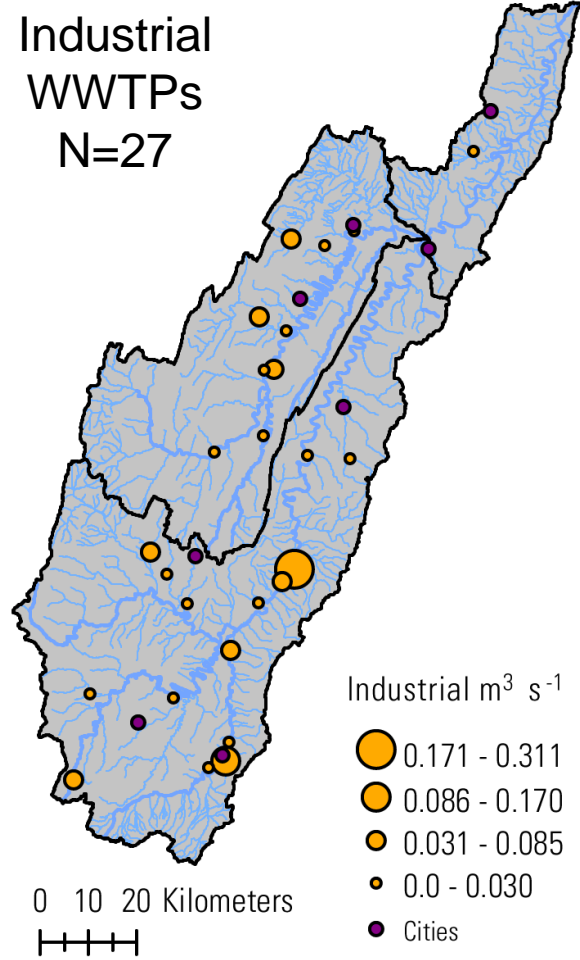


Municipal and Industrial Wastewater Reuse

Municipal
WWTPs
N=70



Industrial
WWTPs
N=27



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

Accumulated Wastewater Ratio (ACCWW%)

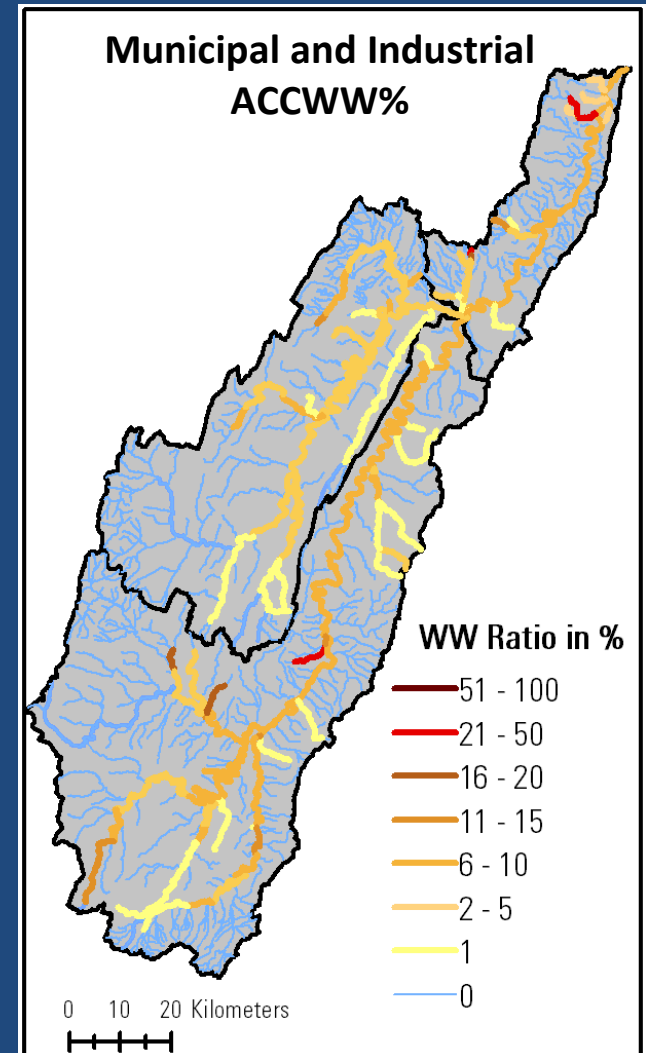
Combine
NHDPlus V2
streamflow and
ECHO WWTP
discharge

