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NEW HAMPSHIRE DEPARTMENT OF Environmental Services

Assessing PFAS Occurrence and Background Concentrations in New Hampshire Soils

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Collaborators

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With support from many others!

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Study purpose

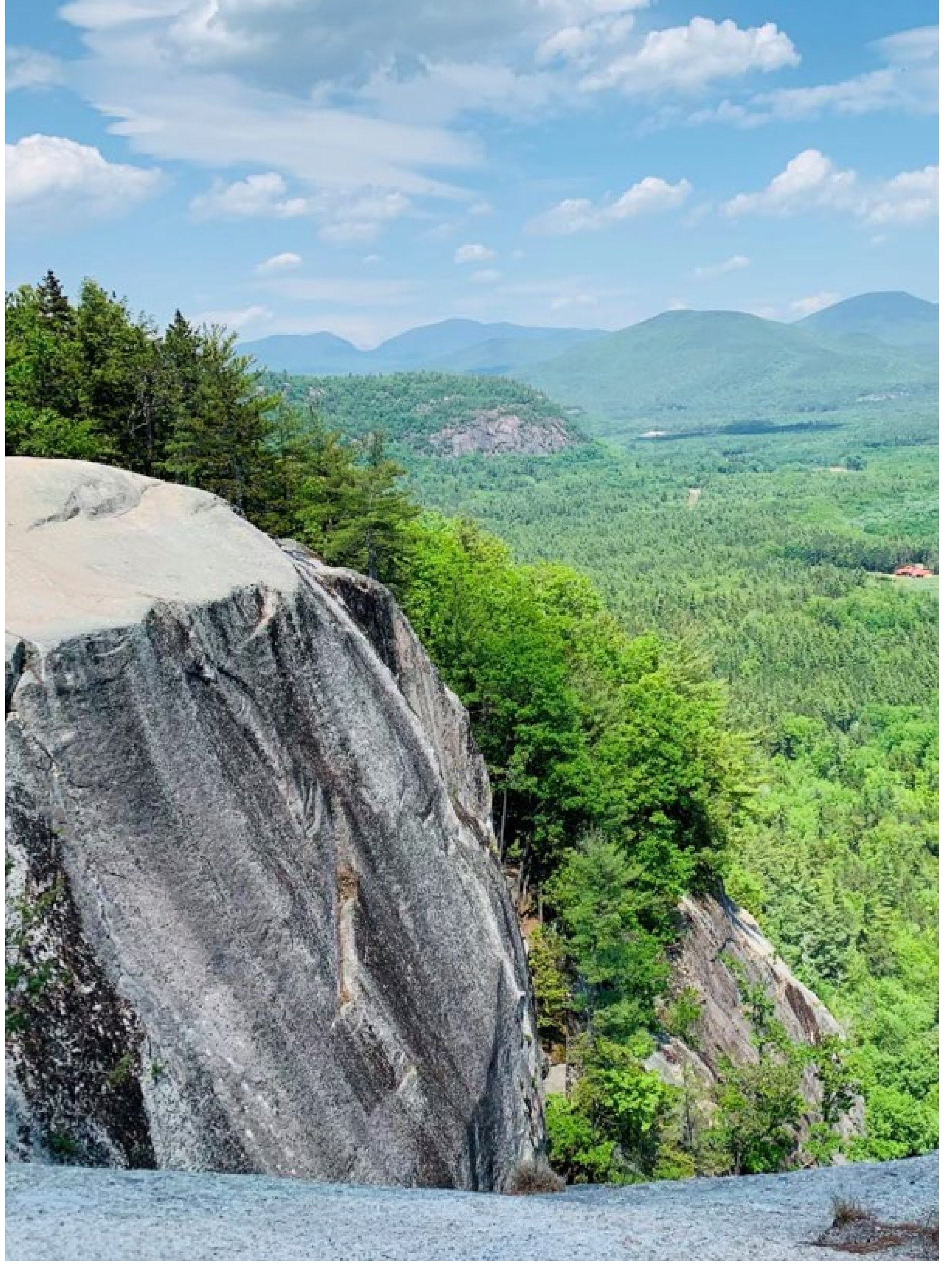
The study was undertaken to:

1. Address data gaps on shallow soil concentrations and partitioning
2. Provide data to support Soil Remediation Standard (SRS) rulemaking:

    485-H:13 *– SRS rulemaking initiated by November 1, 2023 for PFNA, PFOA, PFOS, PFHxS*

5 Factors Evaluated:

- Direct Contact Risk-Based Soil Concentrations
- Leaching-Based Soil Concentrations
- Background Soil Concentrations
- Ceiling Concentrations
- Practical Quantification Limits



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Study goals

1. **Characterize concentrations of PFAS in shallow soil throughout NH in areas NOT known to be impacted by local PFAS sources.**

2. Conduct extensive laboratory experiments to understand how PFAS move from soil and biosolids to water under a variety of environmentally relevant conditions.

