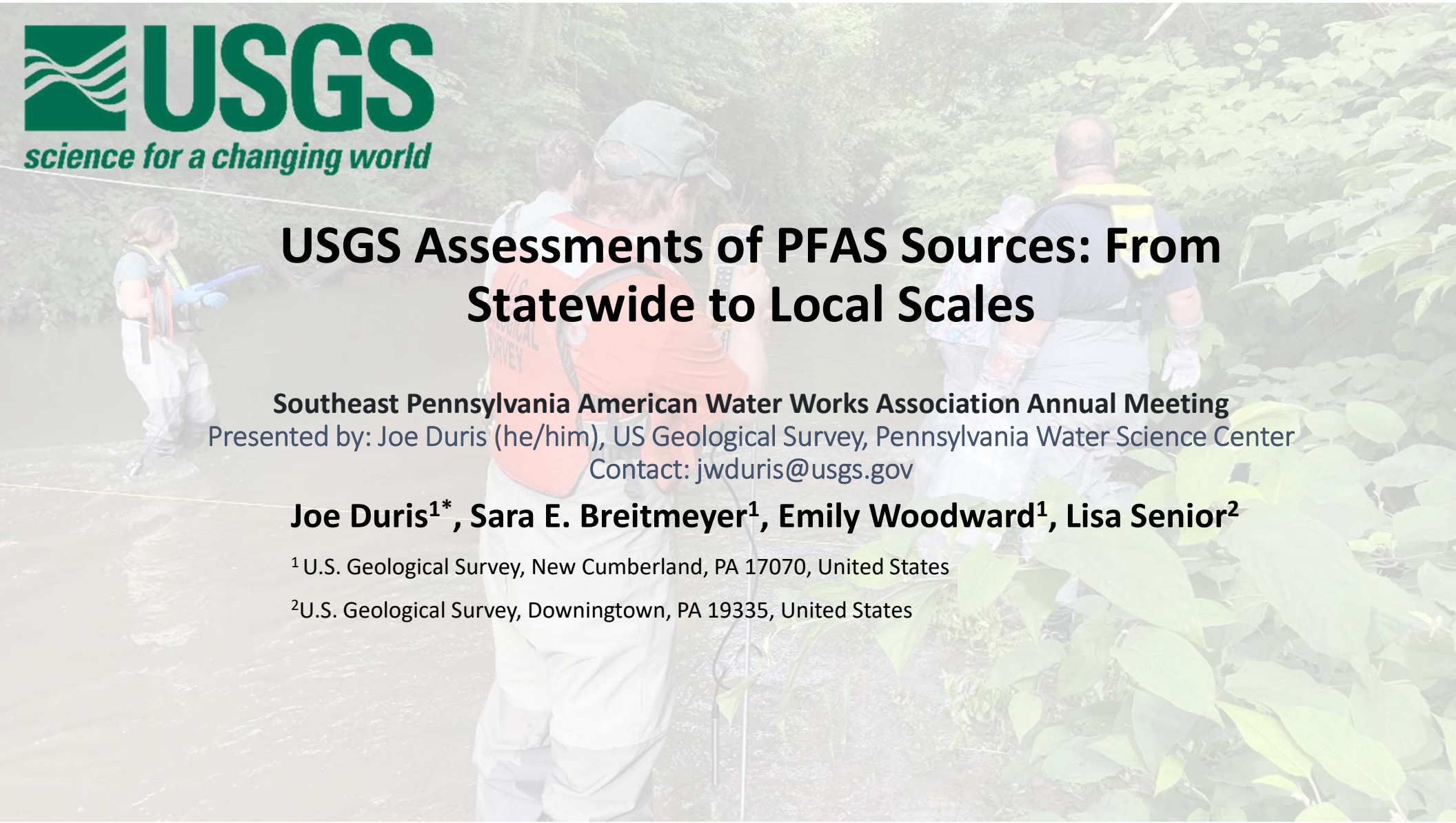


USGS Assessments of PFAS Sources: From Statewide to Local Scales

Southeast Pennsylvania American Water Works Association Annual Meeting

Presented by: Joe Duris (he/him), US Geological Survey, Pennsylvania Water Science Center
Contact: jwduris@usgs.gov

Joe Duris[1*], Sara E. Breitmeyer[1], Emily Woodward[1], Lisa Senior[2]

[1] U.S. Geological Survey, New Cumberland, PA 17070, United States

[2]U.S. Geological Survey, Downingtown, PA 19335, United States

Contributors and Co-authors

PA-DEP Bureau of Clean Water

- Dustin Schull
- Amy Williams
- Tim Wertz
- Staff from regional offices

USGS Pennsylvania Water Science Center

- Lee Eicholtz
- Staff from all 4 field offices

Staff from SRBC

USGS Water Resources Mission Area

- Jacob A. Fleck, Larry B. Barber, Angela M. Hansen

Background

Per and Polyfluoroalkyl substances

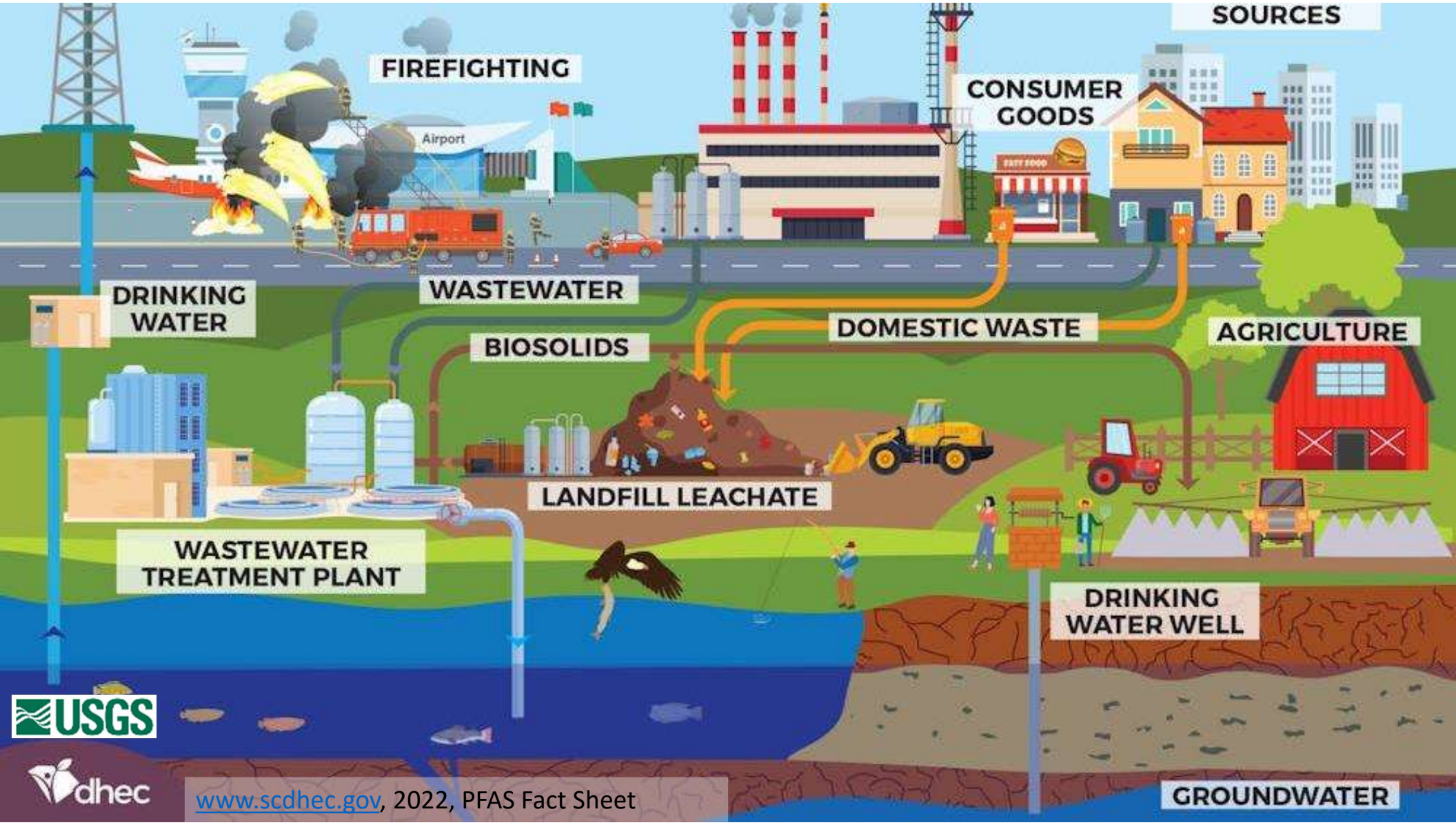
- >4000 different PFAS compounds
- PFAS (the whole group of chemicals)
- Entirely man-made

Common element they are saturated with fluorine

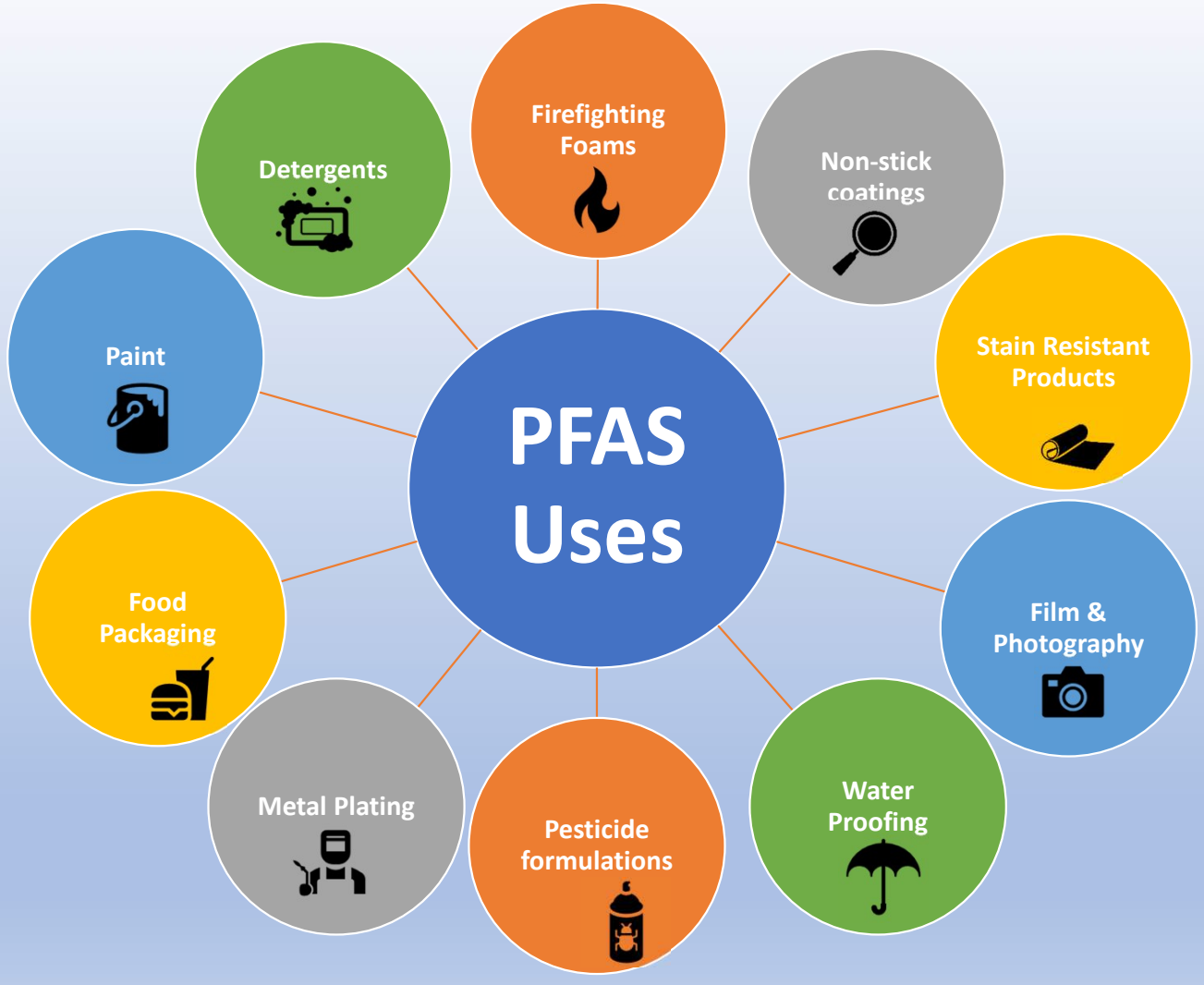
- carboxylic acids (PFOA)
- sulfonic acids (PFOS)
- at least 5 other analytical groupings

Often referred to by length of fluorine saturated carbon chain

- eg. Perfluorooctanoic acid is 8 carbons or “C8”
- We typically measure from C4 to C14