420 of 1,754 stream
segments have
WWTP influence

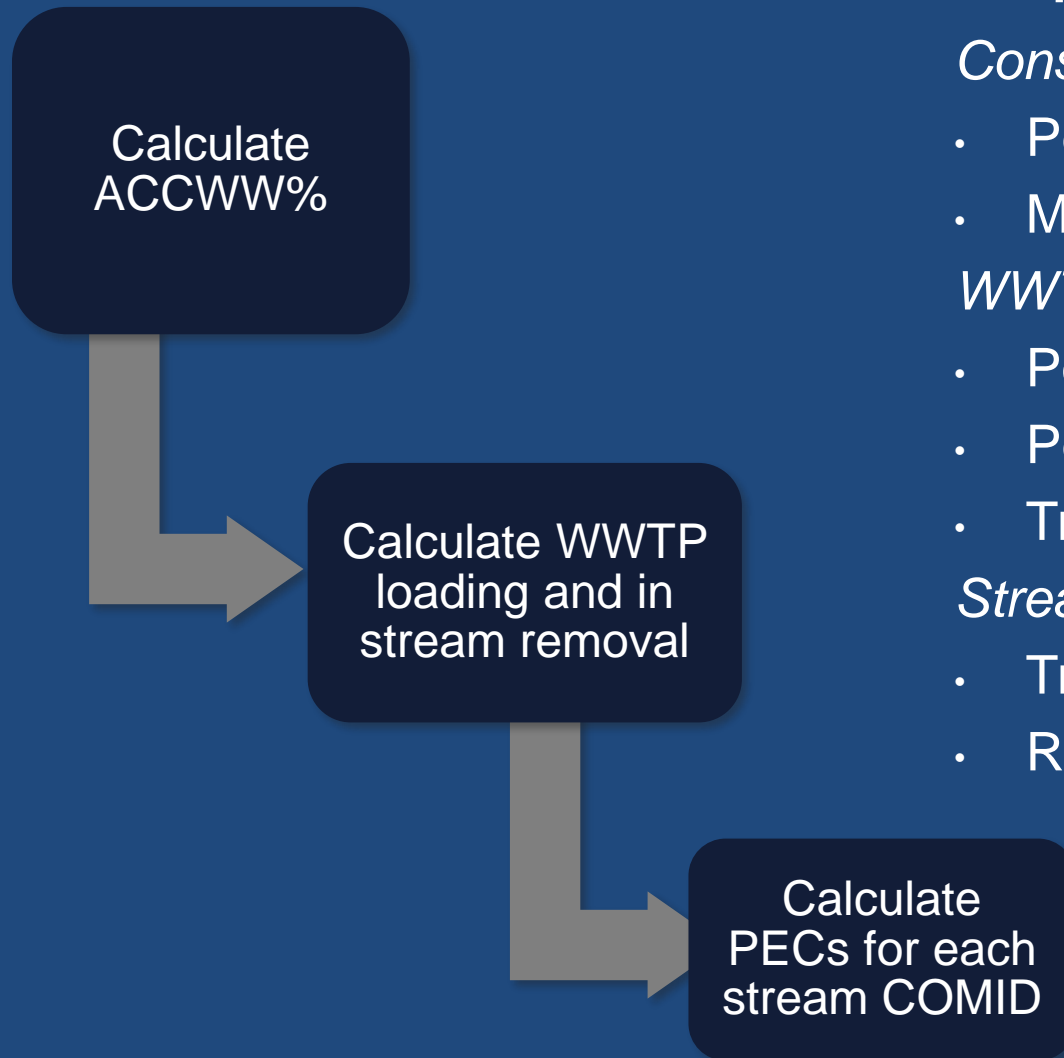
Incoming +
upstream WWTP
discharge

ACCWW% for
each stream
COMID

August flow conditions



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

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

$$RQ = PEC/PNEC_{eq}$$

Sum RQs to
provide
aggregated RI

Calculate RIs
for each stream
COMID

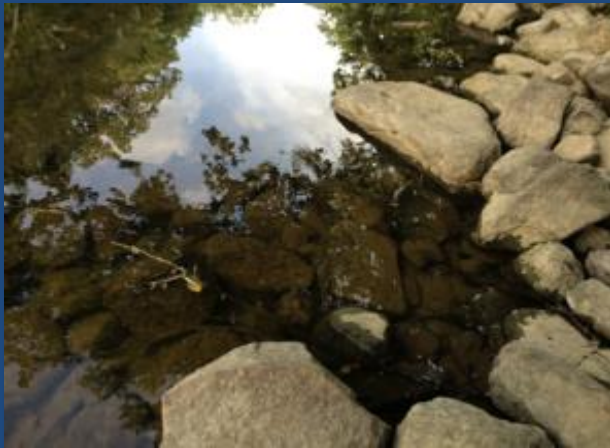
Challenges

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

Integrated Chemical and Biological Assessment

Chemical Profiling

Mobile Laboratory Exposures



Fathead minnow (*Pimephales promelas*)



H																		He																	
Hydrogen 1.00794																		Helium 4.002602																	
Li																		Be																	
Lithium 6.941																		Beryllium 9.012182																	
Na																		Mg																	
Sodium 22.98976928																		Magnesium 24.30469																	
K																		Ca																	
Potassium 39.0983																		Calcium 40.078																	
Rb																		Sr																	
Rubidium 85.4678																		Strontium 87.62																	
Y																		Zr																	
Yttrium 88.90584																		Zirconium 91.224																	
Nb																		Mo																	
Niobium 92.90638																		Molybdenum 95.94																	
Tc																		Ru																	
Technetium 98																		Ruthenium 101.07																	
Rh																		Pd																	
Rhodium 102.9055																		Palladium 106.3635																	
Ag																		Cd																	
Silver 107.8642																		Cadmium 112.411																	
In																		Sn																	
Indium 114.818																		Tin 118.710																	
Sb																		Te																	
Antimony 121.757																		Tellurium 127.6																	
I																		Xe																	
Iodine 126.90545																		Xenon 131.29																	
Cs																		Ba																	
Cesium 132.90545196																		Barium 137.327																	
La																		Ce																	
Lanthanum 138.90547																		Cerium 140.12																	
Pr																		Nd																	
Praseodymium 140.90766																		Neodymium 144.24																	
Pm																		Sm																	
Promethium 144.9127																		Samarium 150.36																	
Eu																		Gd																	
Europium 151.964																		Gadolinium 157.25																	
Tb																		Dy																	
Terbium 158.92535																		Dysprosium 162.5001																	
Ho																		Er																	
Holmium 164.93033																		Erbium 167.259																	
Tm																		Yb																	
Thulium 168.93032																		Ytterbium 173.054																	
Lu																		Hf																	
Lutetium 174.967																		Hafnium 178.49																	
Ta																		W																	
Tantalum 180.94788																		Tungsten 183.84																	
Re																		Os																	
Rhenium 186.207																		Osmium 190.23																	
Ir																		Pt																	
Iridium 192.222																		Platinum 195.083																	
Au																		Hg																	
Gold 196.966569																		Mercury 200.59																	
Tl																		Pb																	
Thallium 204.3833																		Lead 207.2																	
Bi																		Po																	
Bismuth 208.9804																		Polonium 209																	
At																		Rn																	
Astatine 210																		Radon 222																	
Fr																		Ra																	
Francium 223																		Radium 226																	
Ac																		Th																	
Actinium 227																		Thorium 232.0377																	
Pa																		U																	
Protactinium 231																		Uranium 238.02891																	
Np																		Pu																	
Neptunium 237																		Plutonium 244																	
Am																		Cm																	
Americium 243																		Curium 247																	
Bk																		Cf																	
Berkelium 247																		Californium 251																	
Es																		Fm																	
Einsteinium 252																		Fermium 257																	
Md																		No																	
Mendelevium 258																		Nobelium 259																	
Lr																		La																	
Lawrencium 261																		Lanthanum 138.90547																	
Ce																		Pr																	
Cerium 140.12																		Praseodymium 140.90766																	
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Radium 226																		Actinium 227																	
Th																		Pa																	
Thorium 232.0377																		Protactinium 231																	
U																		Np																	
Uranium 238.02891																		Neptunium 237																	
Pu																		Am																	
Plutonium 244																		Americium 243																	
Cm																		Bk																	
Curium 247																		Berkelium 247																	
Cf																		Es																	
Californium 251																		Einsteinium 252																	
Fm																		Md																	
Fermium 257																		Mendelevium 258																	
No																		Lr																	
Nobelium 259																		Lawrencium 261																	

Periodic Table of Elements, 2012

Alkali metals

Alkaline earth metals

Transition metals

Lanthanides

Actinides

Hydrogen

Helium

Lithium

Beryllium

Boron

Carbon

Nitrogen

Oxygen

Fluorine

Neon

Sodium

Magnesium

Aluminum

Silicon

Phosphorus

Sulfur

Chlorine

Argon

Potassium

Calcium

Scandium

Titanium

Vanadium

Chromium

Manganese

Iron

Cobalt

Nickel

Copper

Zinc

Gallium

Germanium

Antimony

Tellurium

Iodine

Xenon

Cesium

Barium

Lanthanum

Cerium

Praseodymium

Neodymium

Europium

Gadolinium

Terbium

Dysprosium

Ytterbium

Lutetium

Actinium

Thorium

Protactinium

Uranium

Neptunium

Plutonium

Americium

Curium

Berkelium

Californium

Einsteinium

Fermium

Mendelevium

Nobelium

Lanthanum

Cerium

Praseodymium

Neodymium

Europium

Gadolinium

Terbium

Dysprosium

Ytterbium

Lutetium

Comprehensive
Contemporaneous

- Photoperiod
- Aeration
- Temperature
- Diet
- 21-d exposure
- Continuous flow
- Weekly water/fish sampling
- Multiple biological endpoints