3. Investigate PFAS groundwater and soil concentrations at two selected sites in NH to compare field observations with soil-to-water transport properties measured in the laboratory.

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Elements of an effective study design for soil assessment

1. **Study goals**
   - How will the data be used?
   - Will the data need to be compared to other results?
2. **Sample network design**
   - Define appropriate scale
   - Determine number of sites needed
   - Site selection
   - Restrictions on location
3. **Sampling methodology**
   - Discrete or composite
   - Sampling depth(s)
   - Sample processing
   - Types of supporting data (TOC, pH, etc.)
4. **Data quality**
   - Lab and Field QA/QC
   - Laboratory reporting limits

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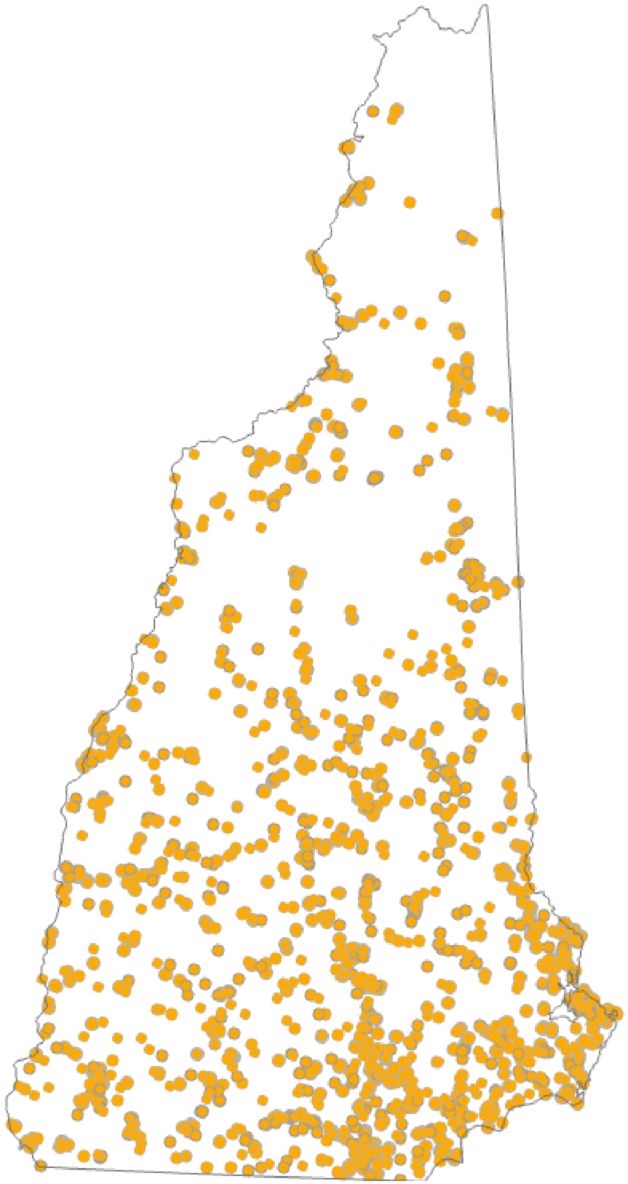
Study design

Study goals: Characterize concentrations of PFAS in shallow soil throughout NH in areas ***not*** known to be impacted by local PFAS sources.

Sample network design

- Sampling limited to lands classified as forested, shrubland, herbaceous, barren, or wetlands.
- Placed a 500-meter buffer around parcels with known and/or potential PFAS contamination/release.
  - Airports
  - WWTPs
  - Fire training areas
  - Landfills
  - Etc.



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Minimizing bias through stratified equal area random sampling

Sample network design

1. The state of NH was gridded into 100 equal-area grid cells.
2. Sites were randomly generated within the grid cells and one sample was taken from each grid cell.
   - Sampling was not easy or convenient, but provided:
     - Equal statewide spatial coverage
     - Minimized bias

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Sampling overview

- At all 100 locations: Sampled from 0 to 6 inches in depth
- At 50 locations: Sampled from 6 to 12 inches in depth
- At 6 locations: Profiles collected in 6-inch increments to a maximum of 36 inches

Soil Analyses	Sites/Locations
PFAS (36 compounds)	Every depth, every location
Total Oxidizable Precursor Assay (TOPA)	50 locations, 0 to 6 inches depth
pH	Every depth, every location
Total Organic Carbon (TOC)	Every depth, every location
Protein	91 locations, 0 to 6 inches depth
% Moisture	Every depth, every location
Visual classification of soils (NRCS USDA Field Book)	Every depth, every location

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Sampling methods

- Land surface was cleared of leaf litter, sticks, etc.
- PFAS-free sampling equipment used (stainless steel trowel, stainless steel bowl, stainless steel auger, etc.)
- Samples at the target depth intervals were collected from 3 separate nearby locations, and homogenized
- Equipment was cleaned between each sample by brushing off loose soil, rinsing with deionized (DI) water, scrubbing with Liquinox® mixed with DI water, followed by a thorough DI water rinse, and finally a PFAS-free liquid chromatography/mass spectrometry (LC-MS) grade water rinse