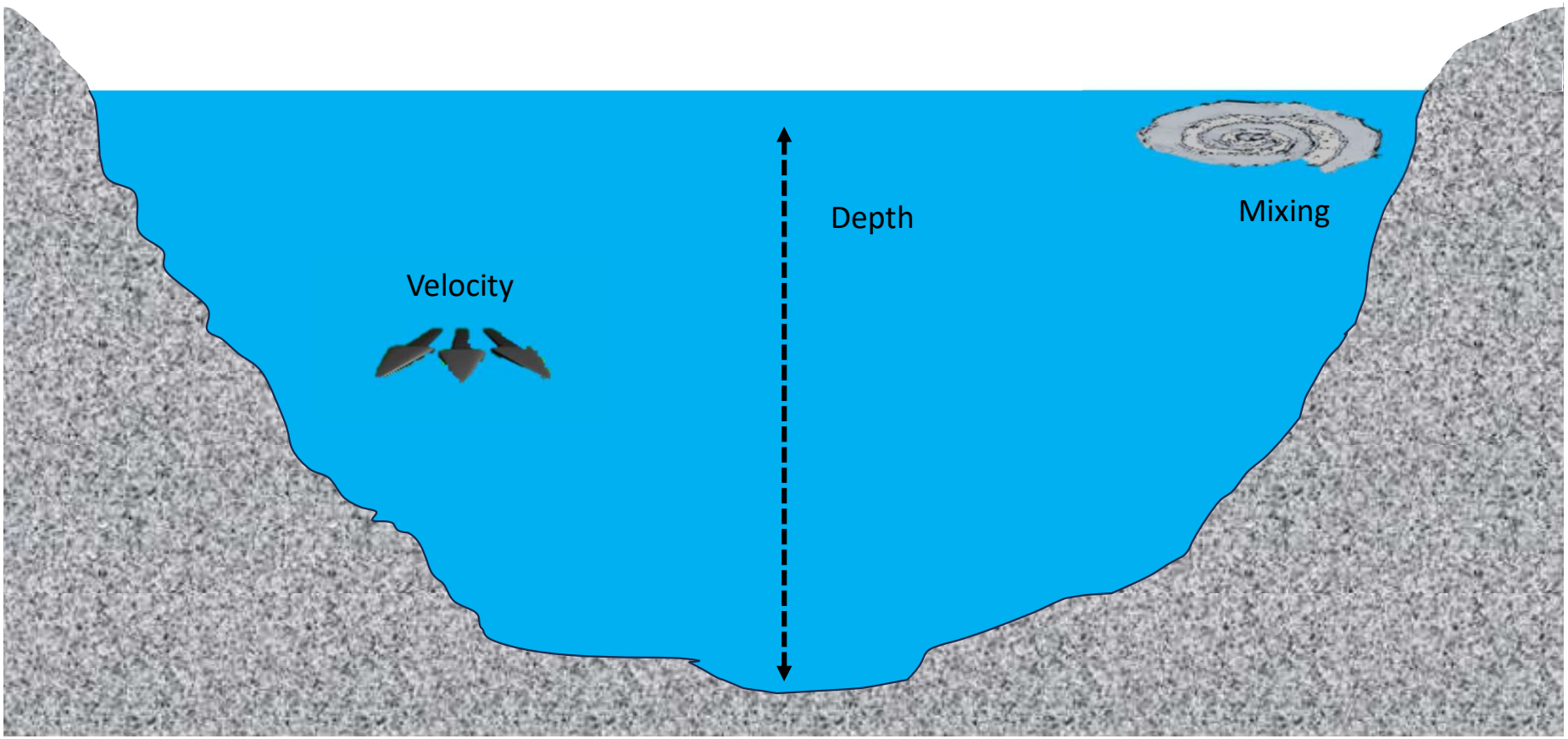
www.scdhec.gov, 2022, PFAS Fact Sheet



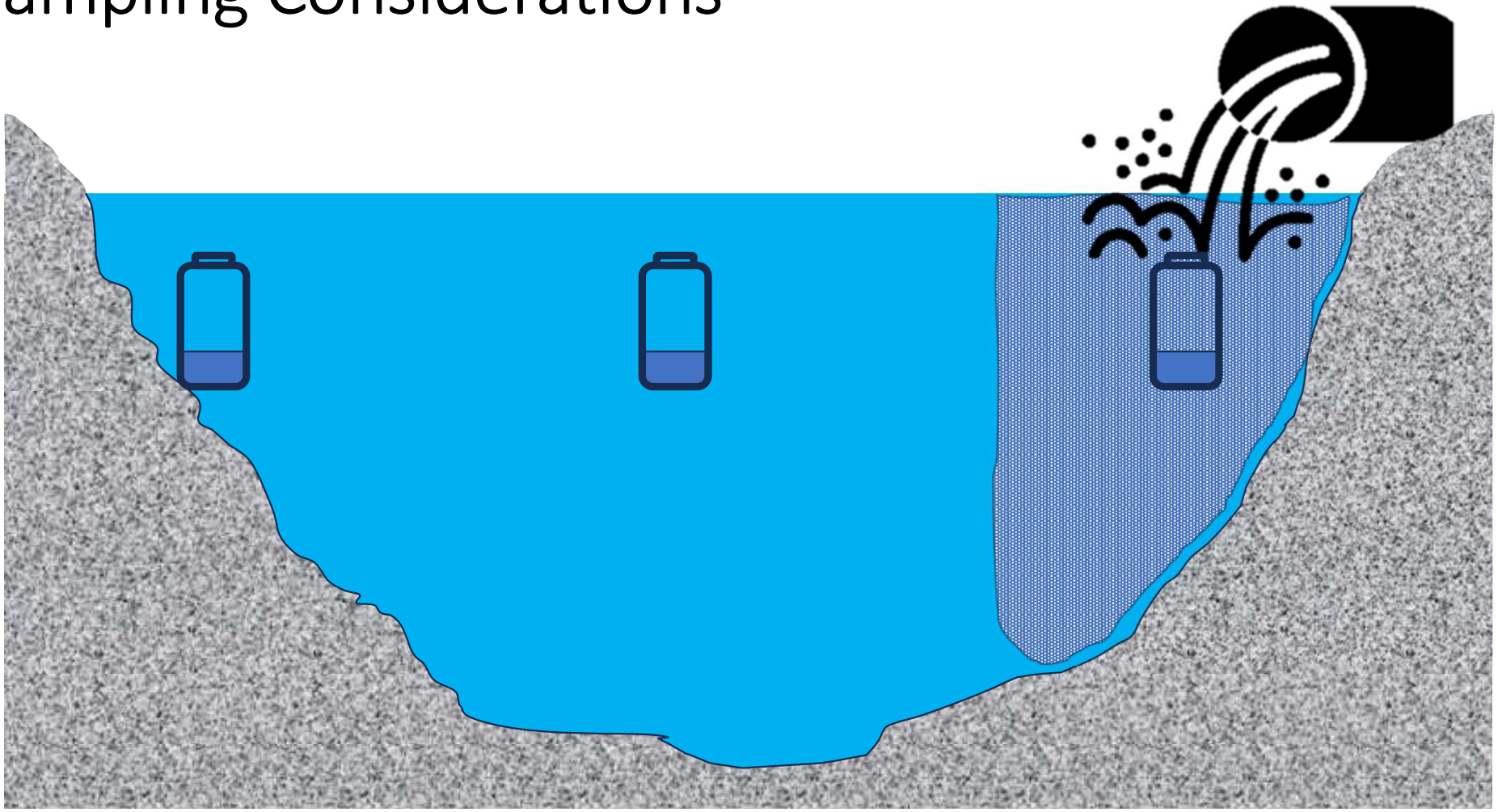
Sampling follows study goals

- **If your goal is broad reconnaissance or trends**
  - **Hand-dip sampling**
  - **Consider mixing, locations, and timing carefully**
- **If you're thinking about mass, loads, or sources**
  - **Representative sampling of flowing water**
  - **Depth/width integration**
  - **Timing of samples with respect to relevant sources**
- **If you're thinking about exposure of aquatic organisms**
  - **Dip/grab samples or collection of aquatic organisms**
  - **Near surface vs below surface**
  - **Serum vs tissue (exposure of organism vs exposure of consumers)**
  - **Sediment**
  - **Surface Foams**
- **Overarching**
  - **What materials are you using to collect your sample?**

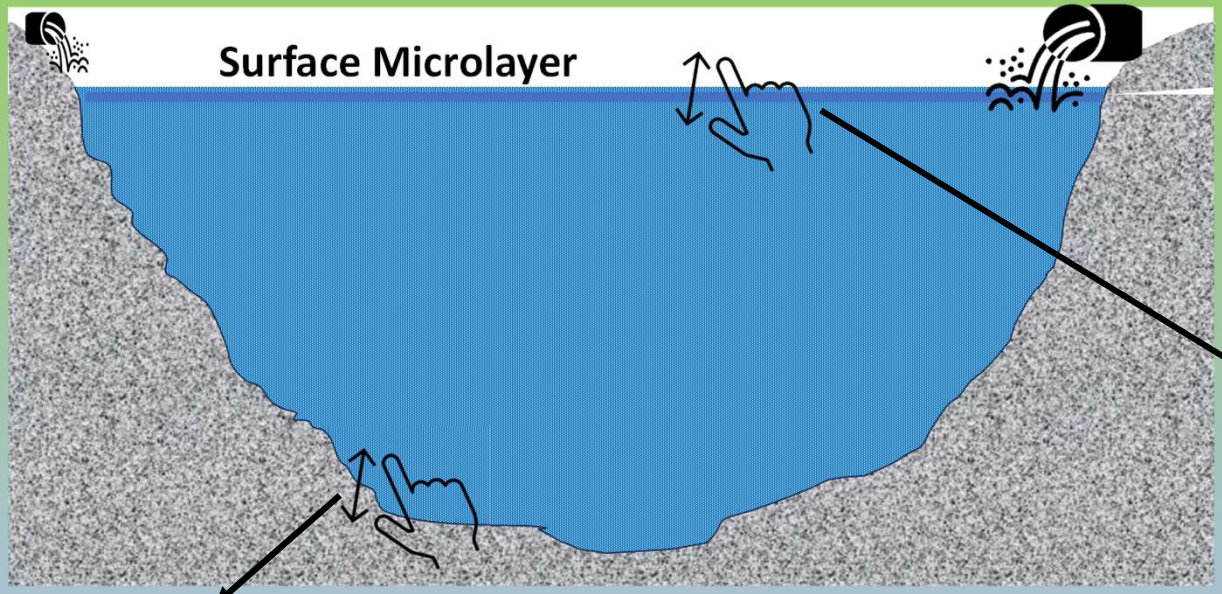
Sampling Considerations



Sampling Considerations

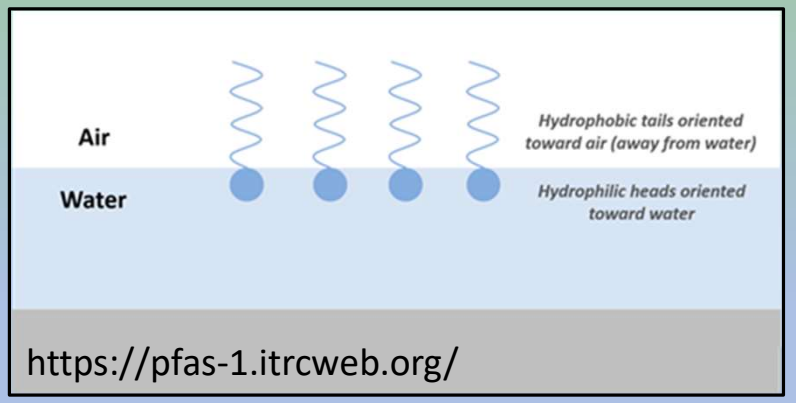


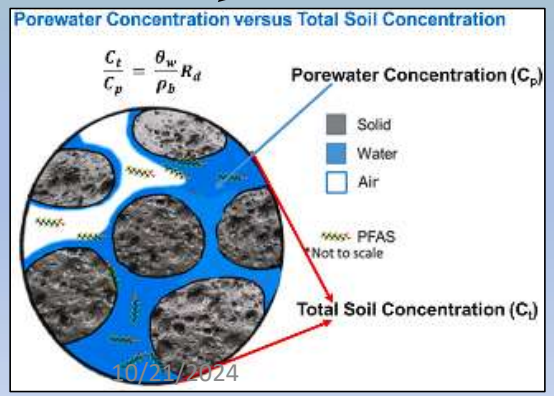
Sampling Considerations



Surface Microlayer can have as much as **18x concentration** as the bulk water.

Schaefer et al., 2022.
10.1016/j.jhazmat.2022.129782

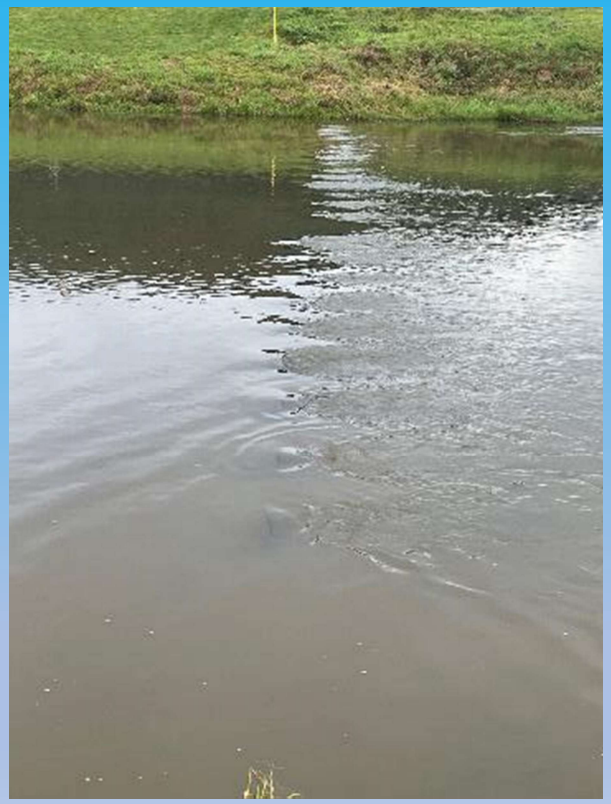




Bulk sediment can have between **1-100x concentration** as the soil/sediment pore water. Increases with chain length.

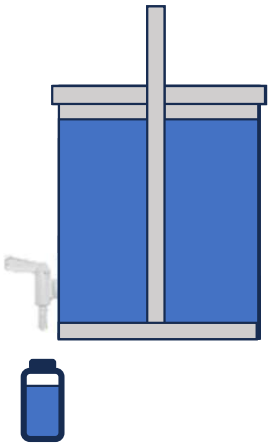
Brusseau and Guo, 2022
10.1016/j.chemosphere.2022.134938

Timing?