Wild Fish Assessment

Shenandoah River Watershed Research

Mobile Lab Fish Exposures

2014: 4 Sites

2015: 3 Sites

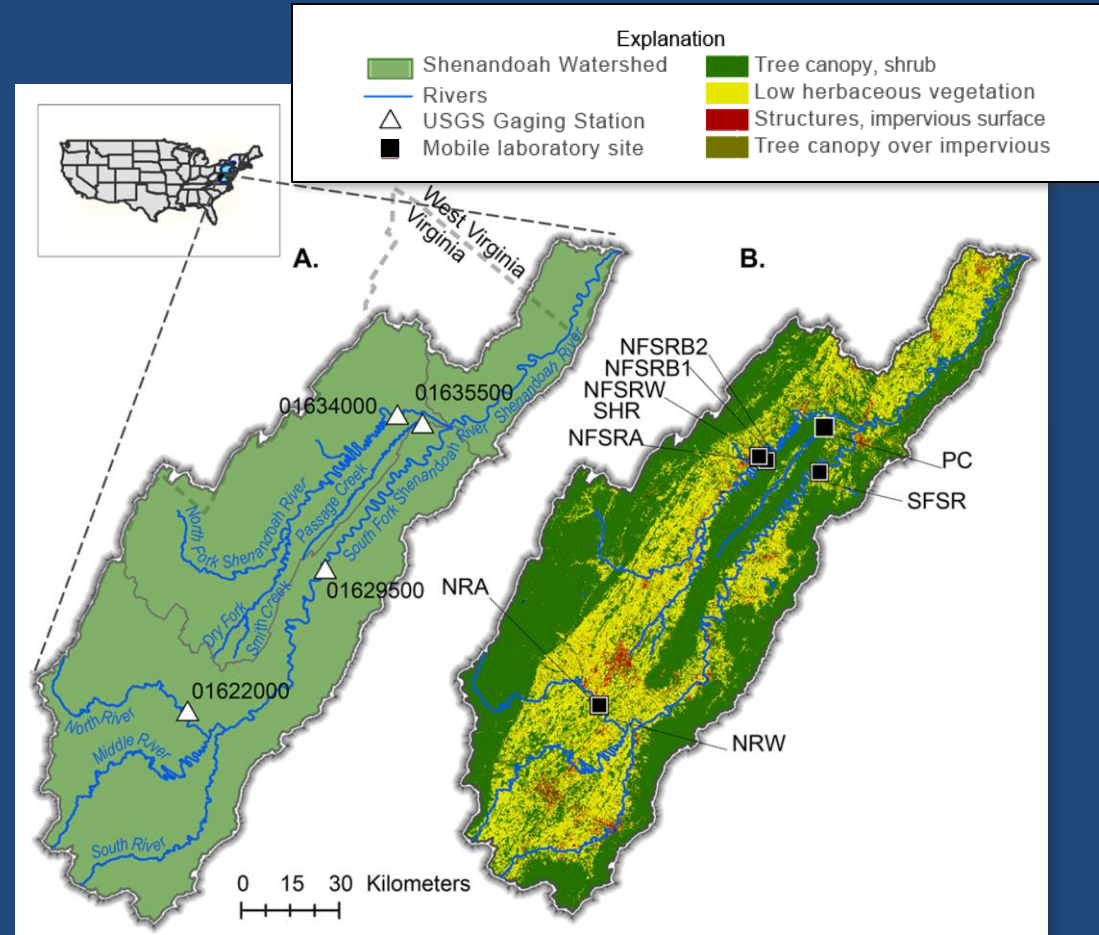
2016: 5 Sites

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

Complex Chemical Mixtures

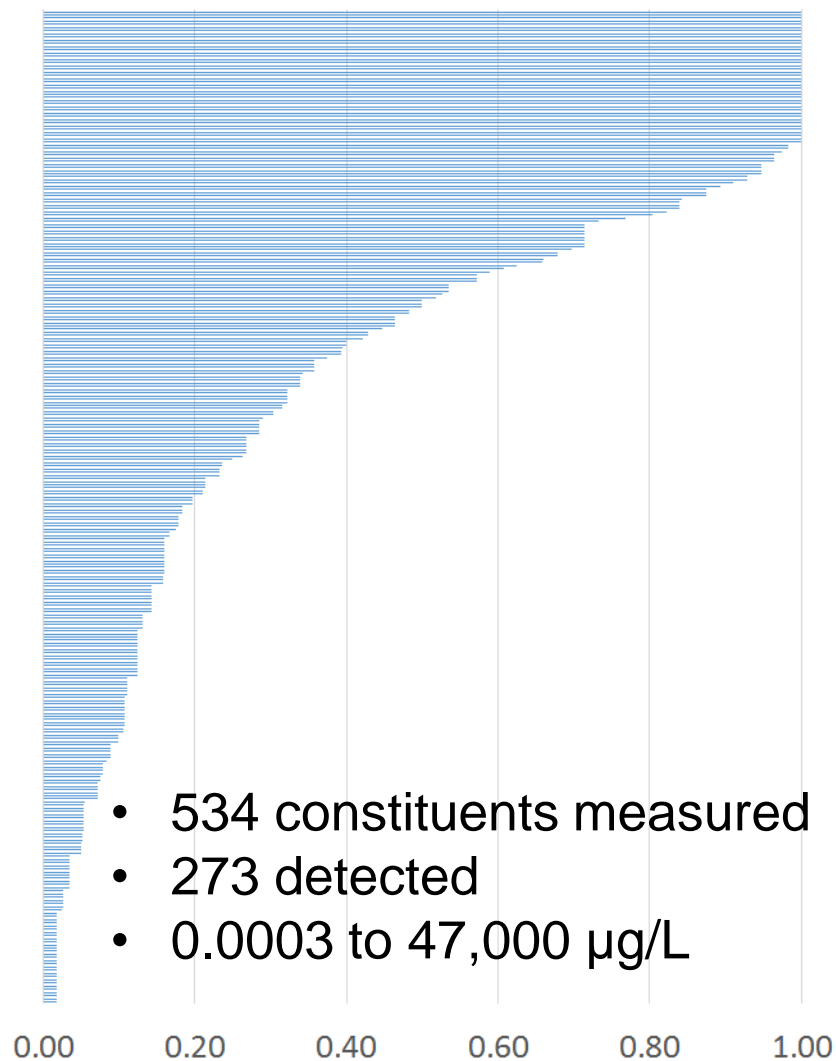
20 Methods in 6 laboratories

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

Biological Effects

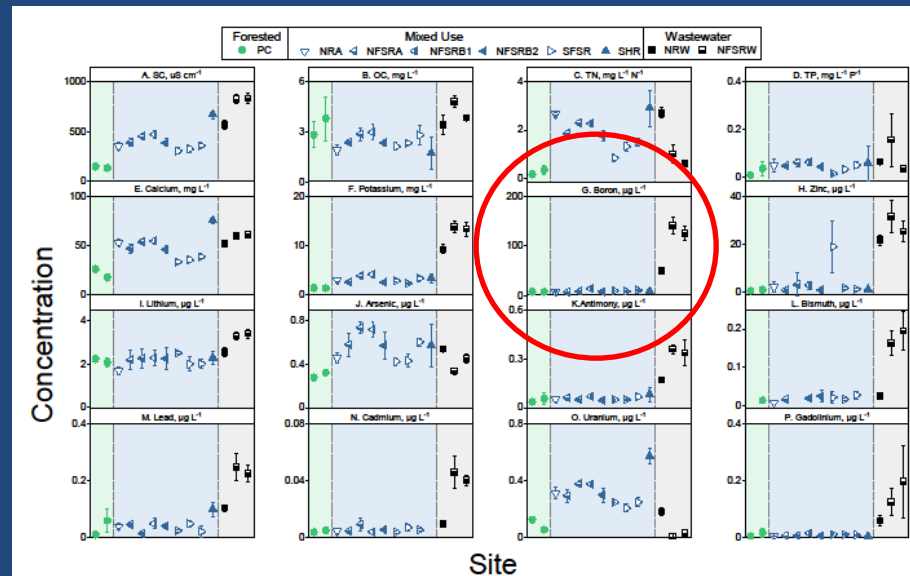
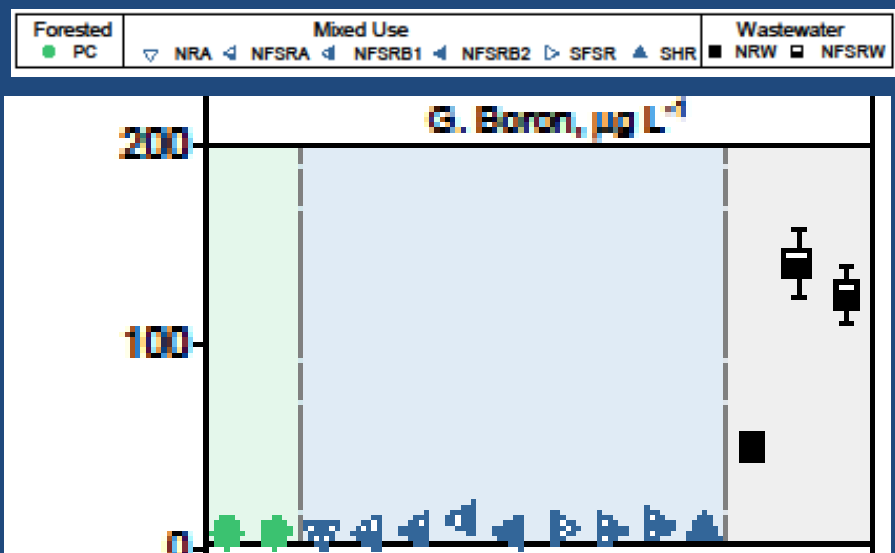
- Chemical structure
- Concentration
- Mode of action
- Exposure pathways
- Target organism