QA/QC

- **Equipment Blanks:** 22 Equipment Blanks collected and measured for PFAS, TOPA, and TOC
- **Source Solution Blanks:** 3 LC-MS grade water and 2 DI water source solution blanks collected for PFAS and TOPA, 2 LC-MS grade water and 1 DI water source solution blank collected for TOC
- **Replicates:** 12 duplicate sets, 3 triplicate sets of soil samples collected for PFAS and TOC, 1 duplicate set and 2 triplicate sets collected for TOPA. 6 duplicate sets and 1 triplicate set collected for protein
- **Matrix Spikes/Matrix Spike Duplicates:** 20 soil samples analyzed

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QA/QC - Results

Blanks

- Equipment blank concentrations (if any) were determined to be unlikely to impact sample results
- Method blank concentrations, when detected, may have impacted some sample results:
  - Data was censored if concentrations were less than 5 x the method blank detection. For soil PFAS results, this resulted in censoring of PFHxA (1 sample), PFBS (25 samples), 6:2 FtS (5 samples)

Duplicates (n = 15)

- Average relative percent difference (RPD) was <25% for all compounds for PFAS analysis, except for PFTrDA (average RPD = 27%)
- Average RPDs ≤20% for TOC, percent moisture, protein (n=5), and pH

Triplicates (n = 3)

- Average relative standard deviation (RSD) was <20% for all compounds for PFAS, TOC, percent moisture, protein (n=1), and pH

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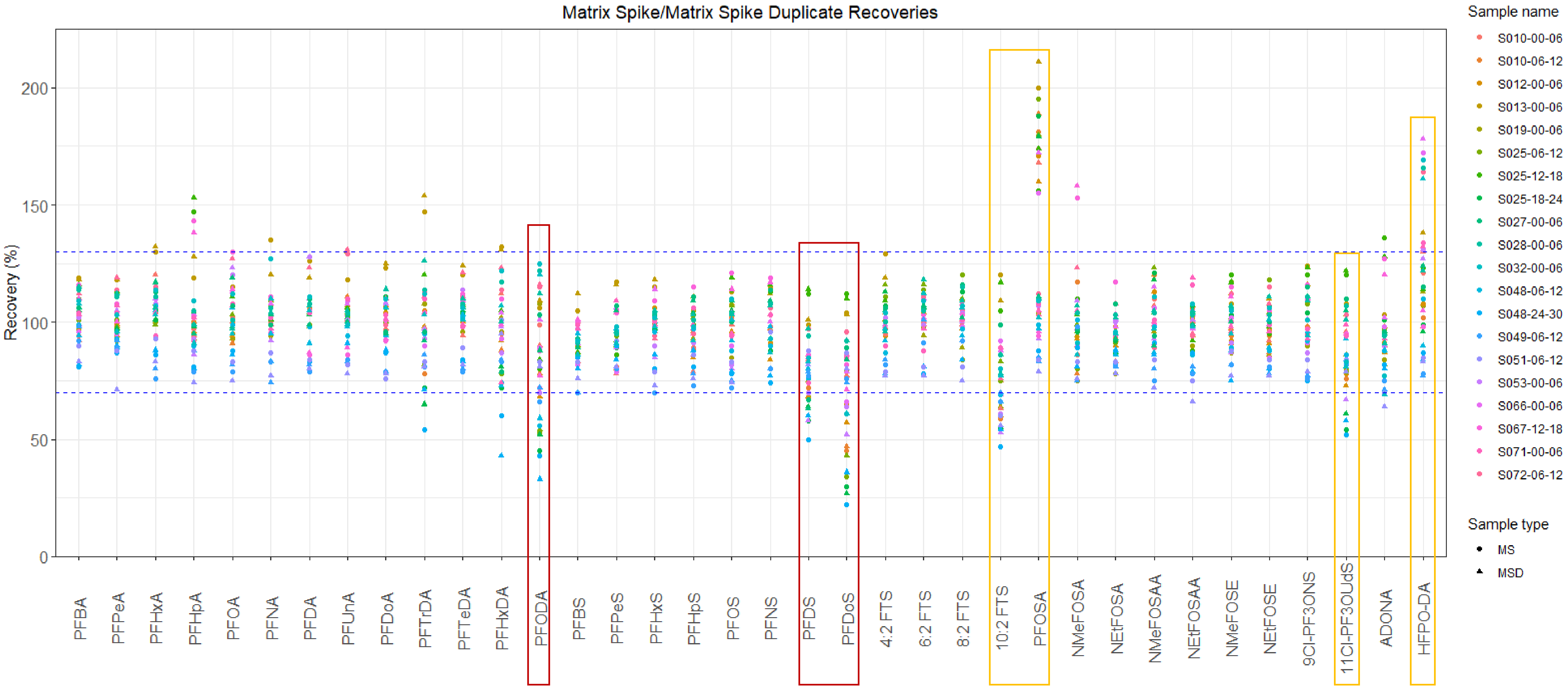
Matrix spike recoveries