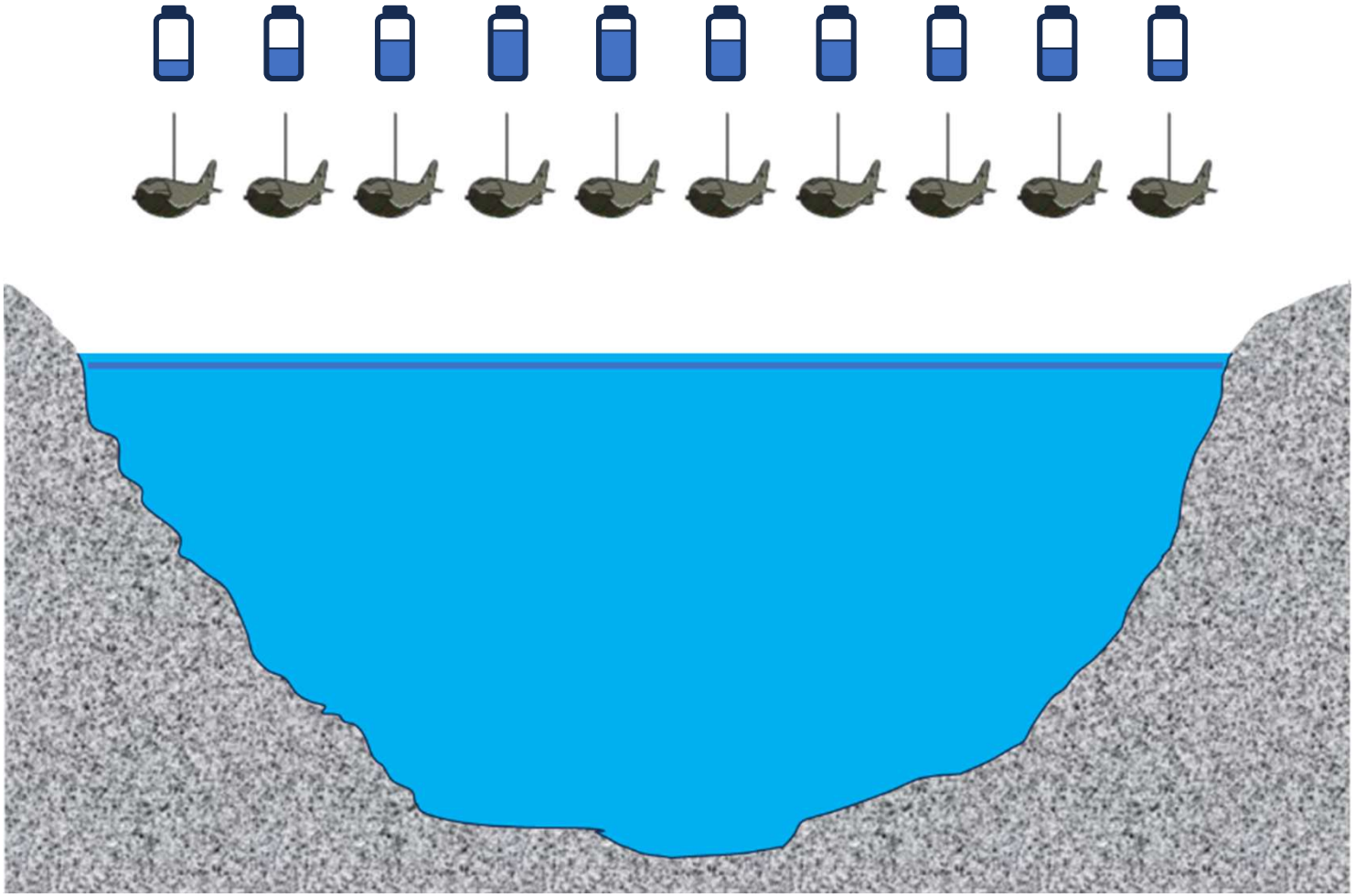
+ 30 minutes =

USGS Integrated sampling



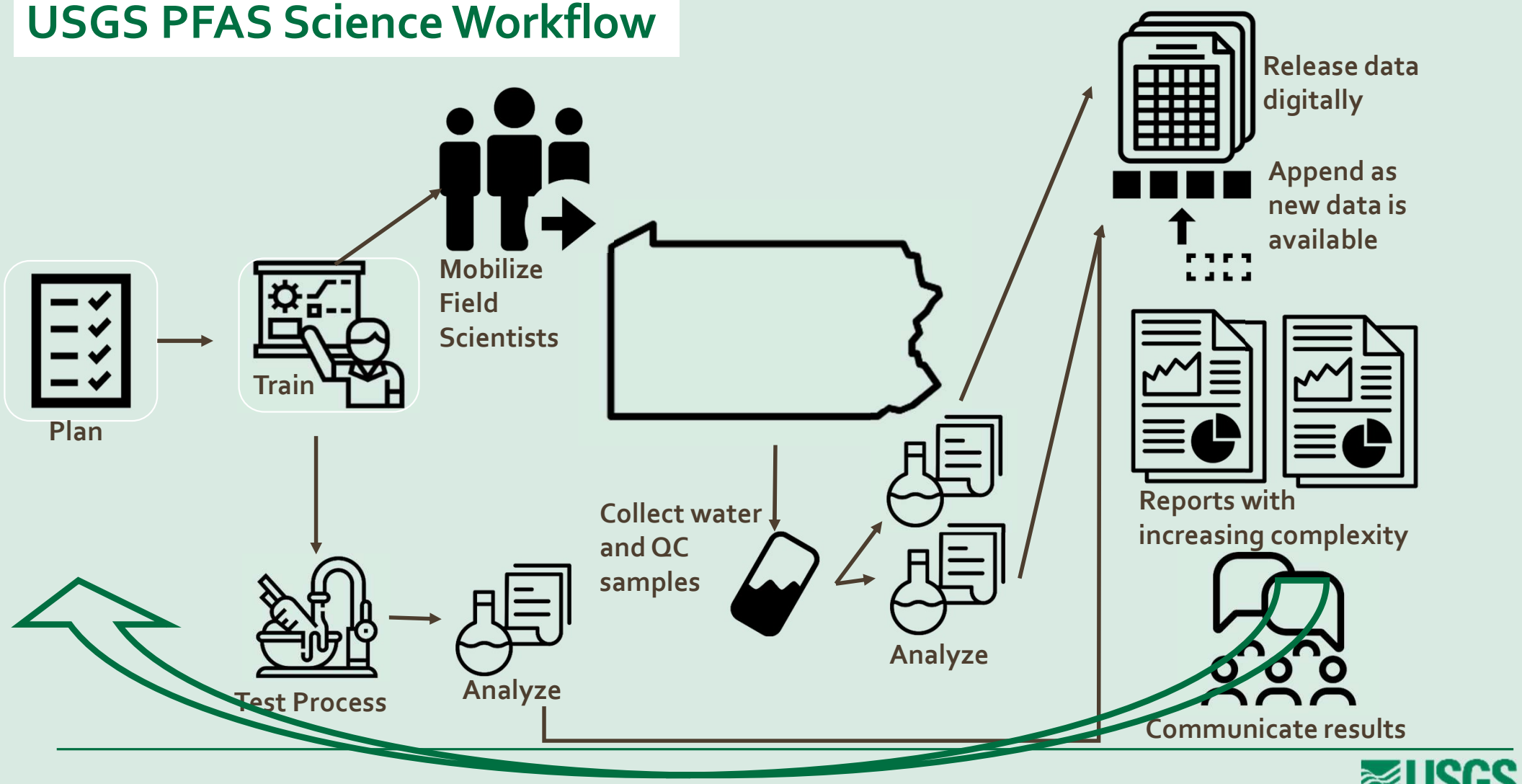
Mix composite sample

Fill analytical bottle



Goal is to represent the water flowing in the entire channel. Top to bottom. Bank to bank.

USGS PFAS Science Workflow



USGS science for a changing world

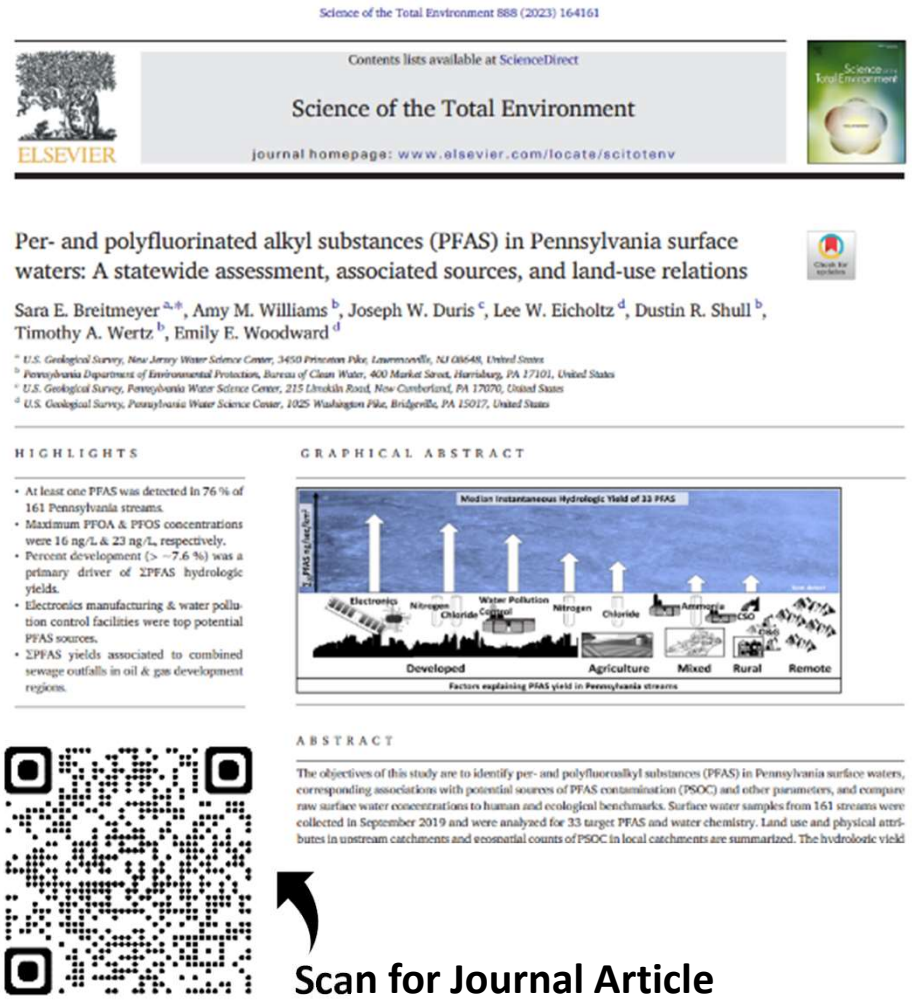
Per- & polyfluorinated alkyl substances (PFAS) in Pennsylvania surface waters: A statewide assessment & associated sources

Sara E. Breitmeyer, Amy M. Williams, Joseph W. Duris, Lee W. Eicholtz, Dustin R. Shull, Timothy A. Wertz, Emily E. Woodward

U.S. Geological Survey & Pennsylvania Department of Environmental Protection (PADEP)

pennsylvania
DEPARTMENT OF ENVIRONMENTAL PROTECTION

USGS



Science of the Total Environment 888 (2023) 164161

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journal homepage: www.elsevier.com/locate/scitotenv

Per- and polyfluorinated alkyl substances (PFAS) in Pennsylvania surface waters: A statewide assessment, associated sources, and land-use relations

Sara E. Breitmeyer [a,*], Amy M. Williams [b], Joseph W. Duris [c], Lee W. Eicholtz [d], Dustin R. Shull [b], Timothy A. Wertz [b], Emily E. Woodward [d]

[a] U.S. Geological Survey, New Jersey Water Science Center, 3450 Princeton Pike, Lawrenceville, NJ 08648, United States
[b] Pennsylvania Department of Environmental Protection, Bureau of Clean Water, 400 Market Street, Harrisburg, PA 17101, United States
[c] U.S. Geological Survey, Pennsylvania Water Science Center, 215 Limekiln Road, New Cumberland, PA 17070, United States
[d] U.S. Geological Survey, Pennsylvania Water Science Center, 1025 Washington Pike, Bridgeville, PA 15017, United States

HIGHLIGHTS

- At least one PFAS was detected in 76 % of 161 Pennsylvania streams.
- Maximum PFOA & PFOS concentrations were 16 ng/L & 23 ng/L, respectively.
- Percent development (> −7.6 %) was a primary driver of ΣPFAS hydrologic yields.
- Electronics manufacturing & water pollution control facilities were top potential PFAS sources.
- ΣPFAS yields associated to combined sewage outfalls in oil & gas development regions.

GRAPHICAL ABSTRACT

ABSTRACT

The objectives of this study are to identify per- and polyfluoroalkyl substances (PFAS) in Pennsylvania surface waters, corresponding associations with potential sources of PFAS contamination (PSOC) and other parameters, and compare raw surface water concentrations to human and ecological benchmarks. Surface water samples from 161 streams were collected in September 2019 and were analyzed for 33 target PFAS and water chemistry. Land use and physical attributes in upstream catchments and geospatial counts of PSOC in local catchments are summarized. The hydrologic yield

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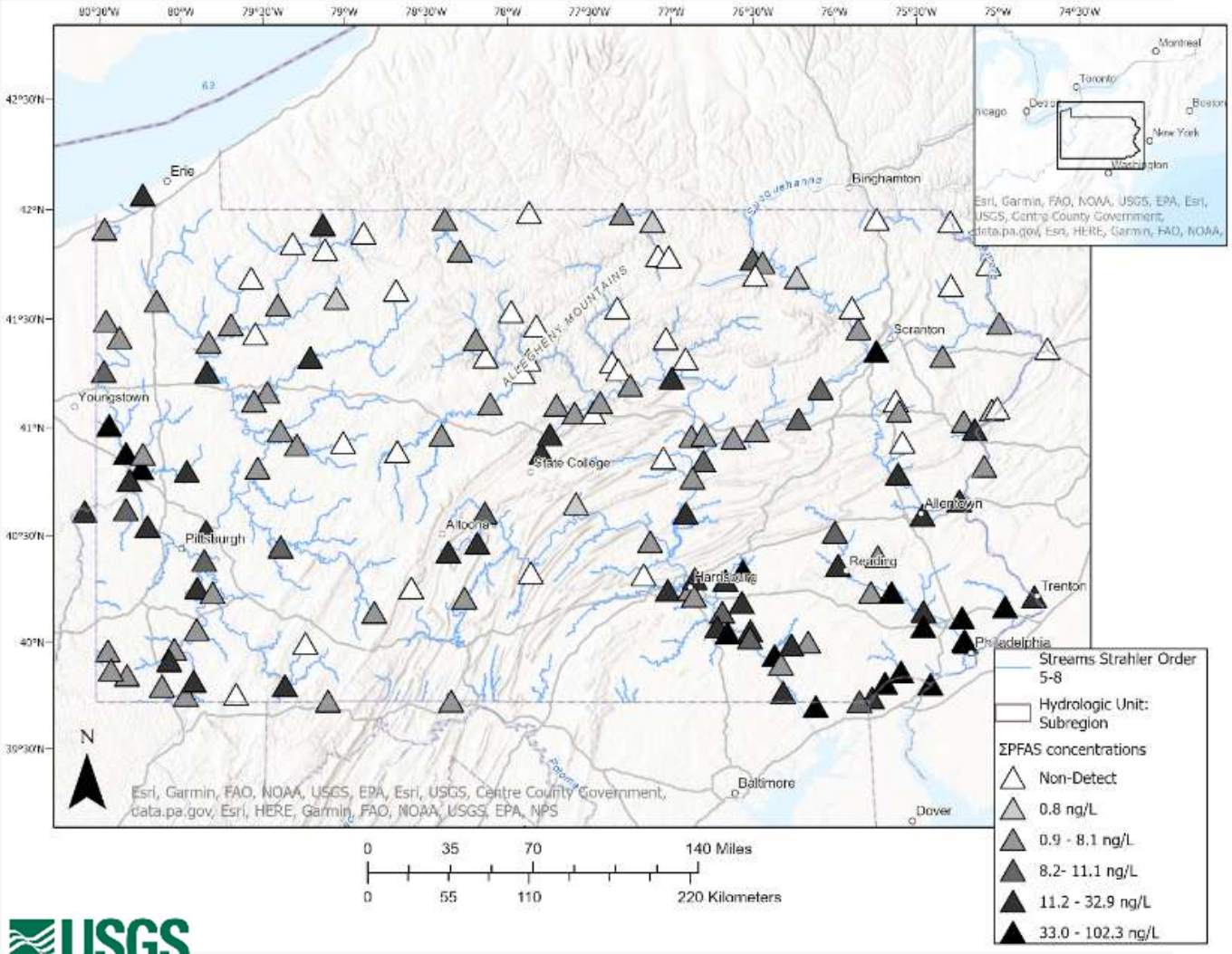
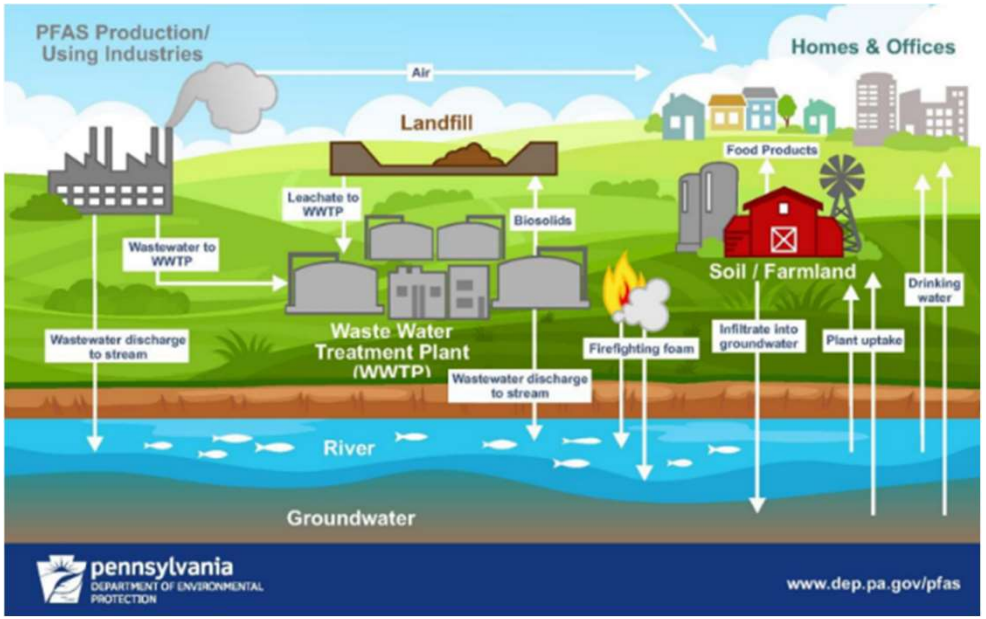


Pennsylvania Water Quality Network Streams (n=161)

- Sampled once- September 2019
- 33 target PFAS concentrations (EPA draft method 1633)
- Samples also measured for: pH, alkalinity, total dissolved solids, total nitrogen (TN), ammonia, chloride, & sulfate



Geospatial Analysis

- Land use (upstream catchment)
  - Wetland
  - Cropland
  - Development
- Potential PFAS sources
- (local catchment)
  - Sinkholes
  - Water pollution control facilities
  - Military installations
  - Airports
  - Fire training schools
  - Combined sewer overflow outfalls
  - Oil & gas wells
  - Land recycling cleanup locations
  - Superfund sites
  - Major groups of EnviroFACTS industries
  - (manufacturing/service facilities w/ permitted discharges)