All detection frequency, fraction



Inorganic Contaminants

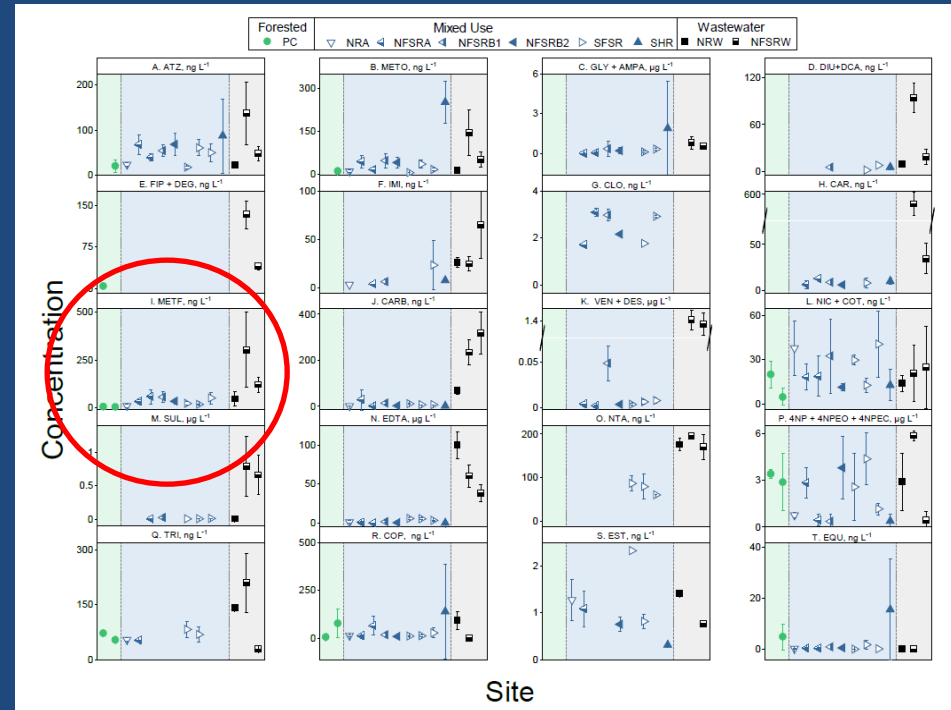
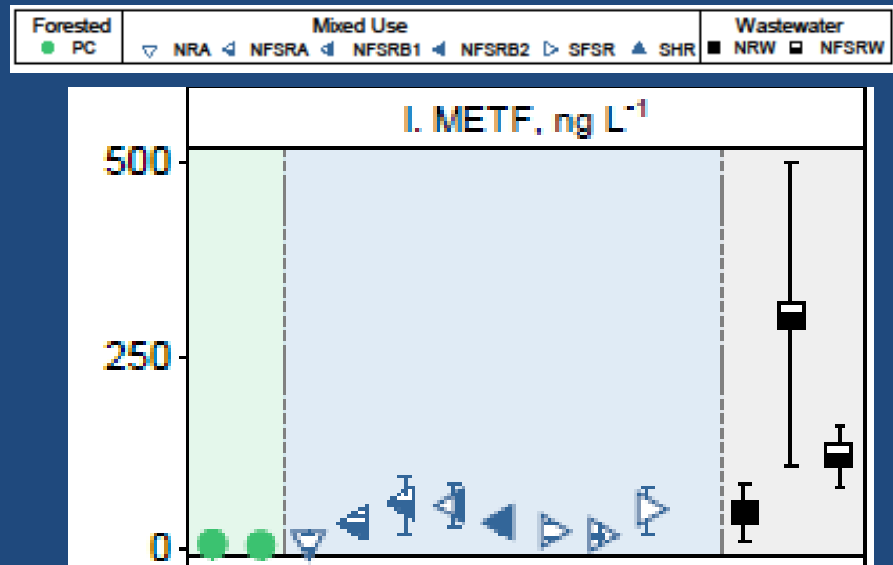
- >60 Nutrients and Elements
- Range of sources and behaviors
- Range of biological effects