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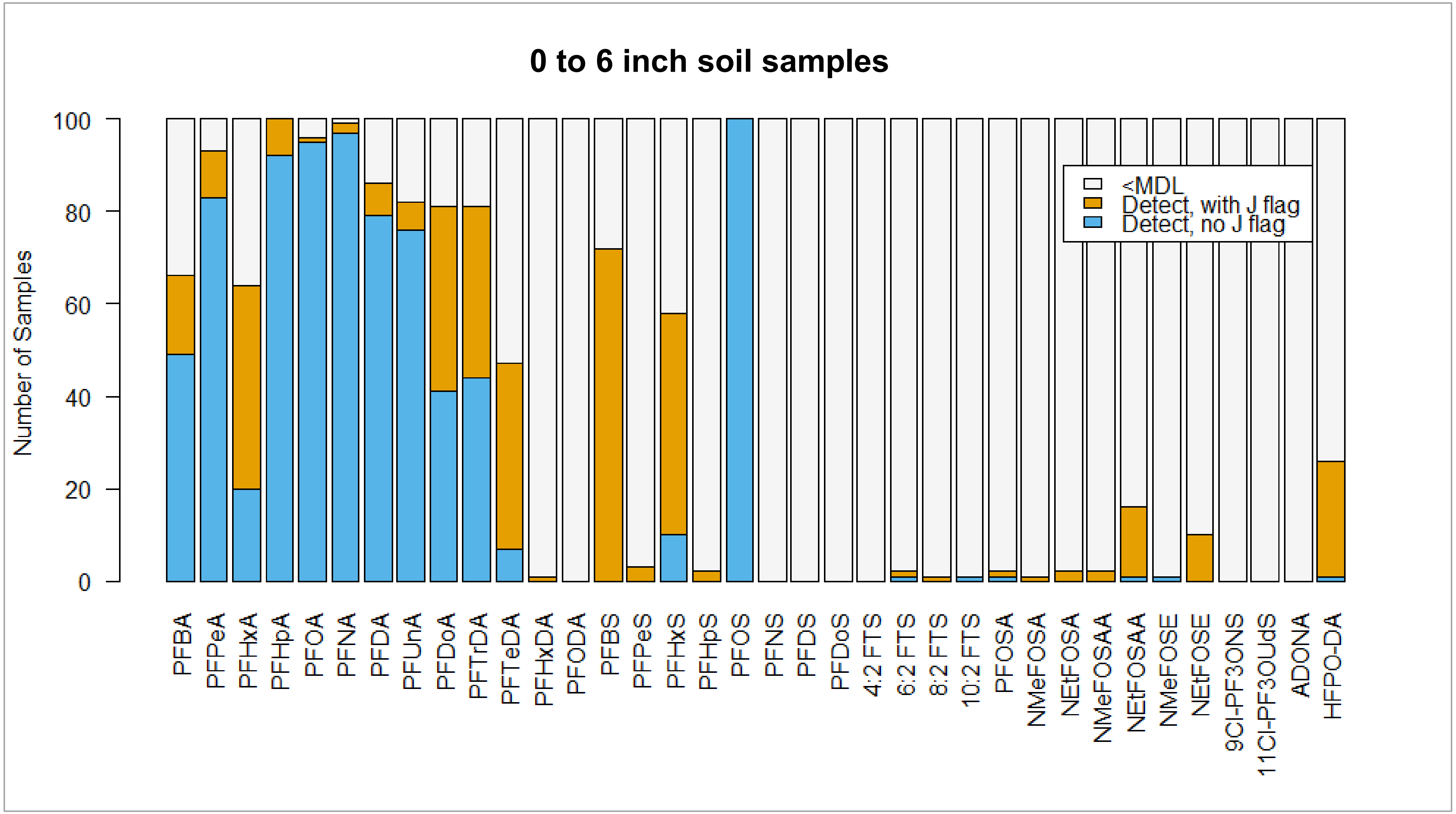
MS = Matrix Spike MSD = Matrix Spike Duplicate