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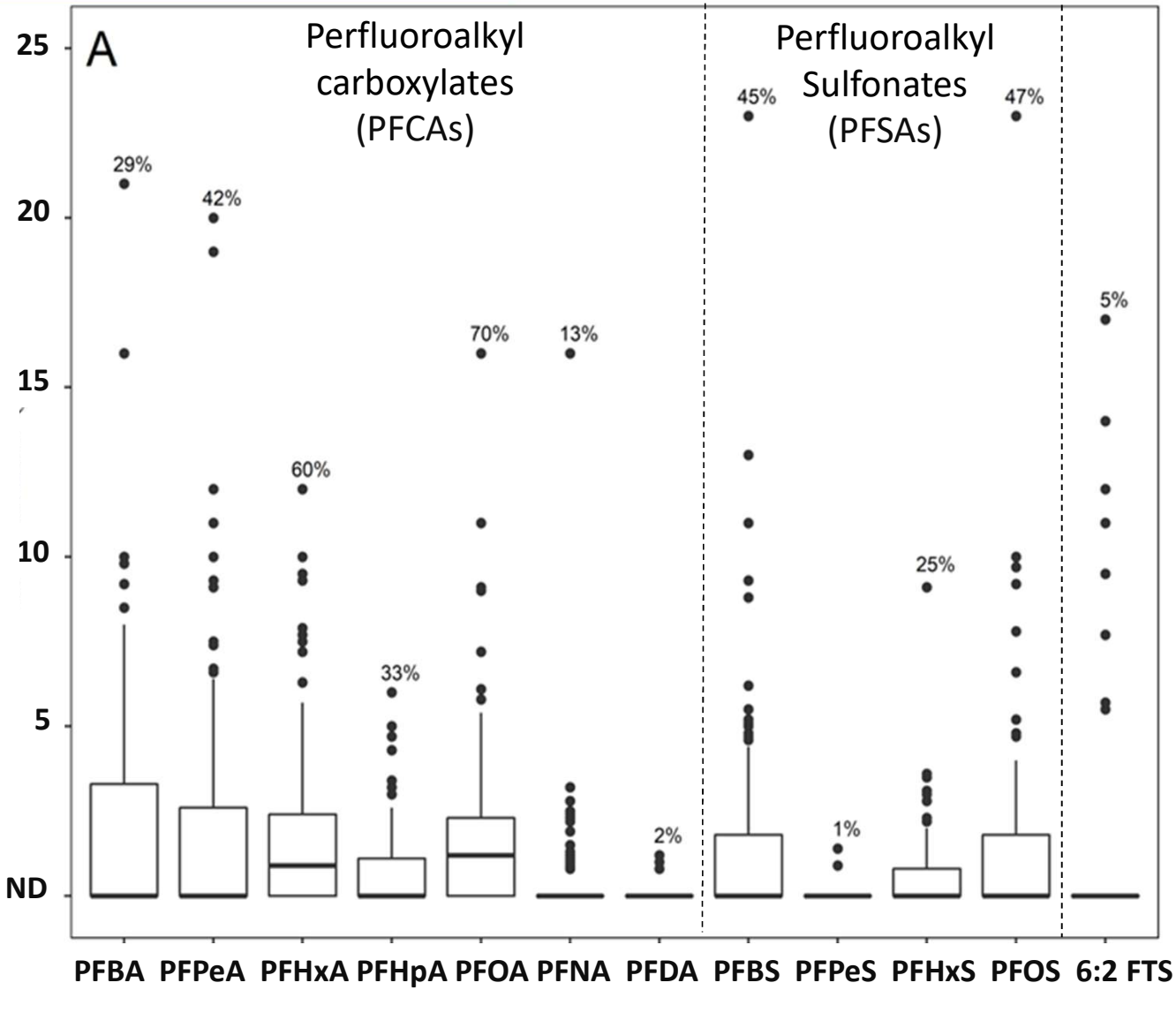
Detected PFAS concentrations (ng/L) n=161 streams



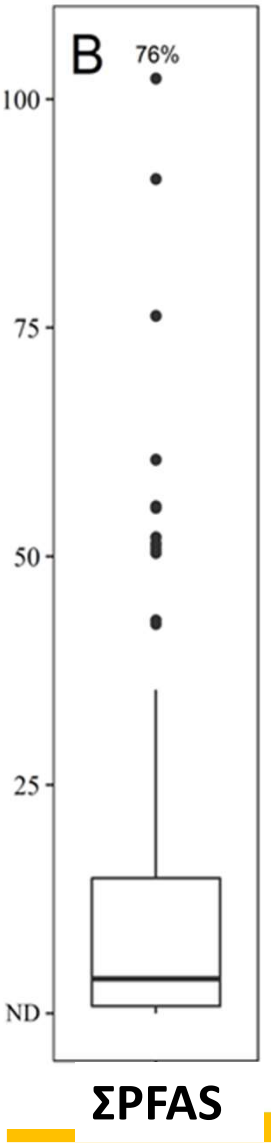


Figure from: Breitmeyer et al. (2023).

USGS

Urbanization & PFAS

- n=161 streams
- 38 total input features
- Total PFAS yield (median)= $11.9\,\frac{\mathrm{ng}}{\mathrm{s}}/\mathrm{km}^2$
- dev_pct,
- % development

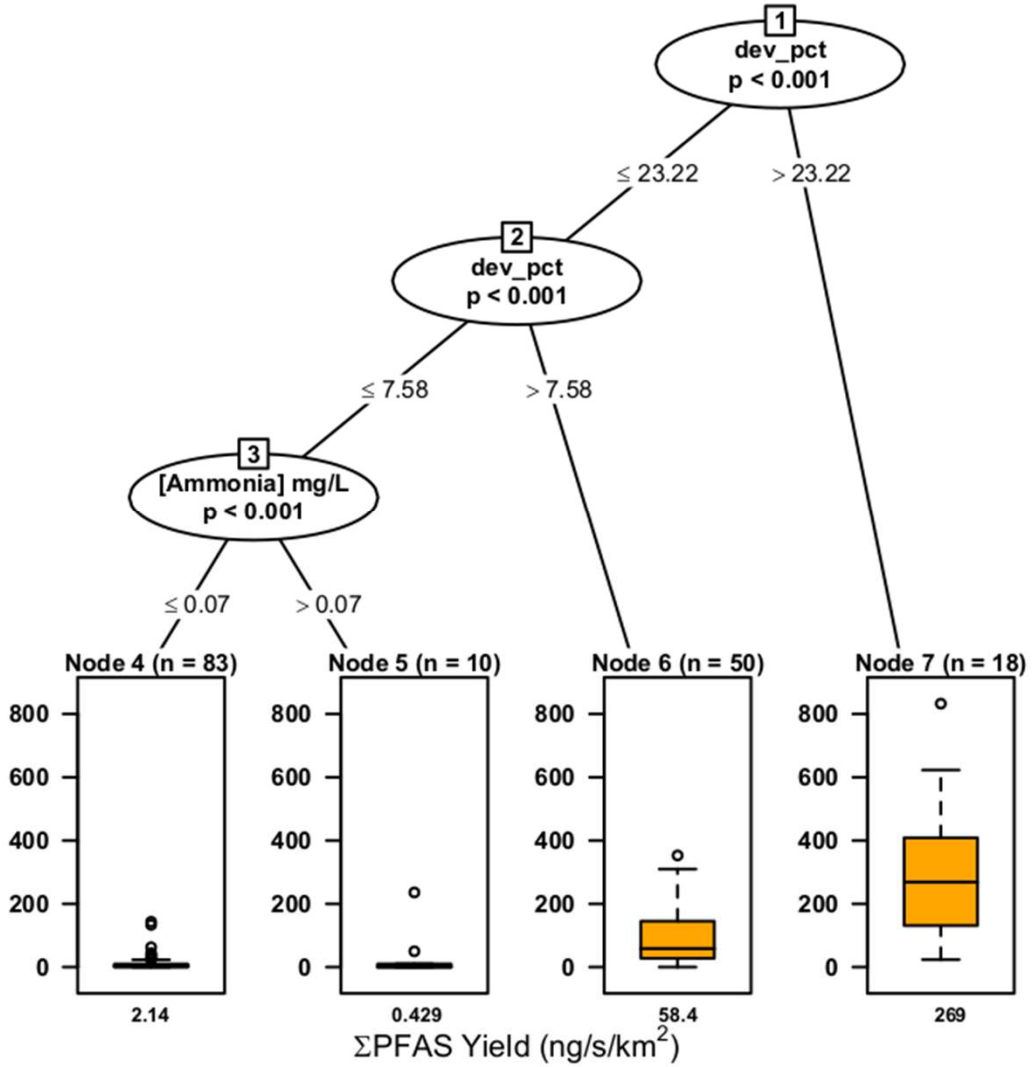
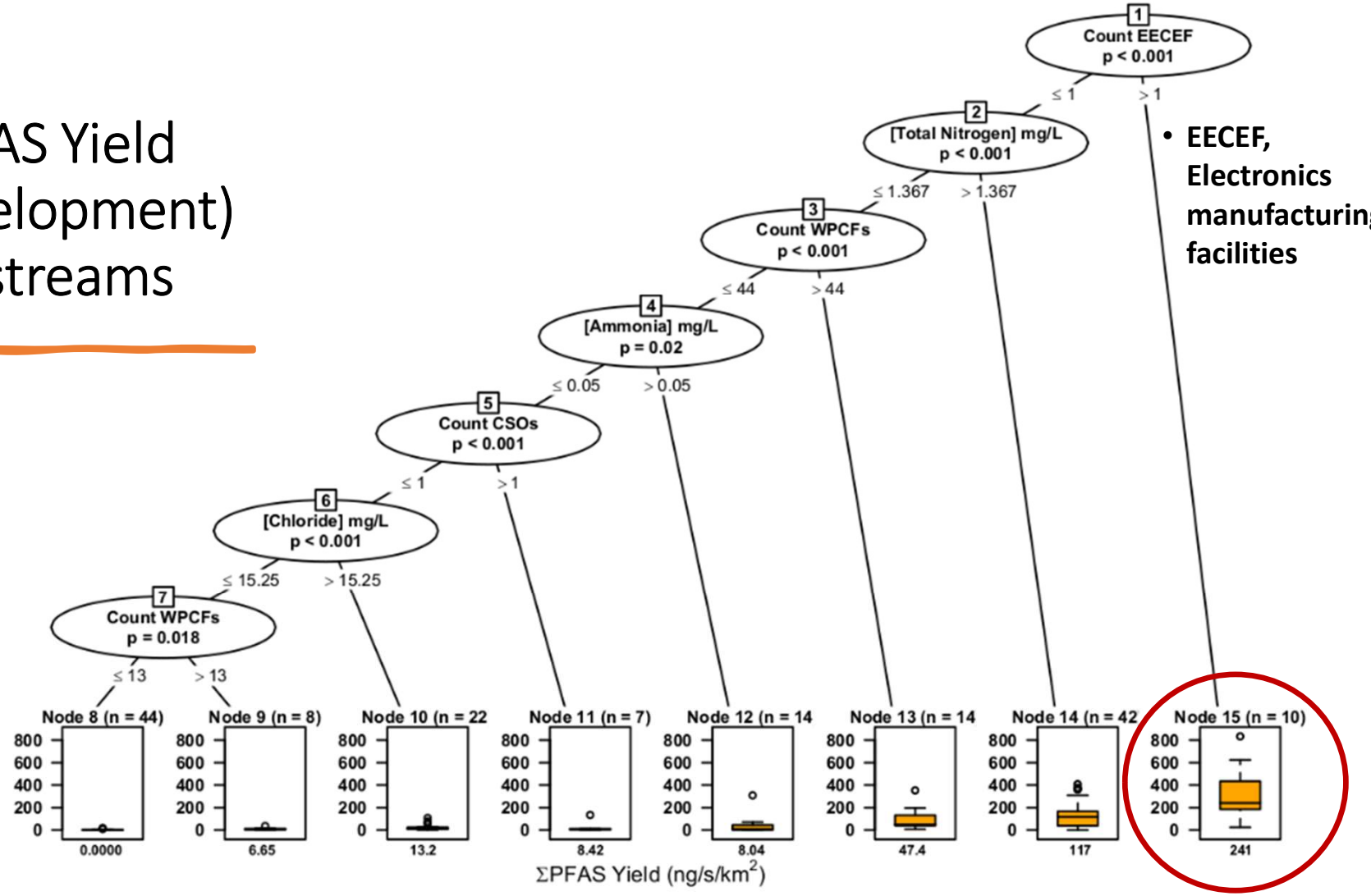


Figure from: Breitmeyer et al. (2023).

USGS

Total PFAS Yield (no development) n= 161 streams



- **EECEF, Electronics manufacturing facilities**

Figure from: Breitmeyer et al. (2023).

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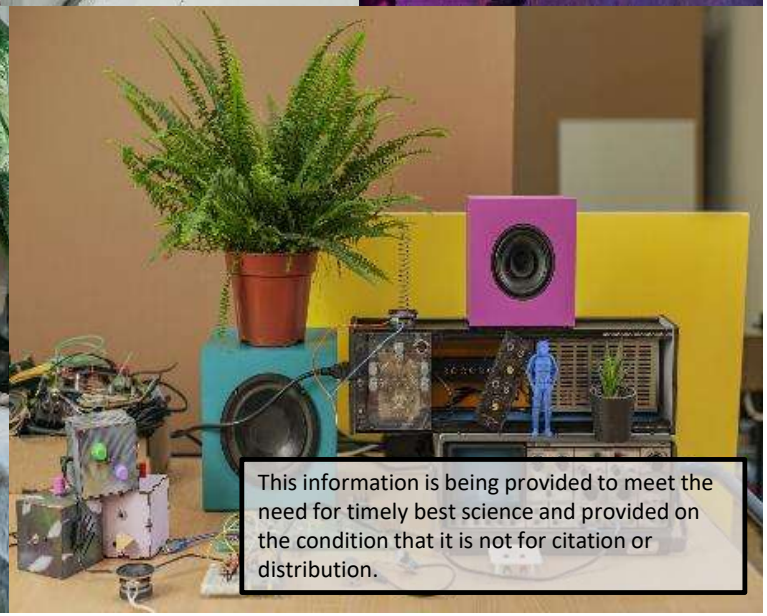
Electronic & Other Electrical Equipment & Components (Except Computer Equipment):

- Electrical industrial apparatus
- Household appliances
- Electrical lighting & wiring
- Radio & television
- Phones
- Electronic components & accessories





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Total PFAS Yield

Excluded:

- Development
- Highest outlier site

WPCF, water pollution control facilities
CSO, combined sewage overflow outfall

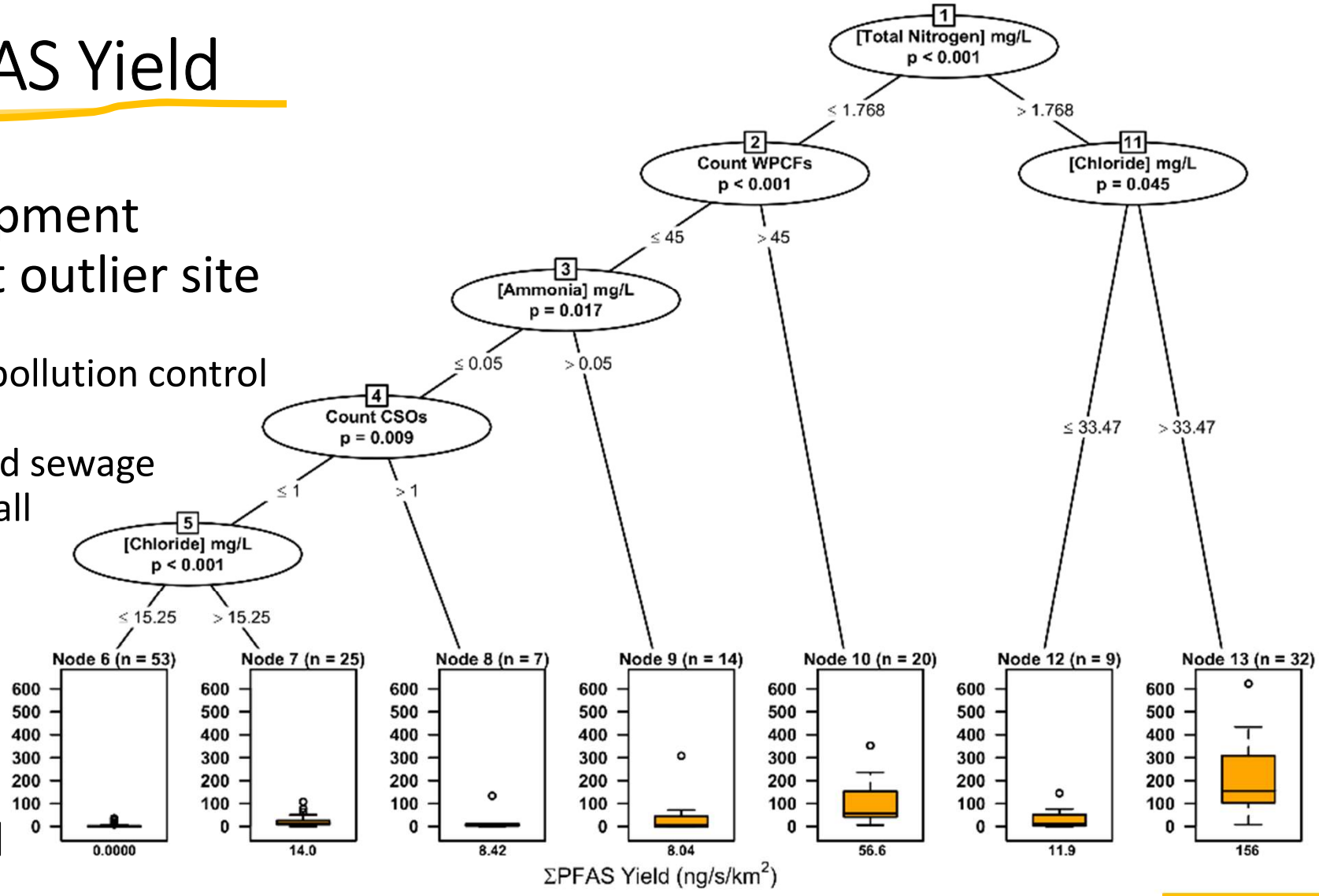
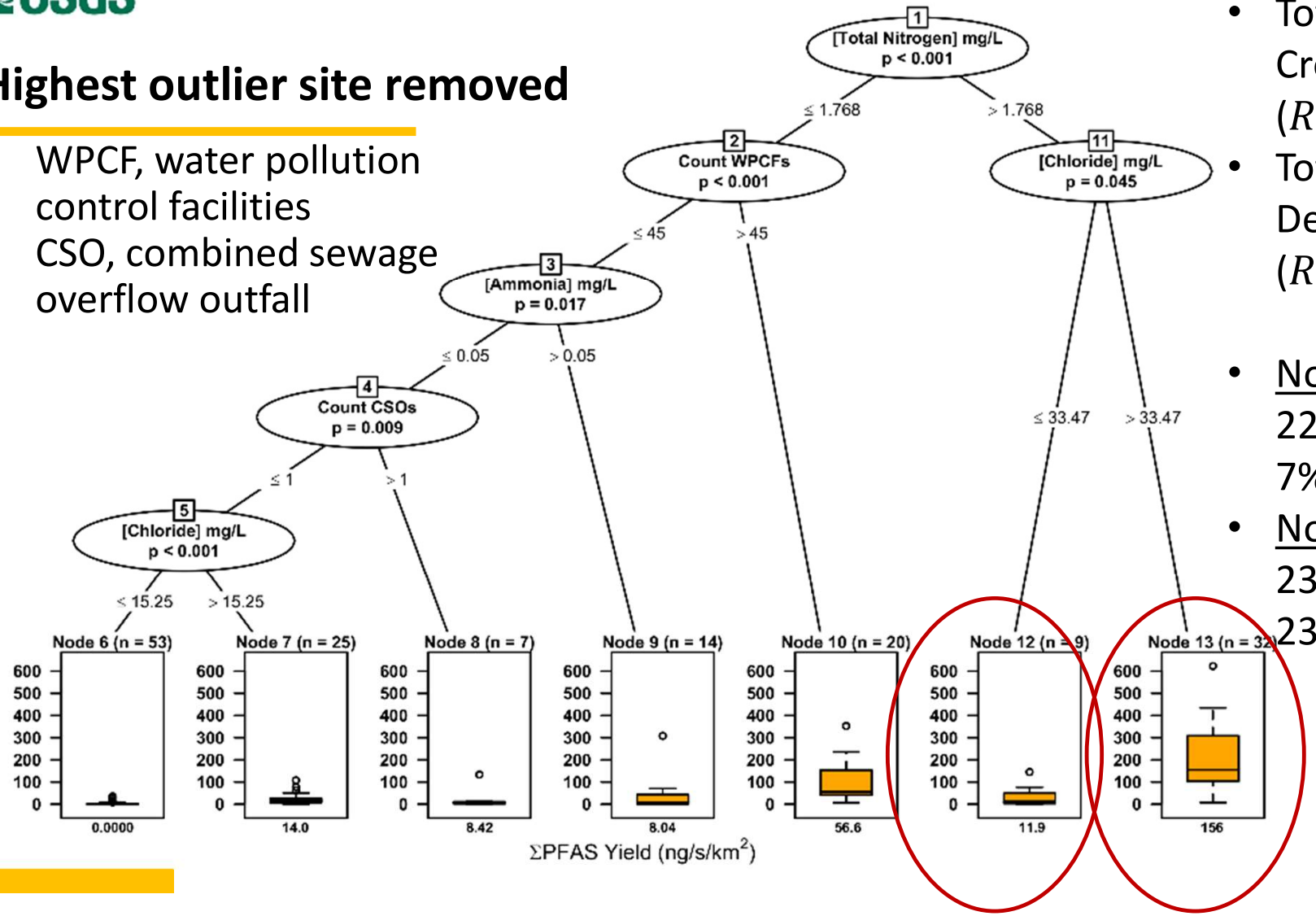


Figure from: Breitmeyer et al. (2023).

USGS

Highest outlier site removed

- WPCF, water pollution control facilities
- CSO, combined sewage overflow outfall



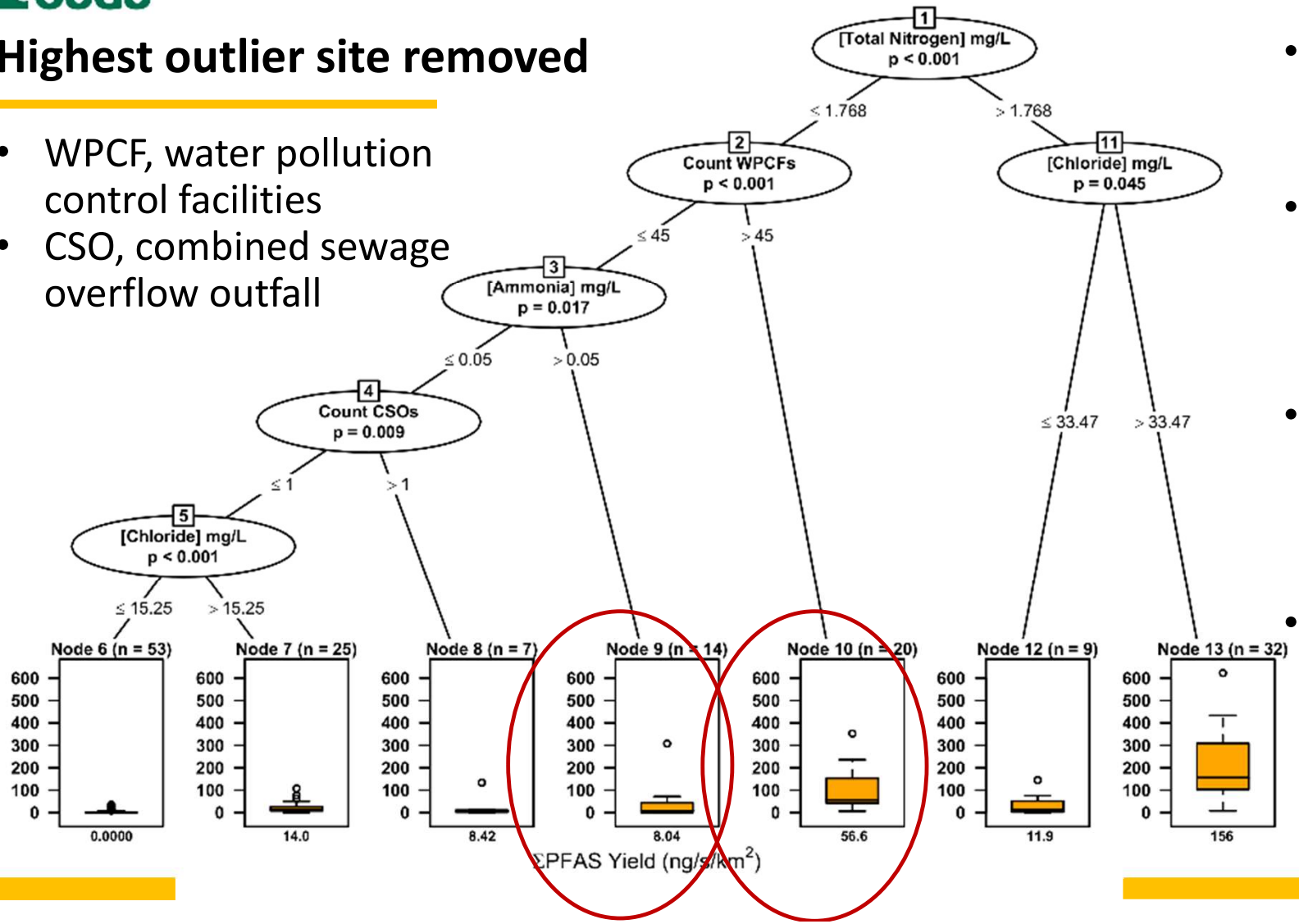
- Total PFAS & Cropland (R^2=0.35, p<0.001)
- Total PFAS & Development (R^2=0.77, p<0.001)

- <u>Node 12:</u>
  22% Cropland
  7% Developed
- <u>Node 13:</u>
  23% Cropland
  23% Developed

Figure from: Breitmeyer et al. (2023).

Highest outlier site removed

- WPCF, water pollution control facilities
- CSO, combined sewage overflow outfall

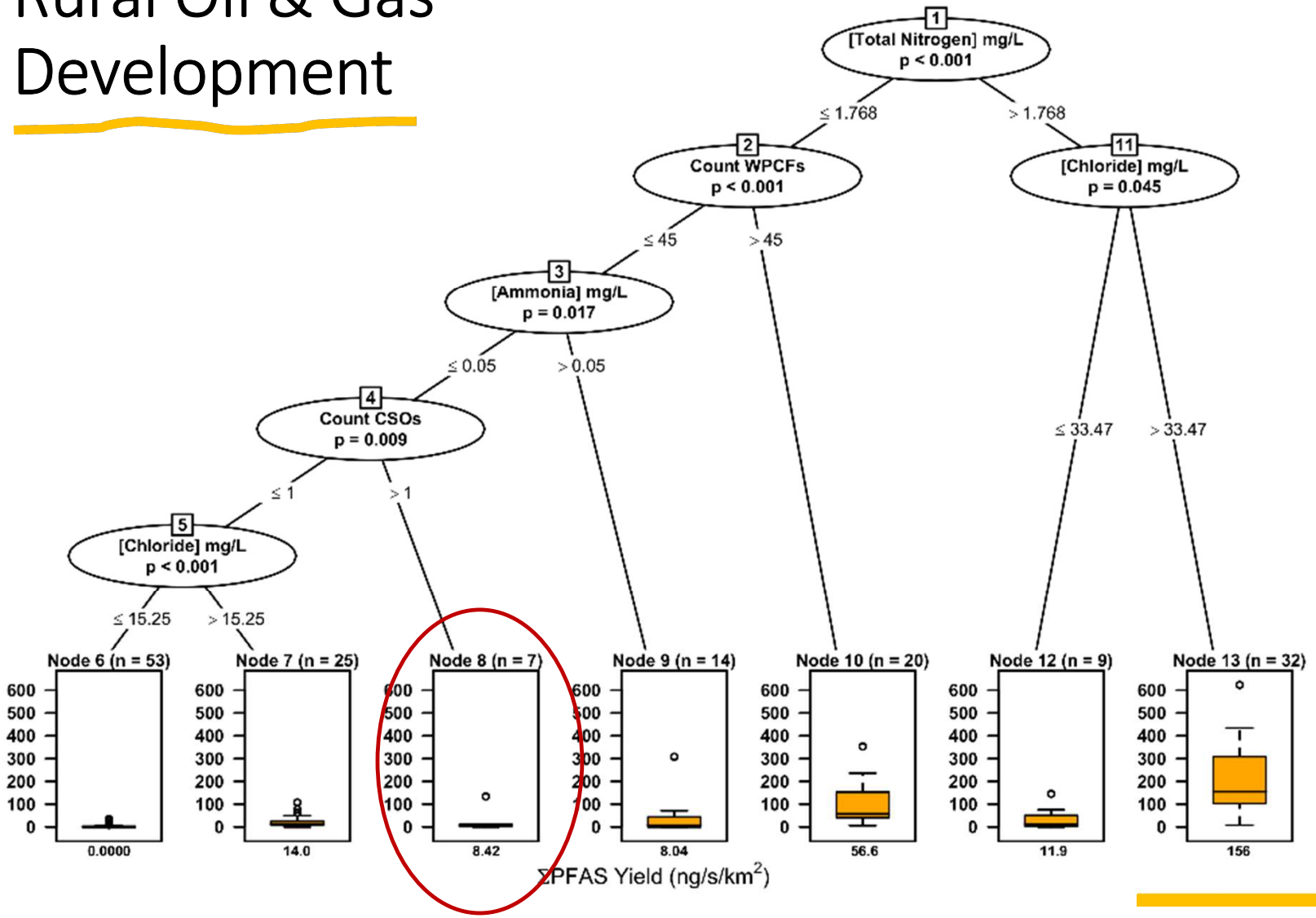


- Total PFAS & Cropland (R^2=0.35, p<0.001)
- Total PFAS & Development (R^2=0.77, p<0.001)

- <u>Node 9:</u>
  8% Cropland
  7% Developed
  (86% Open Space)
- <u>Node 10:</u>
  12% Cropland
  9% Developed

Figure from: Breitmeyer et al. (2023).