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

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

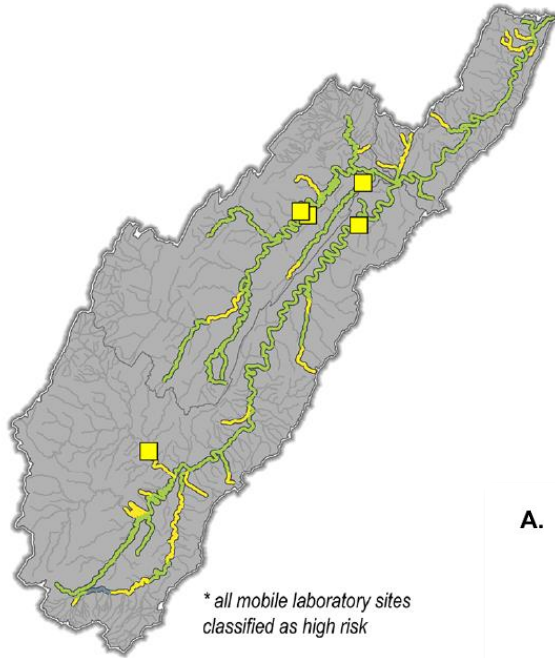
PNEC_{eq} Risk Quotient Ranking

Benzo[a]pyrene	--	--	50.0	--	--	--	207.6	94.7	--	>200
Fenpyroximate	86.6	--	--	--	24.5	--	--	--	91.3	175
Acetylhexamethyltetrahydronaphthalene	--	--	--	--	--	--	--	--	46.8	
Fipronil	4.3	--	--	--	--	--	--	--	49.4	150
17-alpha-Ethinylestradiol	--	--	24.3	--	--	--	--	--	--	
4-Nonylphenoldiethoxylate	15.5	--	15.9	17.2	16.8	15.4	3.4	3.4	16.7	125
Caffeine	8.9	35.2	13.8	33.4	--	7.1	30.6	32.4	17.0	
Nitrogen total	1.1	15.7	7.6	12.4	10.1	15.8	15.1	13.5	4.2	100
Diethylenetriaminepentaacetic acid	0.4	--	--	0.6	--	6.3	--	1.4	119.5	
Nitrite plus nitrate	0.5	11.0	4.2	7.5	6.1	9.9	10.0	8.3	0.8	
Nitrate	0.4	8.4	3.2	5.6	4.6	7.5	7.7	6.2	0.6	50
Phosphorus total	0.9	3.9	2.9	5.1	4.5	6.4	2.2	6.2	5.2	
Bisphenol A	3.9	3.2	4.5	--	--	8.4	--	--	--	
Azithromycin	--	--	--	--	--	1.9	--	--	32.8	25
Triclocarban	1.5	--	0.6	0.5	0.3	--	--	--	3.9	
Propiconazole	--	--	2.8	--	--	--	2.0	0.3	--	
Hexazinone	1.9	--	--	--	--	--	--	--	--	
Ciproflaxacin	--	--	--	--	--	--	--	0.1	1.9	
Imidacloprid	--	0.2	1.8	0.3	--	2.1	0.5	0.4	2.7	10
17-beta-Estradiol	--	--	1.2	--	--	--	--	--	--	
Fluoranthene	--	--	--	--	--	--	1.1	0.9	--	
Triclosan	0.6	0.5	0.7	0.5	--	1.3	--	--	1.4	
Copper	0.4	0.5	0.5	0.6	0.5	0.8	0.5	0.7	1.0	
Clothianidin	--	--	0.6	0.6	0.4	--	--	0.6	--	5
Benzophenone	--	--	--	--	--	--	--	--	0.5	
Fipronil desulfinyl	--	--	--	--	--	--	--	--	0.4	
Sertraline	--	--	--	0.9	--	--	--	--	0.2	
Citalopram	--	--	--	1.0	--	--	--	0.0	0.2	
Nickel	0.2	0.2	0.2	0.1	0.1	0.4	--	0.2	0.3	
Prometon	--	--	0.2	0.2	--	--	0.1	0.2	0.3	
Estrone	--	0.2	0.1	0.2	0.1	0.2	0.1	--	0.1	0
	PC Forested	NRA	NFSRA	NFSRB1	NFSRB2	SFSR	SHR	NRW	NFSRW	
				Mixed Use				Wastewater		

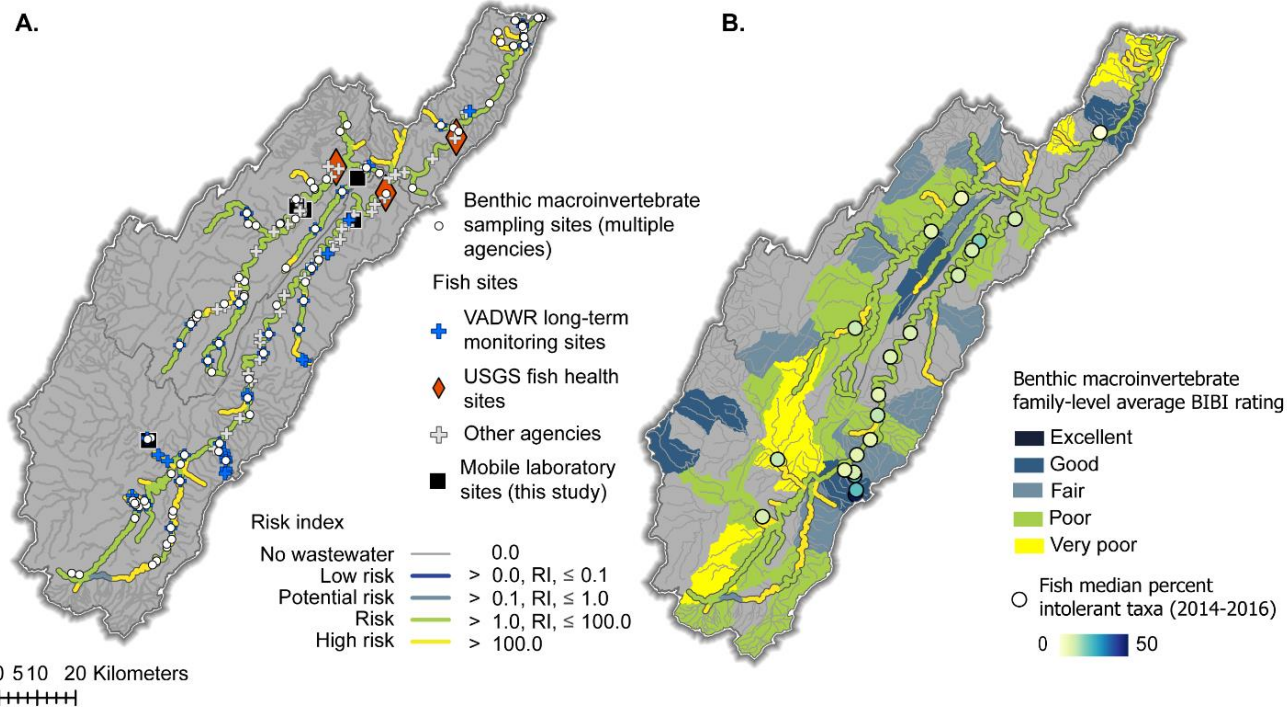
- Top 25th percentile includes nutrients, trace elements, and organic contaminants
- Similar RQ rankings across sites and landscape characteristics

WW Risk Index and Aquatic Community Health

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



No wastewater — 0.0
 Low risk — > 0.0, RI, ≤ 0.1
 Potential risk — > 0.1, RI, ≤ 1.0
 Risk — > 1.0, RI, ≤ 100.0
 High risk — > 100.0