J-flagged data



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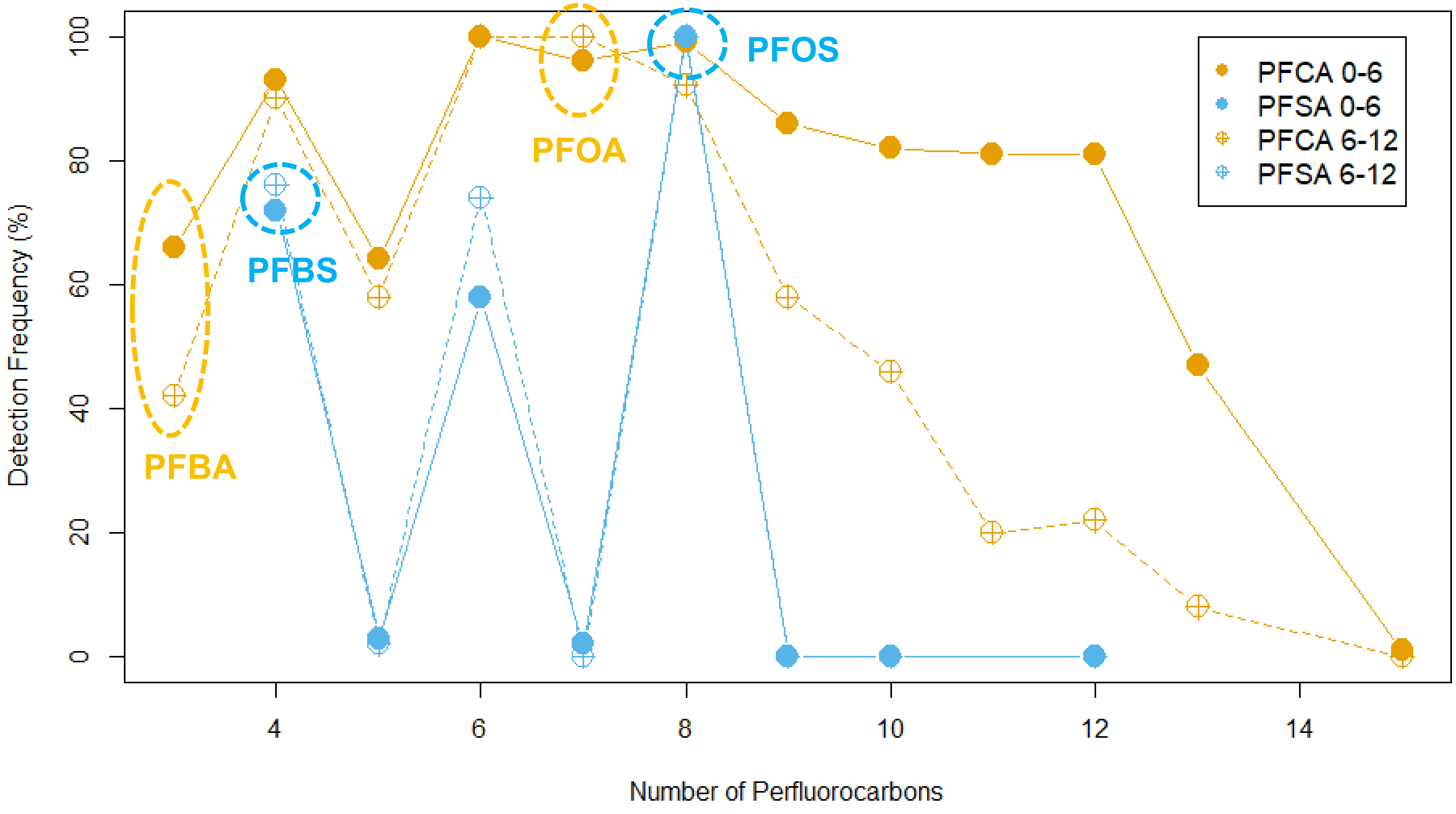
Detection frequency



Detection Frequency of Other Compounds (%)		
	0 to 6 inch soil samples	6 to 12 inch soil samples
4:2 FTS	0	0
6:2 FTS	2	0
8:2 FTS	1	0
10:2 FTS	1	0
PFOSA	2	2
NMeFOSA	1	0
NEtFOSA	2	0
NMeFOSAA	2	2
NEtFOSAA	16	2
NMeFOSE	1	0
NEtFOSE	10	0
9Cl-PF3ONS	0	0
11Cl-PF3OUdS	0	0
ADONA	0	0
HFPO-DA	26	24