Rural Oil & Gas Development

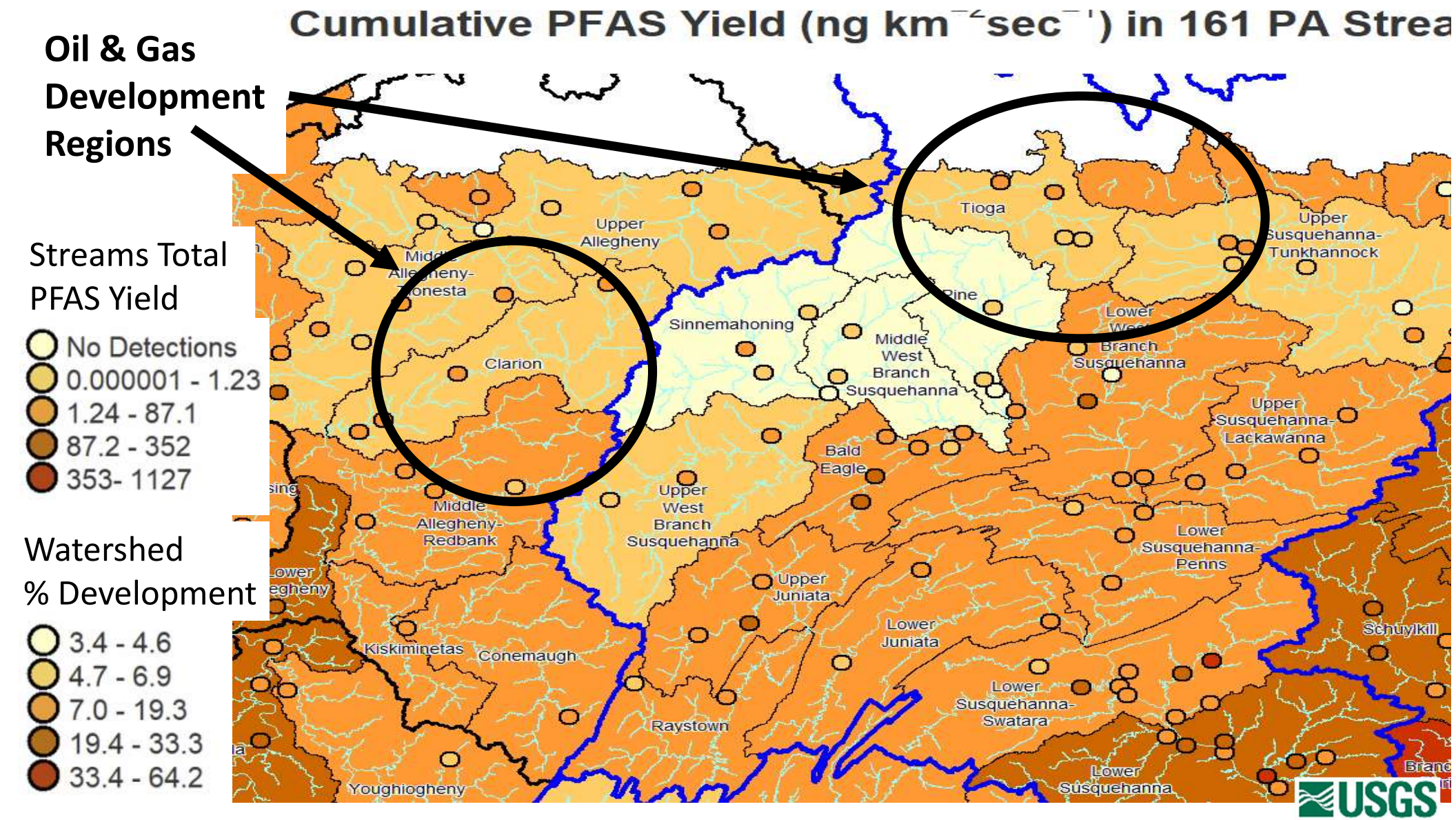


Highest outlier site removed

- WPCF, water pollution control facilities
- CSO, combined sewage overflow outfall

Figure from: Breitmeyer et al. (2023).

USGS


Cumulative PFAS Yield (ng km⁻²sec⁻¹) in 161 PA Strea
Oil & Gas Development Regions
Streams Total PFAS Yield
No Detections
0.000001 - 1.23
1.24 - 87.1
87.2 - 352
353- 1127
Watershed % Development
3.4 - 4.6
4.7 - 6.9
7.0 - 19.3
19.4 - 33.3
33.4 - 64.2
Upper Allegheny
Tioga
Upper Susquehanna-Tunkhannock
Sinnemahoning
Clarion
Middle West Branch Susquehanna
Lower West Branch Susquehanna
Upper Susquehanna-Lackawanna
Bald Eagle
Middle Allegheny-Redbank
Upper West Branch Susquehanna
Lower Susquehanna-Penns
Upper Juniata
Lower Juniata
Kiskiminetas
Conemaugh
Schuylkill
Lower Susquehanna-Swatara
Raystown
Youghiogheny
Lower Susquehanna
USGS

Conclusions – Statewide Scale PFAS Source Attribution

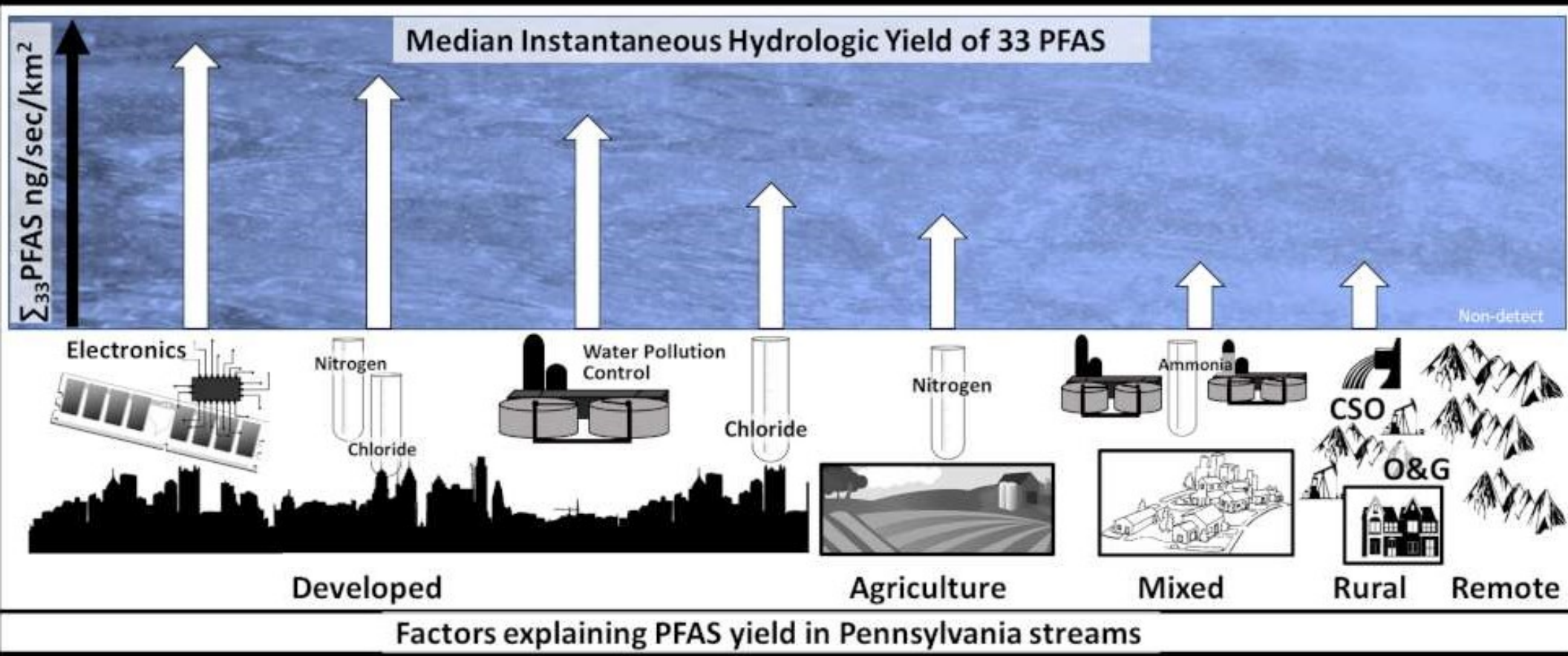
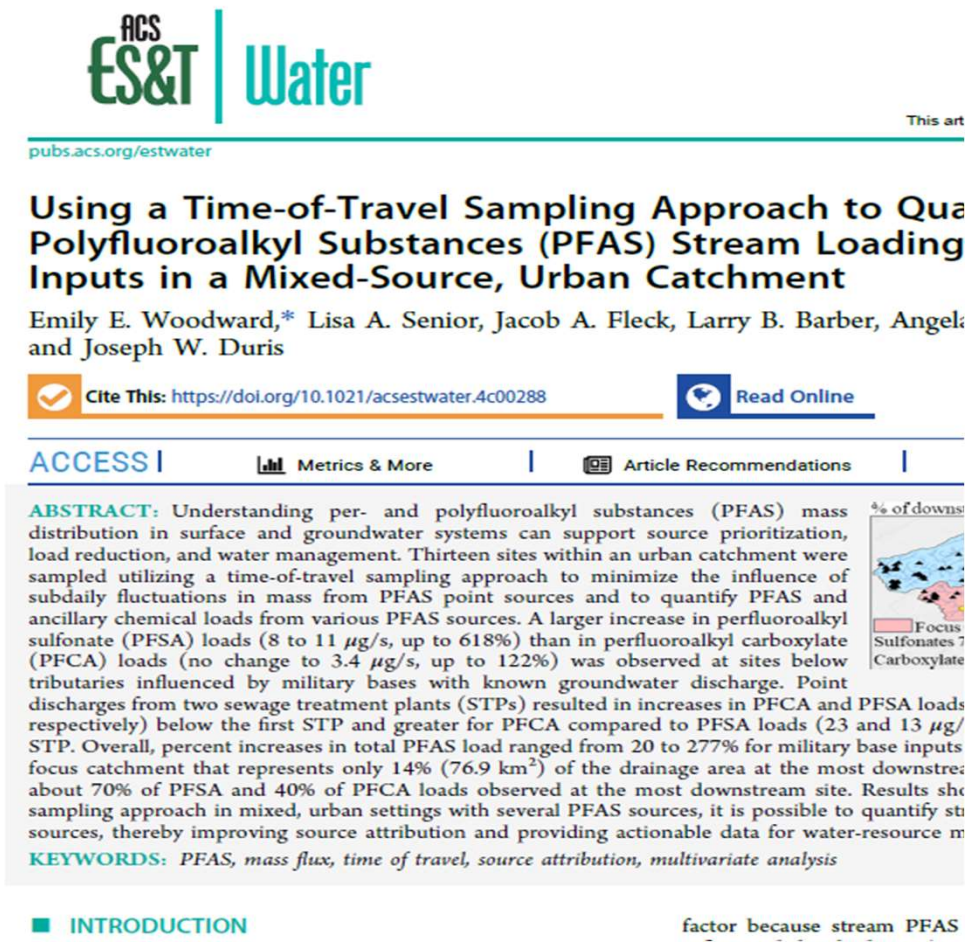


Figure from: Breitmeyer et al. (2023).

Conclusions – Statewide Scale PFAS Source Attribution

- Our study provides the first PA state-wide survey of PFAS concentrations, yields, & total pfas association with potential sources in surface waters.
- This preliminary study is key for future study designs.
- Further temporal monitoring is necessary to determine whether PFAS relations to chloride are impacted by season and/or hydrology.
- Future experimental designs should focus on PFAS trends in surface water, further evaluate associated sources through the targeted sampling of individual PFAS & allow for PFAS attribution from multiple sources.
- Additionally, future studies that incorporate beyond EPA Draft Method 1633 & utilize both targeted & non-targeted analysis will provide better understanding of the breadth of PFAS present.
- For abatement efforts, focus should be on whether associations exist between PFAS contamination & types of water pollution control or electronics manufacturing facilities, & respective wastewater treatment techniques.
- Evaluation of proximal sources & multiple spatial scale effects will help further define the potential effects of PFAS sources.



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Using a Time-of-Travel Sampling Approach to Qua Polyfluoroalkyl Substances (PFAS) Stream Loading Inputs in a Mixed-Source, Urban Catchment

Emily E. Woodward,* Lisa A. Senior, Jacob A. Fleck, Larry B. Barber, Angela and Joseph W. Duris

Cite This: https://doi.org/10.1021/acsestwater.4c00288

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ABSTRACT: Understanding per- and polyfluoroalkyl substances (PFAS) mass distribution in surface and groundwater systems can support source prioritization, load reduction, and water management. Thirteen sites within an urban catchment were sampled utilizing a time-of-travel sampling approach to minimize the influence of subdaily fluctuations in mass from PFAS point sources and to quantify PFAS and ancillary chemical loads from various PFAS sources. A larger increase in perfluoroalkyl sulfonate (PFSA) loads (8 to 11 μg/s, up to 618%) than in perfluoroalkyl carboxylate (PFCA) loads (no change to 3.4 μg/s, up to 122%) was observed at sites below tributaries influenced by military bases with known groundwater discharge. Point discharges from two sewage treatment plants (STPs) resulted in increases in PFCA and PFSA loads respectively) below the first STP and greater for PFCA compared to PFSA loads (23 and 13 μg/ STP. Overall, percent increases in total PFAS load ranged from 20 to 277% for military base inputs focus catchment that represents only 14% (76.9 km^2) of the drainage area at the most downstrea about 70% of PFSA and 40% of PFCA loads observed at the most downstream site. Results sh sampling approach in mixed, urban settings with several PFAS sources, it is possible to quantify st sources, thereby improving source attribution and providing actionable data for water-resource m

KEYWORDS: *PFAS, mass flux, time of travel, source attribution, multivariate analysis*

% of downs

Focus
Sulfonates
Carboxylate

INTRODUCTION

factor because stream PFAS

Local Assessment of PFAS Loading

A Time-of-Travel Sampling Approach to Evaluate PFAS in the Neshaminy Creek Watershed

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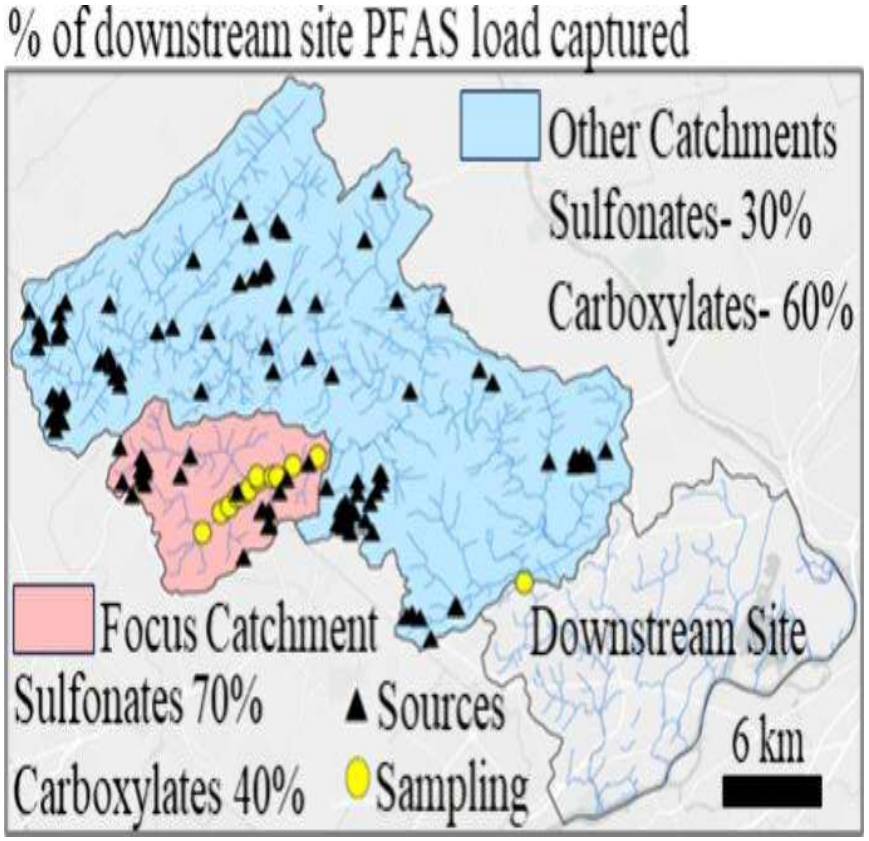
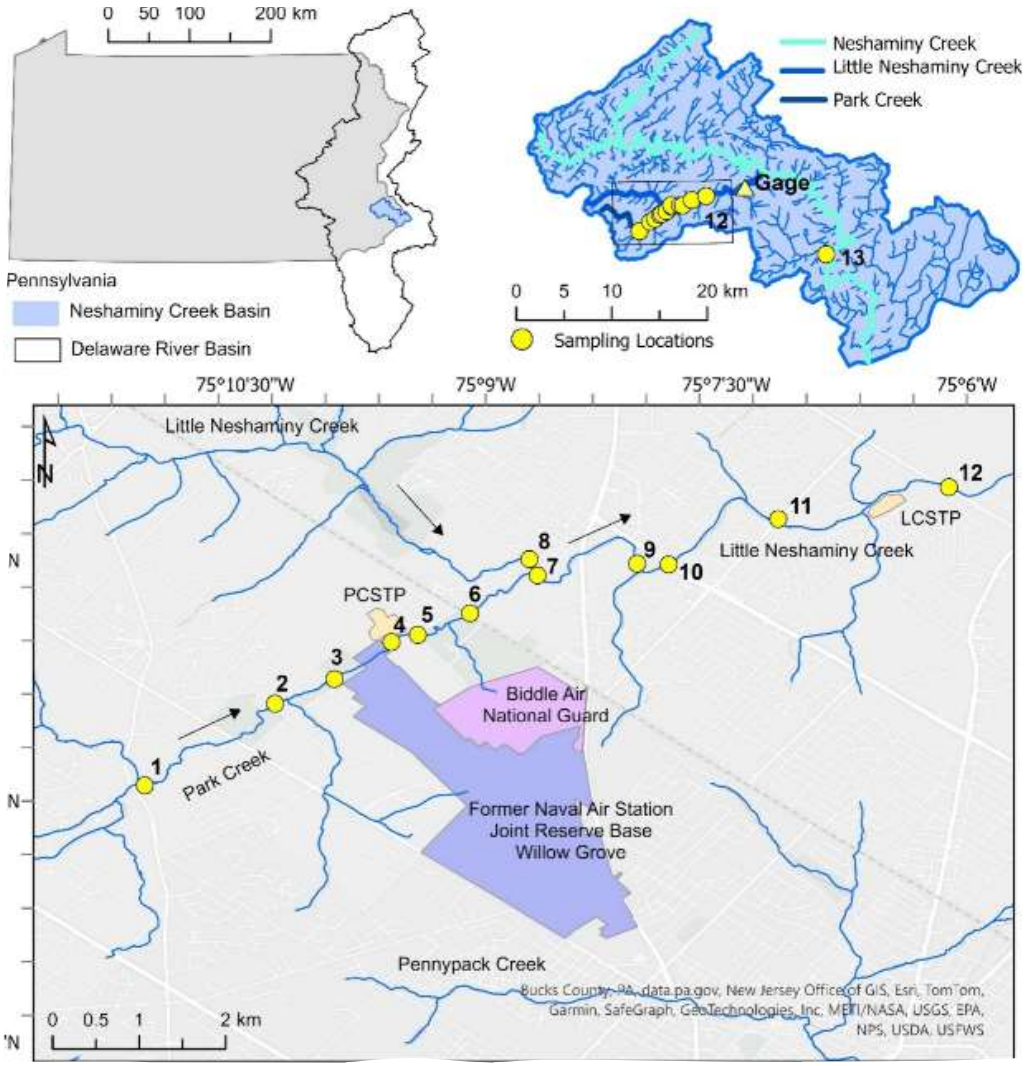
Background