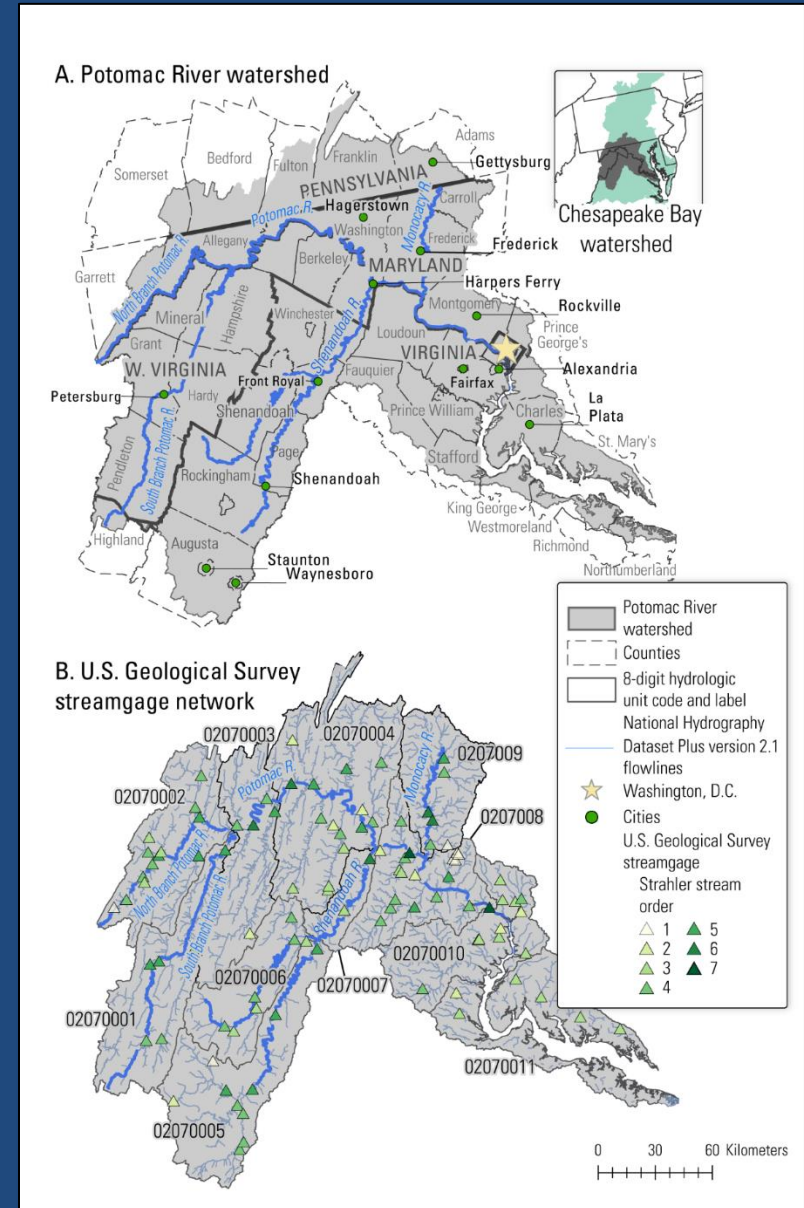


Landscape *predicts* Chemistry *predicts* Biology

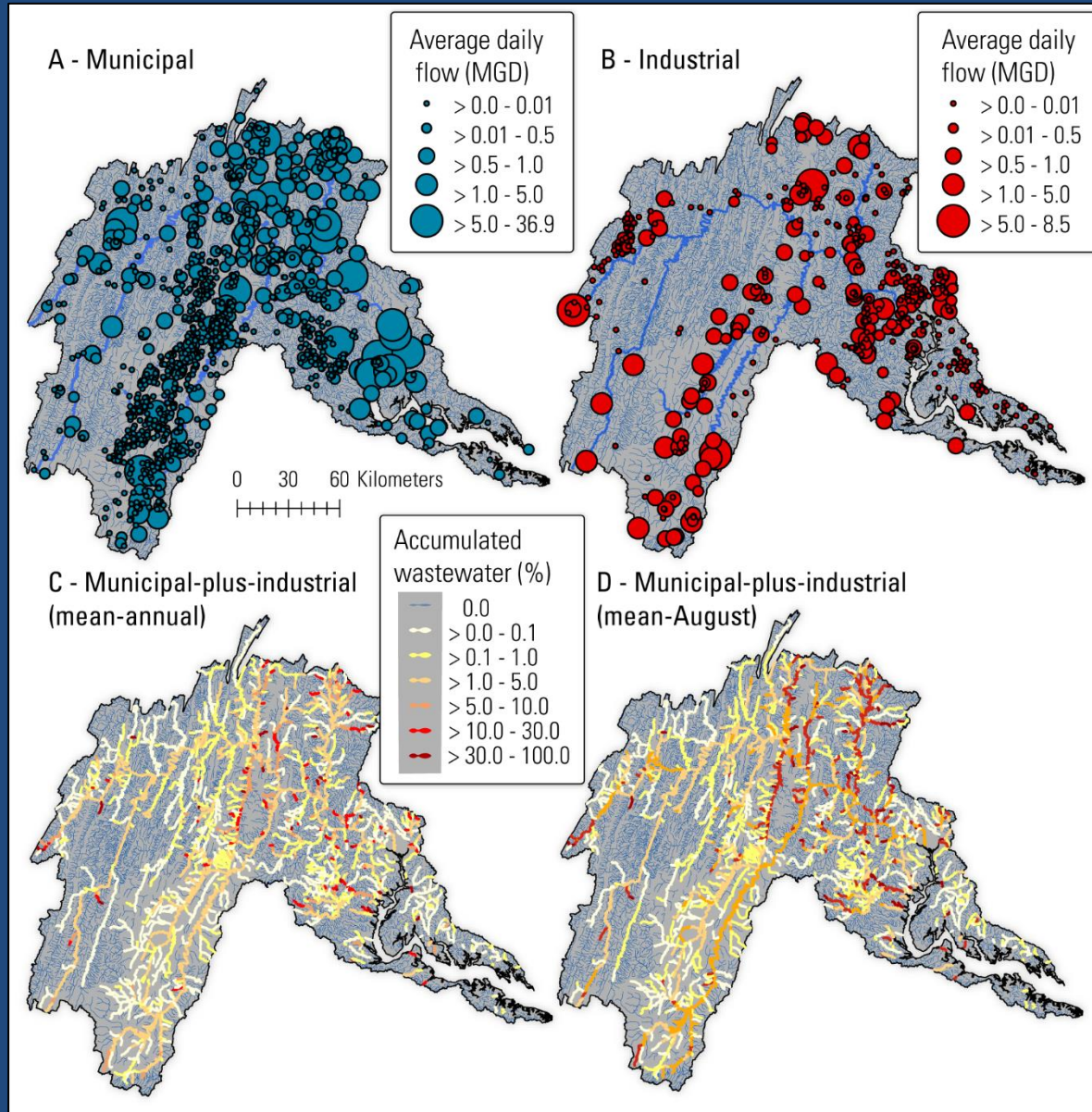
- Widespread occurrence of complex chemical mixtures related to multiple sources and landscape activities
- MECs in WWTP effluents and streams generally below $PNEC_{eq}$
- Fathead minnow exposures indicate physiological, histological, transcriptomic, and metabolomic effects consistent with exposure 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