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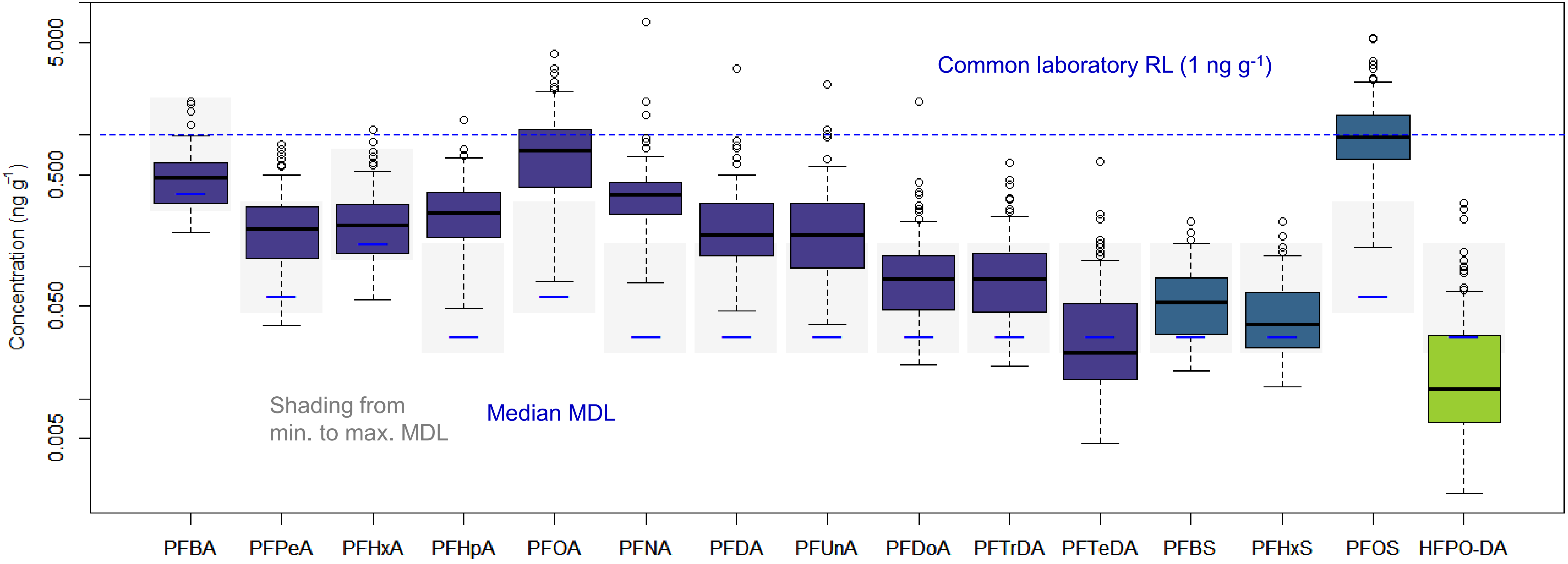
Results with ROS

ROS = Regression on Order Statistics

0 to 6 inch soil samples



Colored boxes span 25th – 75th percentile; median shown as thick black line; whiskers extend up to 1.5 times the interquartile range