- Sources of PFAS are often in close proximity spatially
- Sub-daily fluctuations in mass discharge can affect our understanding of PFAS sources
- Moving past concentrations and evaluating mass contributions is essential to understanding source
  - Streamflow measurements necessary
- When tracking PFAS, other chemicals can often help attribute source



Setting

- Park Creek, Little Neshaminy Creek, and Neshaminy Creek.
- Focus reach –
  - Park Creek & Little Neshaminy in area of Willow Grove Naval Air Base and Biddle Air National Guard Station
  - Park Creek STP
  - Log College STP
  - Reach is 14% of drainage area the drains to site 13 (Neshaminy at Langhorne on PA213
  - Underlain by Stockton Formation (fractured sandstone aquifer)
- Active pumping of water supplies (public, domestic, industrial)
- Mixture of residential, urban, suburban, industrial, and commercial land cover



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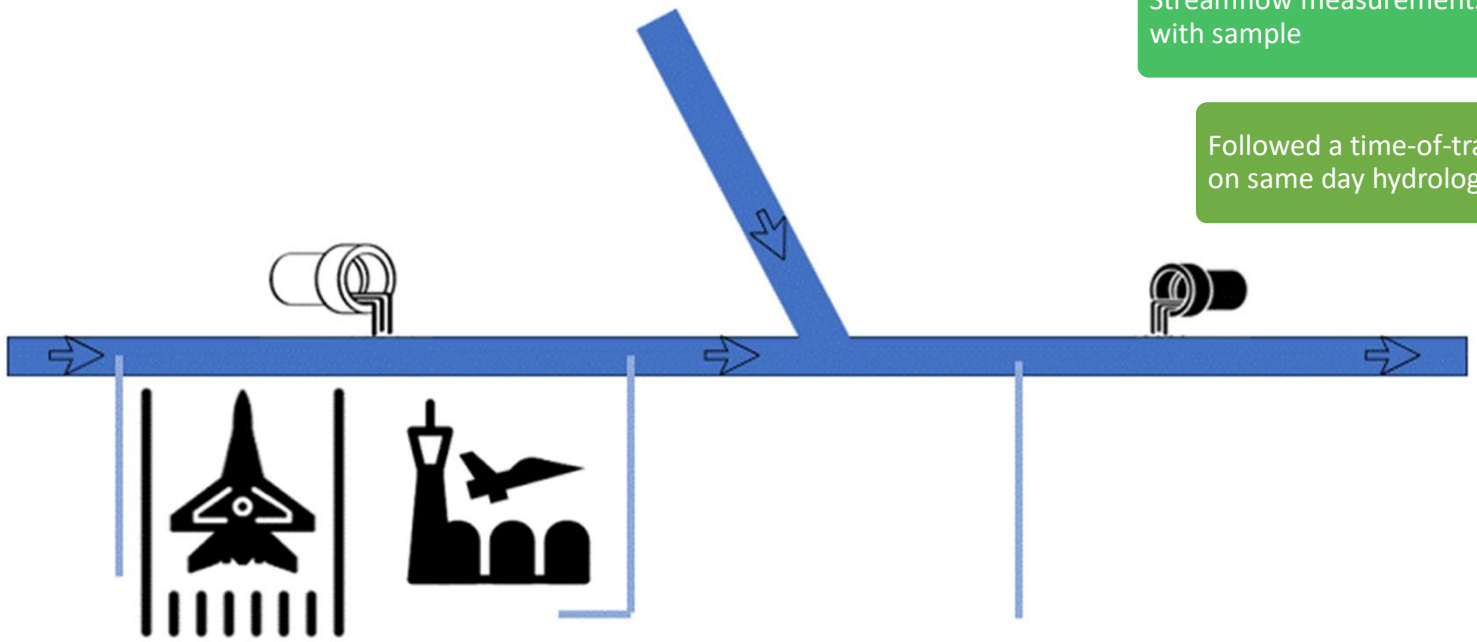
Sampling

Samples collected by USGS staff over 3 days.

Integrated stream sampling

Streamflow measurements concurrent with sample

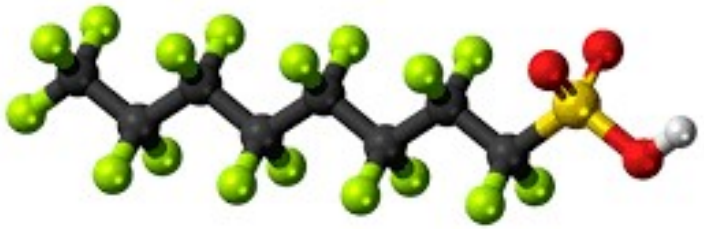
Followed a time-of-travel approach based on same day hydrologic conditions



USGS

Analysis Performed on Water Samples

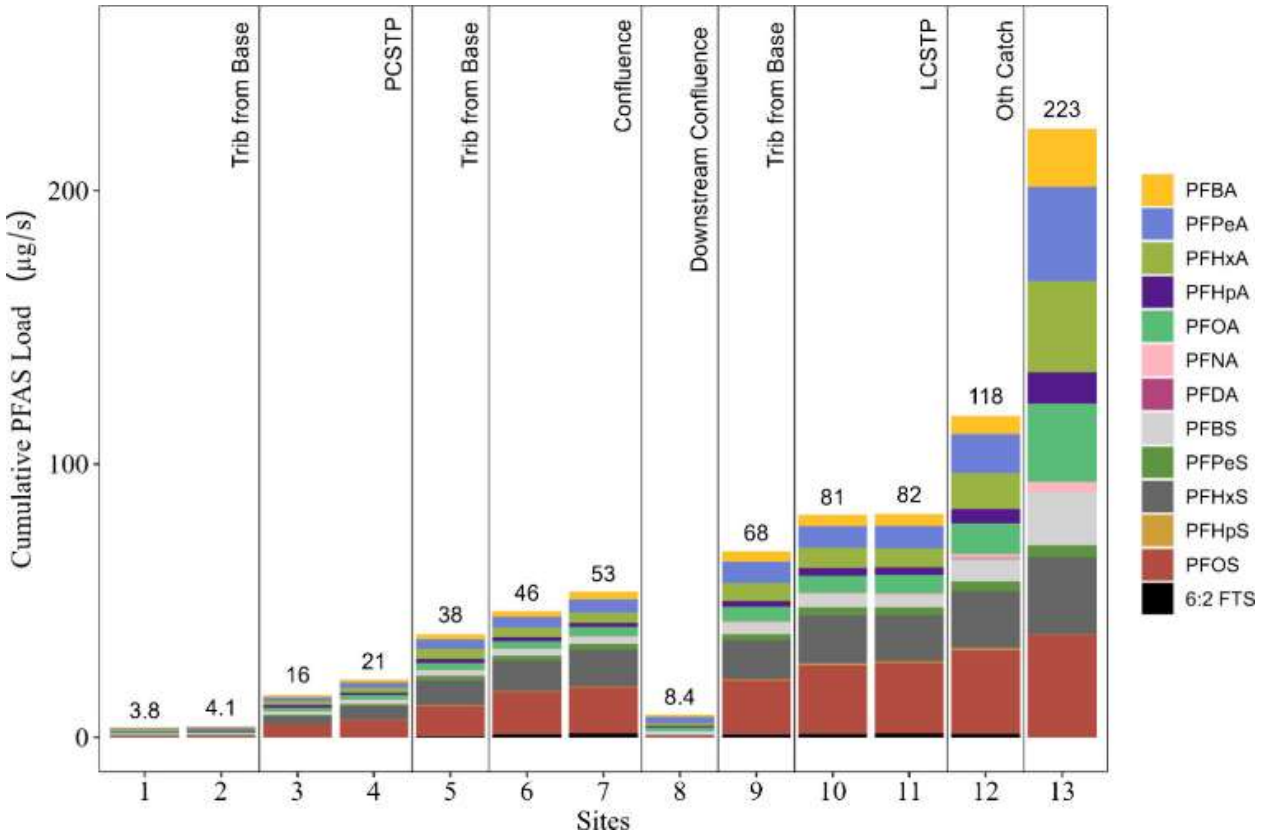
- **PFAS (1633)**
- **Total Oxidizable Percursors Analysis (TOPA)**
- **Dissolved Organic Carbon (DOC)**
- **Optical Properties (absorbance and fluorescence)**
- **Pharmaceutical compounds**
- **Volatile Organic Compounds (VOCs)**
- **Major ions**
- **Trace elements**
- **Physiochemical water properties (pH, specific conductance, dissolved oxygen, temperature, streamflow)**



USGS

Cumulative PFAS Load from Upstream to Downstream

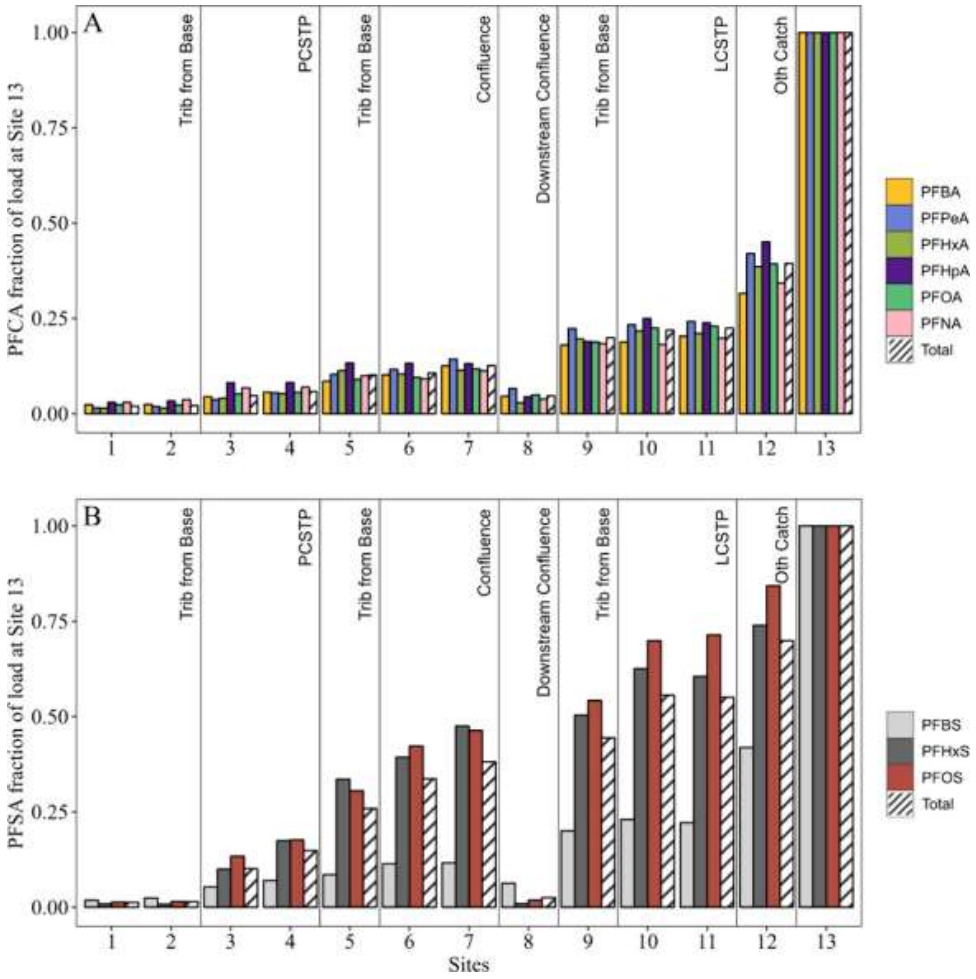
- PFAS demonstrate conservative mass behavior
- Greater than 50% of the PFAS load at Langhorne can be attributed to 14% of the drainage area
- Bases sources account for ~33% of Σ_{40}PFAS load, while STPs account for approximately 53% of Σ_{40}PFAS load at Langhorne