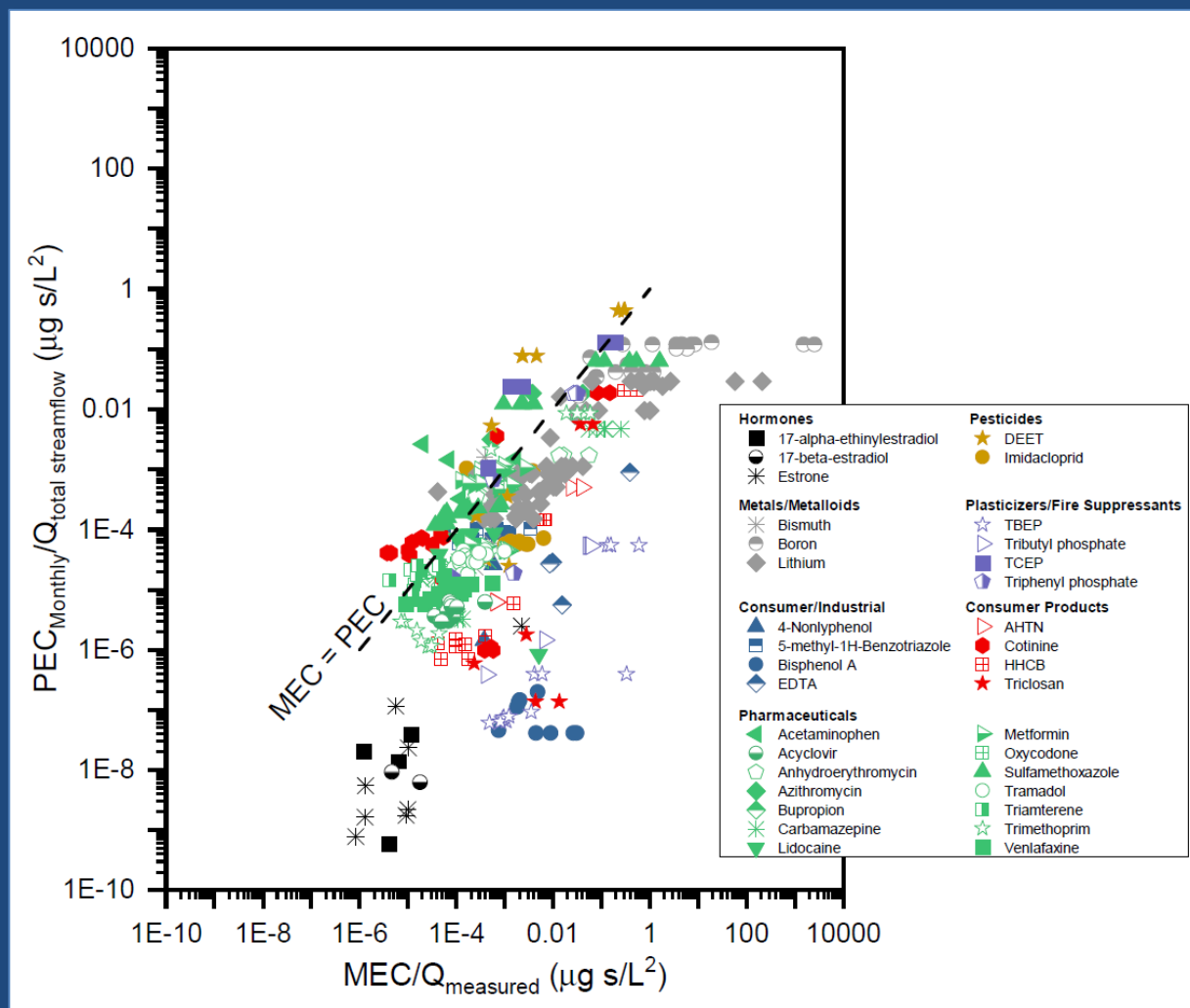


Expanding Coverage and Capabilities

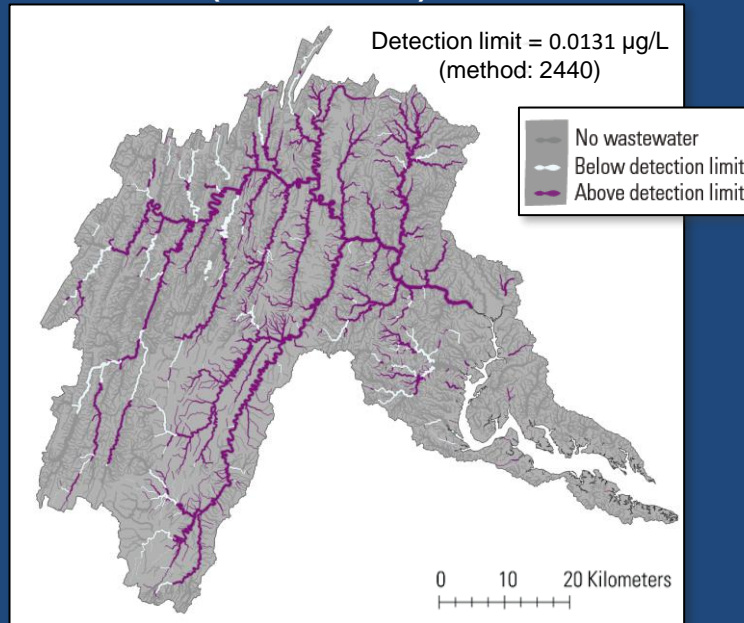


Validation and Verification

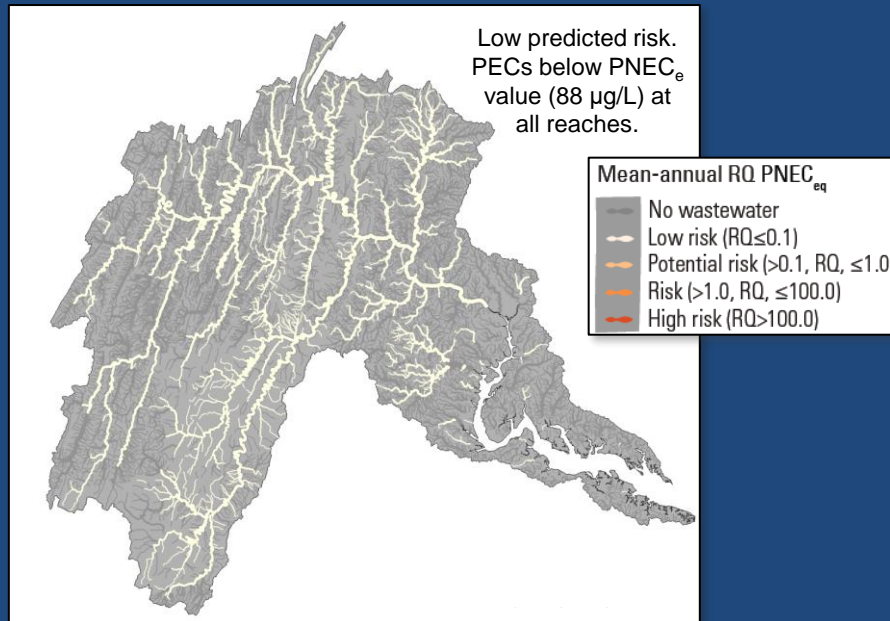
- Stream sampling validation of model predictions planned for summer 2022
- Predictions compared to measured environmental concentrations compiled from the USEPA Water Quality Portal and ScienceBase data releases allow evaluation of general patterns
- Modeling and evaluation of industrial discharged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



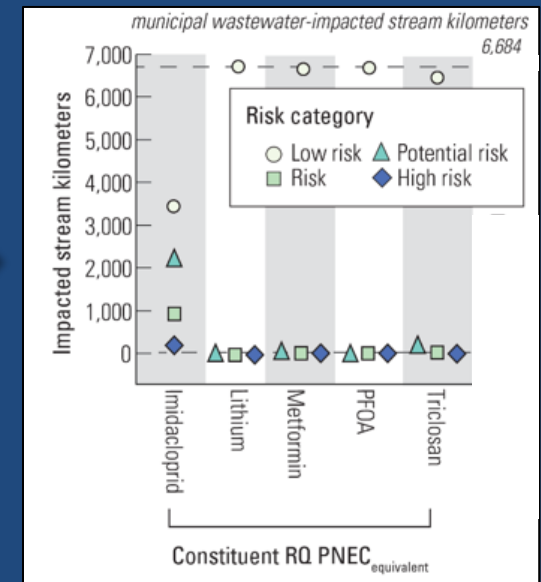
Metformin PECs (mean-annual)



Metformin risk quotients (mean-annual)