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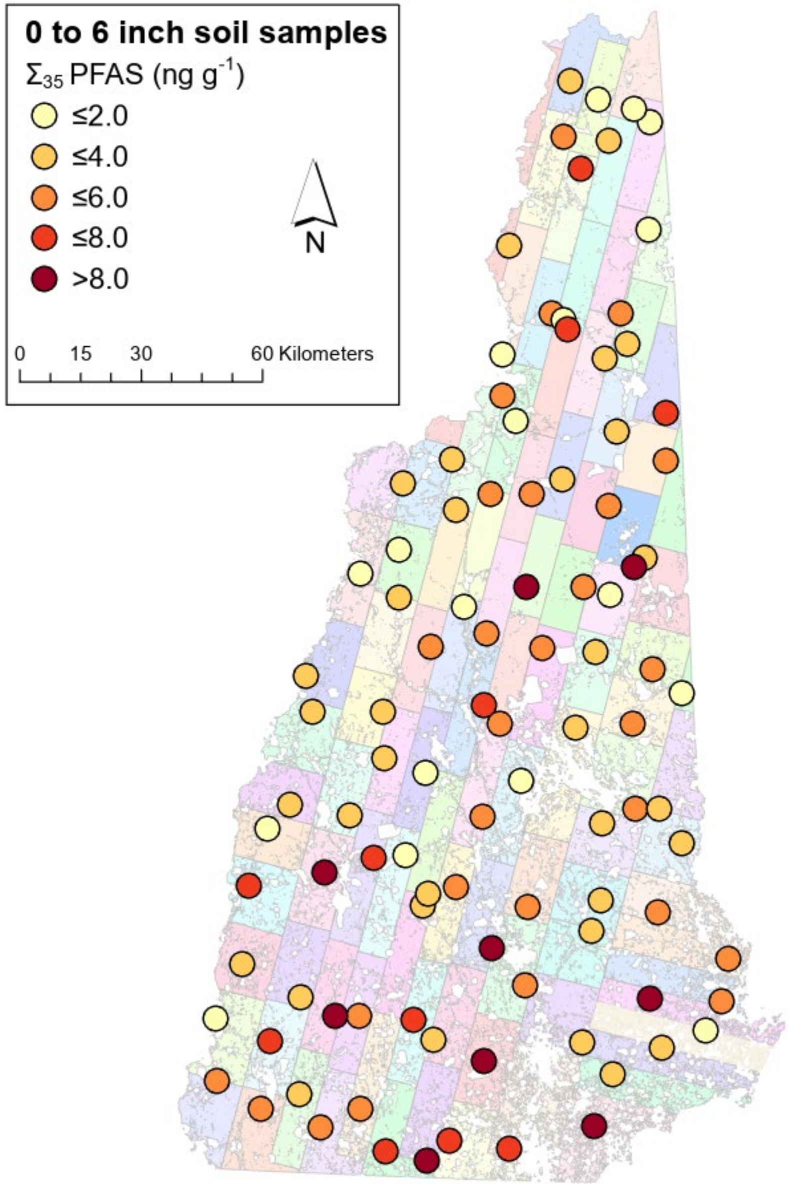
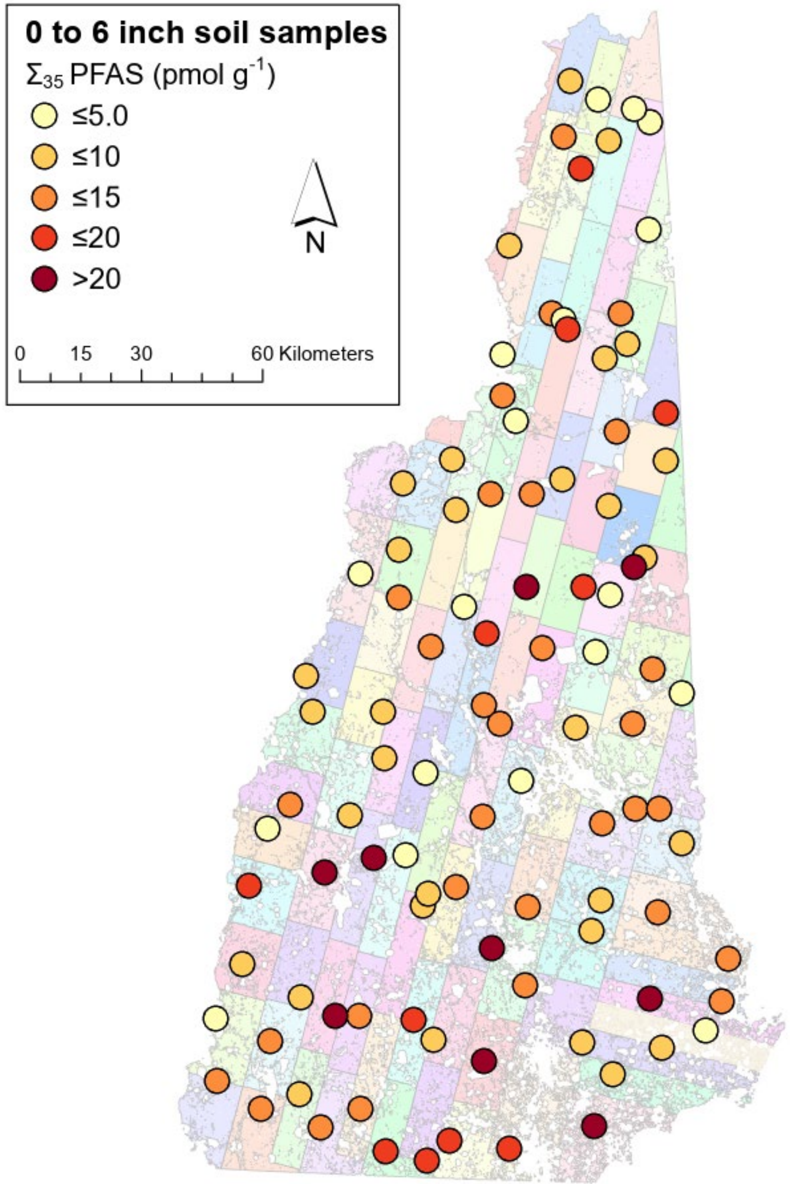
PFAS Sum (Σ_{35}PFAS)





Σ_{35} PFAS calculated assuming ND concentration is 0

Only data for primary samples is shown (no replicates): same for the following maps