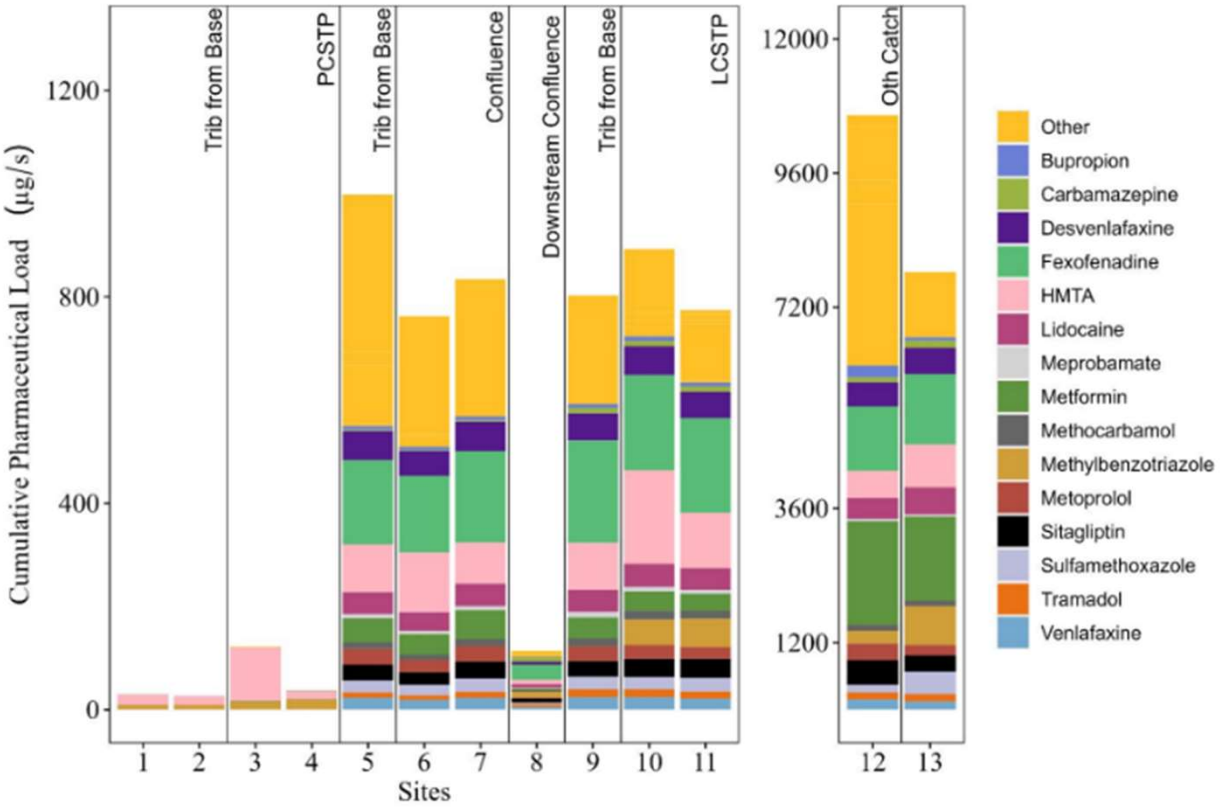
USGS

Carboxylate & Sulfonate Attribution

- ~70% of PFSA at Langhorne are attributable to the focus reach
  - ~40% of PFCA
- Largest increases in PFOS and PFHxS occurred downstream of base inputs

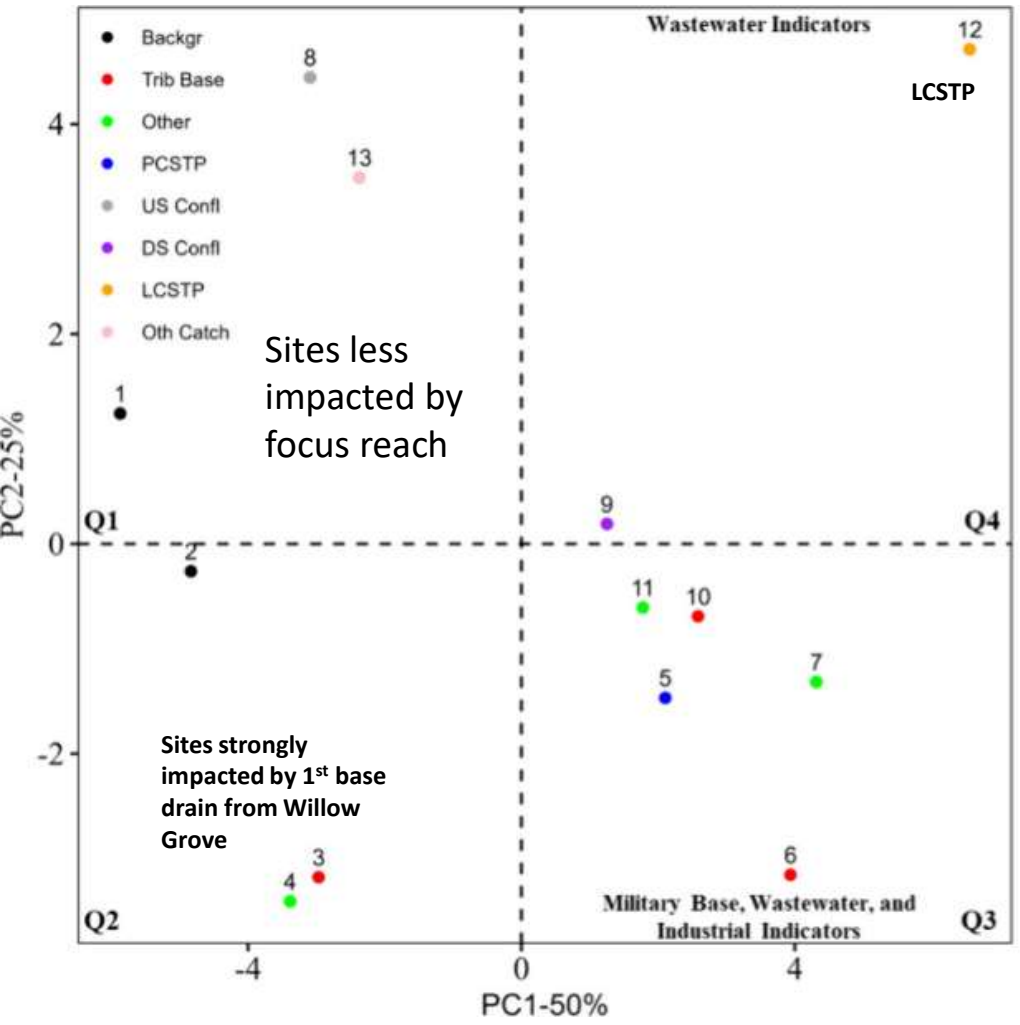


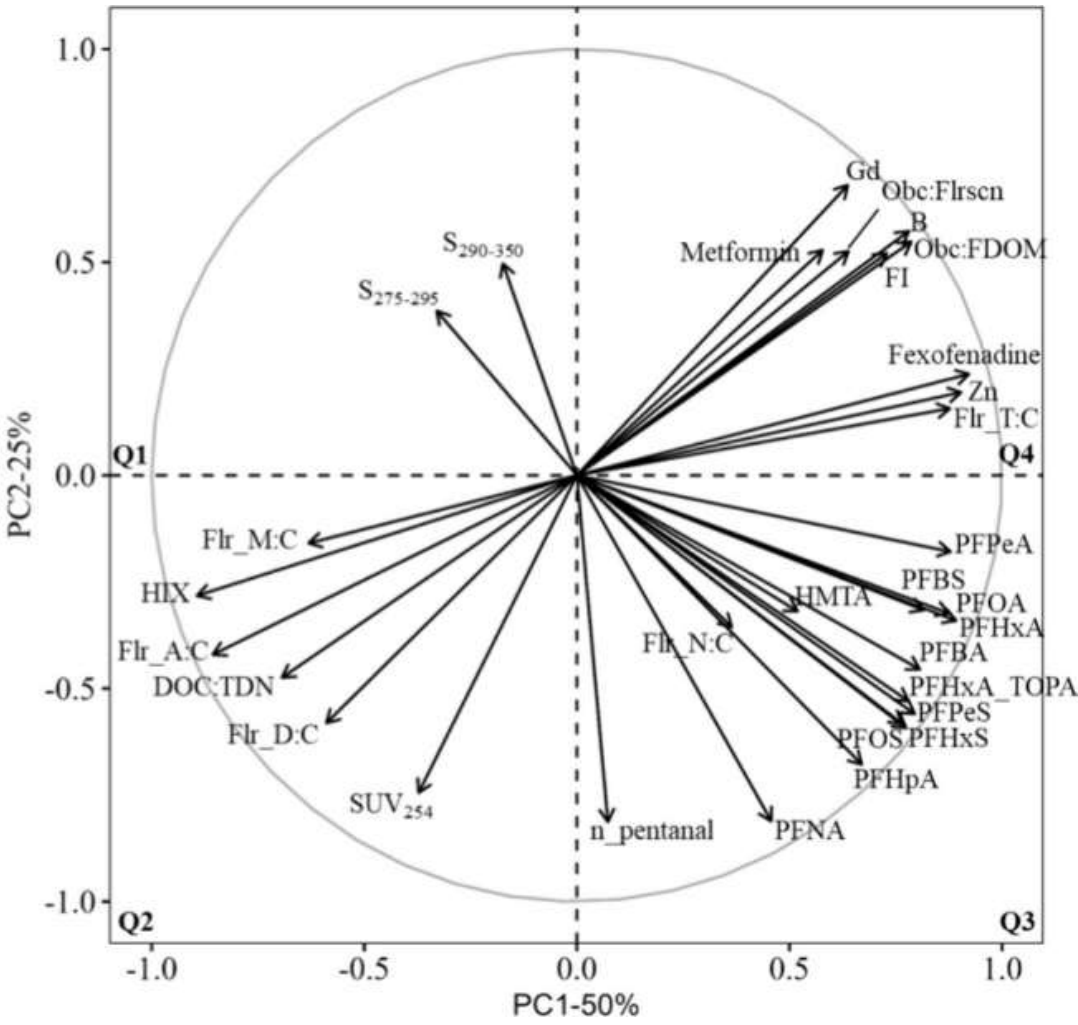
USGS



Cumulative Pharmaceutical Loads

- Not conserved mass
- Defines clear contributions from the STPs
- PCSTP increase load by ~800 ug/sec
- LCSTP increases load by ~10,000 ug/sec (almost 10x)
  - 10 grams/second, 1 kg per 100 seconds!


Backgr
Trib Base
Other
PCSTP
US Confl
DS Confl
LCSTP
Oth Catch
Wastewater Indicators
LCSTP
Sites less impacted by focus reach
Sites strongly impacted by 1st base drain from Willow Grove
Military Base, Wastewater, and Industrial Indicators
Q1
Q2
Q3
Q4
PC1-50%
PC2-25%


Gd
Obc:Flrscn
B
Obc:FDOM
FI
Metformin
S290-350
S275-295
Fexofenadine
Zn
Flr_T:C
Flr_M:C
HIX
Flr_A:C
DOC:TDN
Flr_D:C
SUV254
n_pentanal
Flr_N:C
HMTA
PFNA
PFPeA
PFBS
PFOA
PFHxA
PFBA
PFHxA_TOPA
PFPeS
PFOS:PFHxS
PFHpA
Q1
Q2
Q3
Q4
PC1-50%
PC2-25%

Conclusions – Small-scale PFAS Source Attribution

- Sewage Treatment Plants are an important source of PFAS in Neshaminy Creek
  - Similar load to military bases
- A small part of a drainage area (14%):
  - Contributes over 50% of the total load for the entire drainage (~600 km2)
  - Contributes over 70% of the PFSA load
  - Contributes over 40% of the PFCA load
- Time-of-travel sampling minimizes the influence of diurnal variation of source inputs
- Attributing PFAS load to individual sources and source areas is a useful tool for water resource managers

Sampling Scale and PFAS Attribution

There is some agreement between statewide source assessments and local source assessments

- Urban land cover
- Wastewater Infrastructure

However, smaller watersheds could have other important sources than those important at the state-wide level

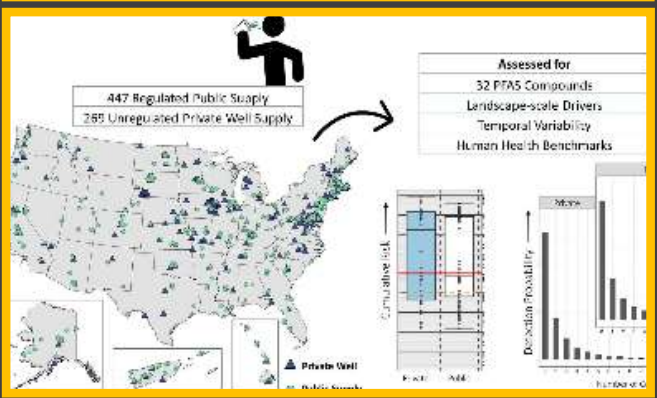
- i.e. military bases, selected industries

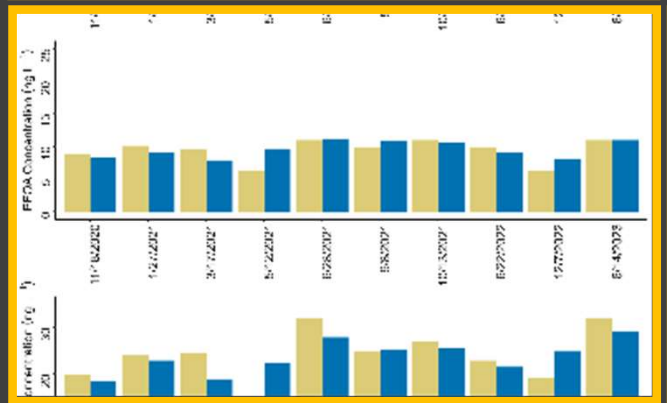
At any scale, robust sampling and flow measurements are essential to understand mass gain and losses

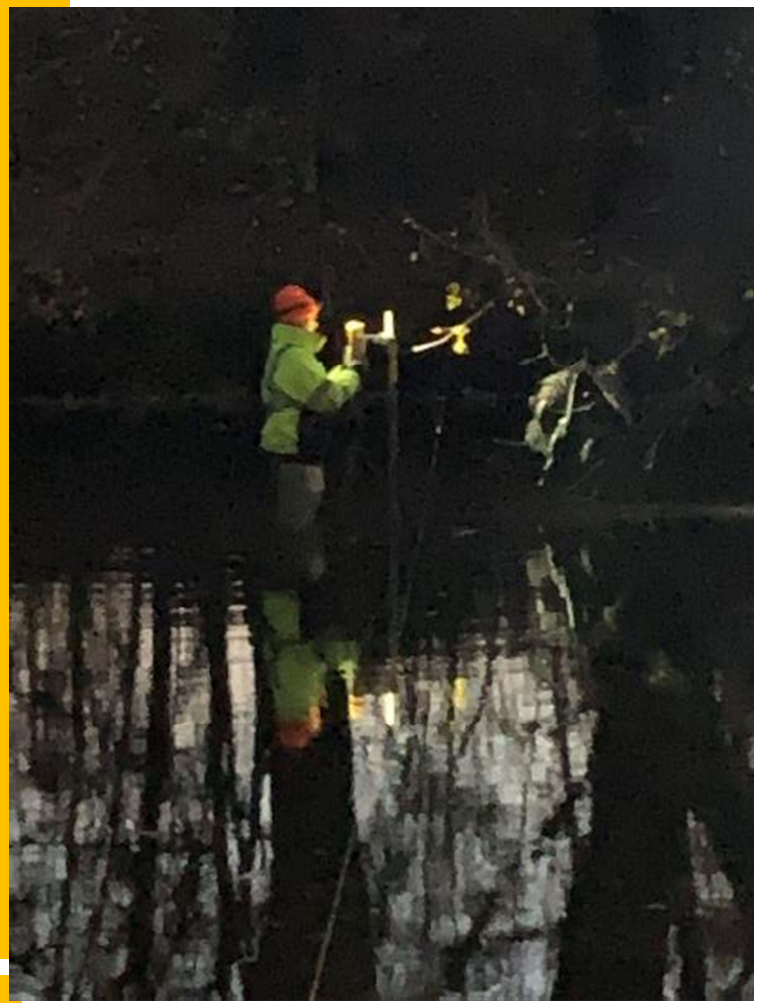
USGS

USGS PAWSC PFAS Research Interests

- PFAS sources related to existing detections of PFAS in public water supplies
- Determine relation between existing detections in SW, GW, and PWS
- Evaluate concurrent trends in source water and PWS
- Test for differences between PFAS in PWS with GW vs SW as sources
- Model potential toxicity from existing PWS PFAS detections
- Evaluate domestic supplies for PFAS and elucidate sources







Thank You

Contact information

Joe Duris

717-730-6930

jwduris@usgs.gov

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