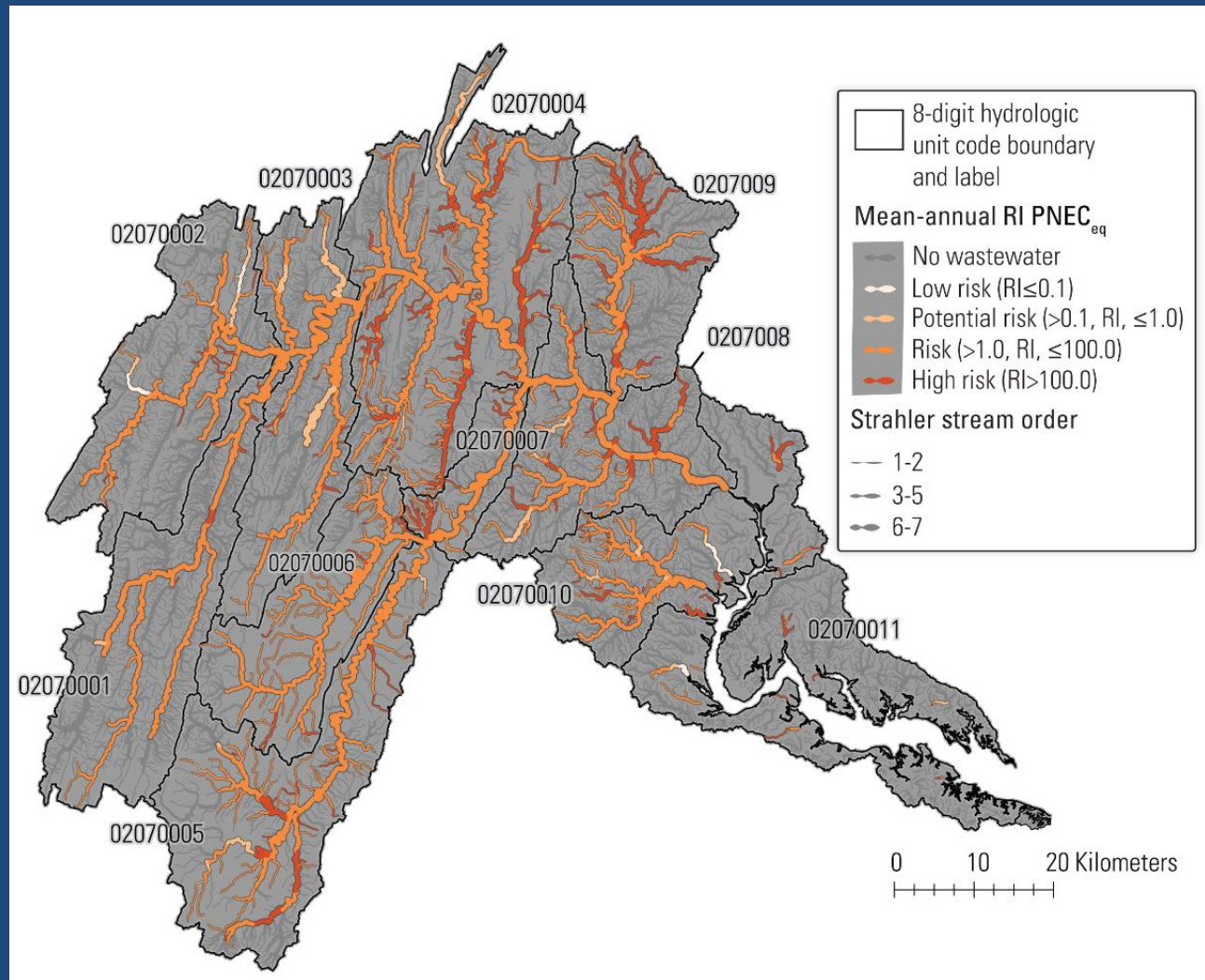
Potential risk posed
varies by individual
contaminant.



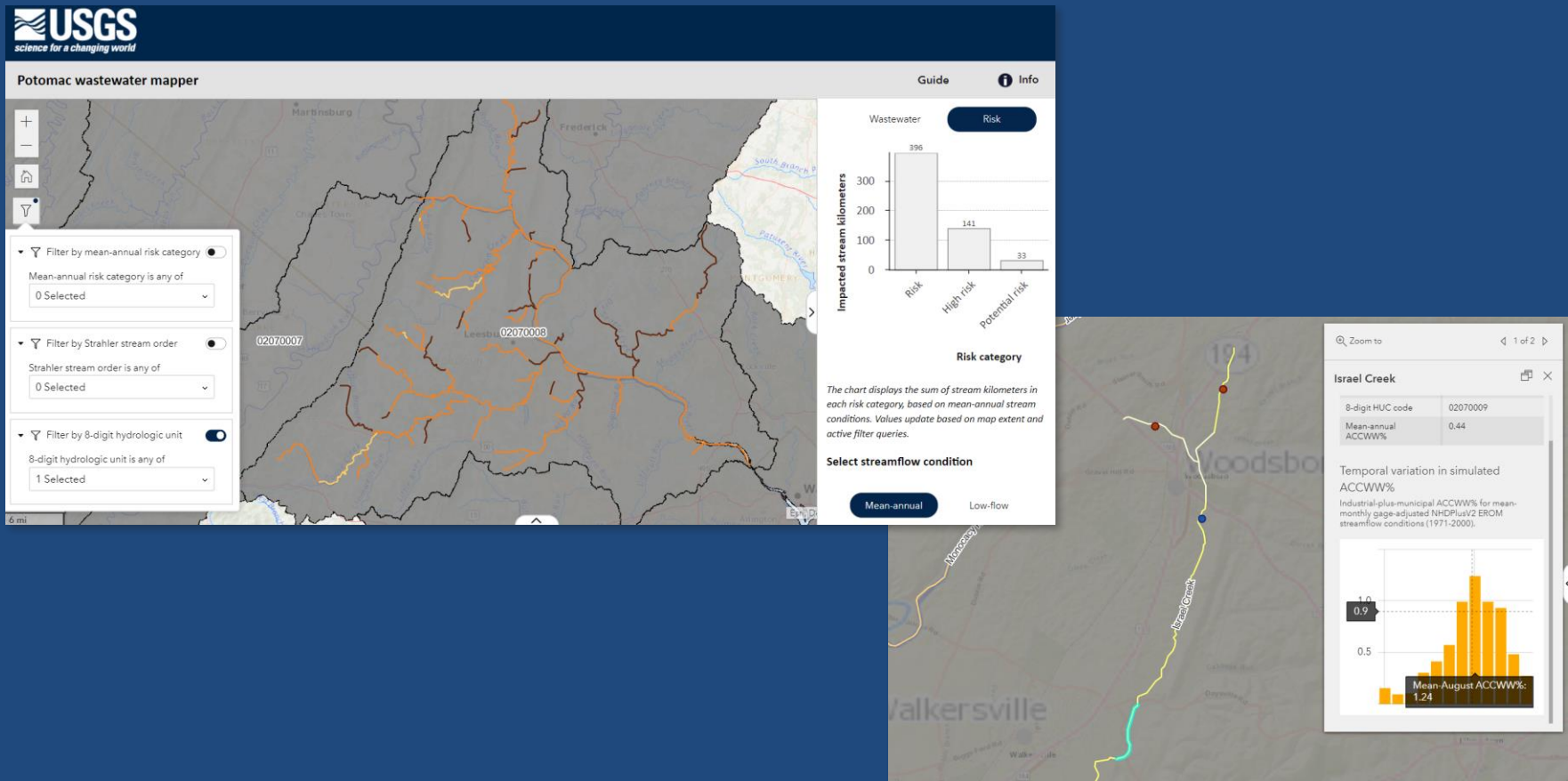
Ecological Risk From Contaminant Mixtures

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.

A photograph of a river flowing through a dense forest. The water is dark and turbulent, with white foam from rapids visible. Large, dark rocks are scattered throughout the riverbed and along the banks. The surrounding trees are lush green, and the sky is overcast and grey. The overall scene is a natural, somewhat somber landscape.

Thank you

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