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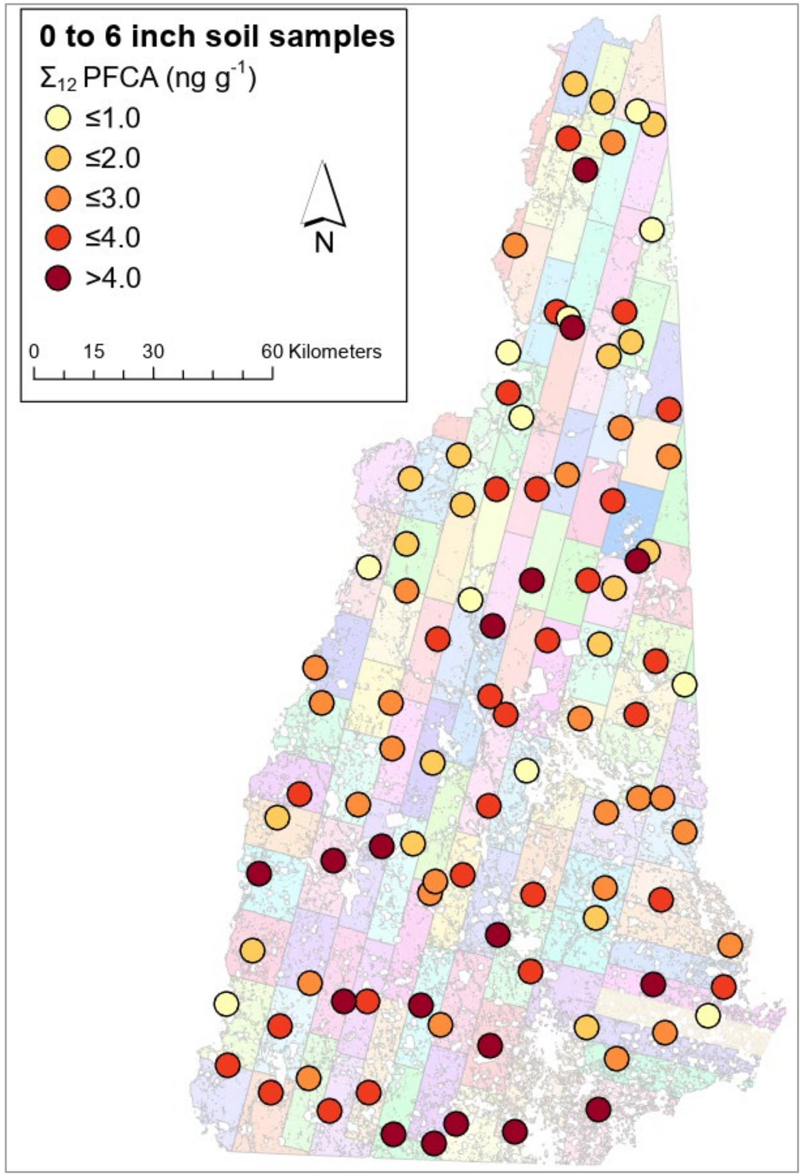
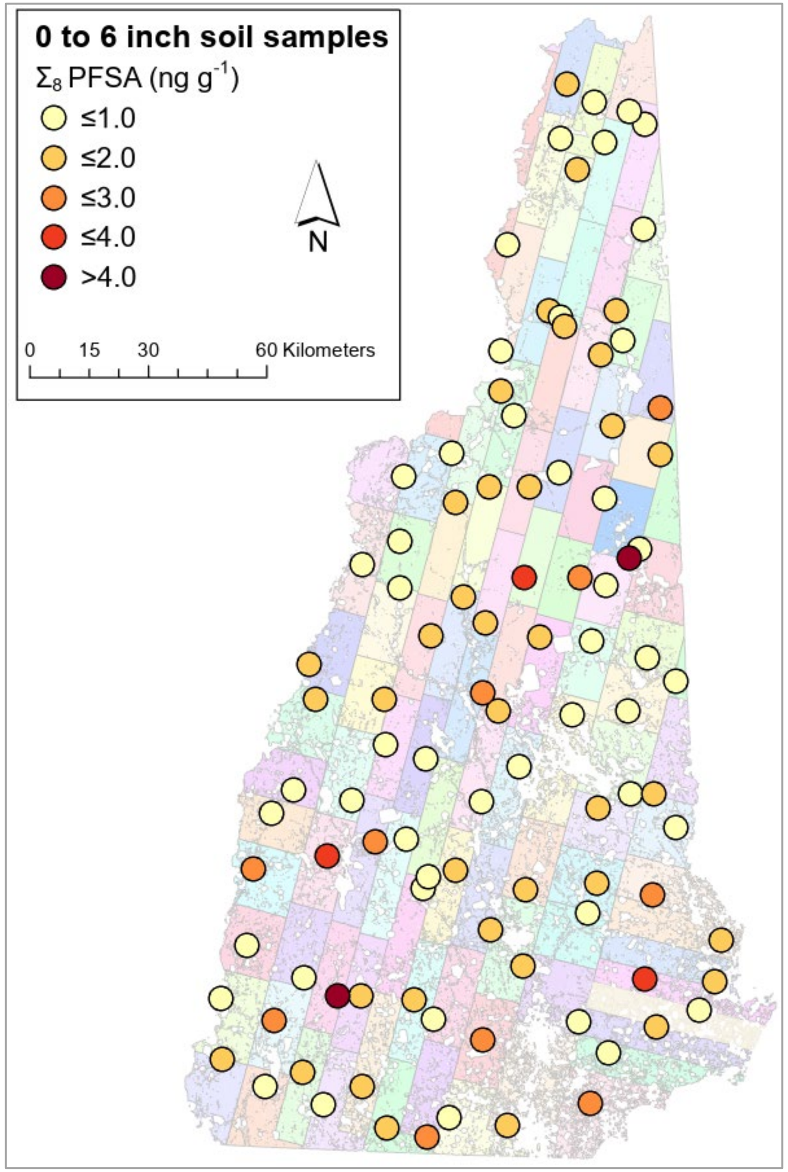
PFCA and PFSA

Σ_{12} PFCA and Σ_8 PFSA calculated assuming ND concentration is 0





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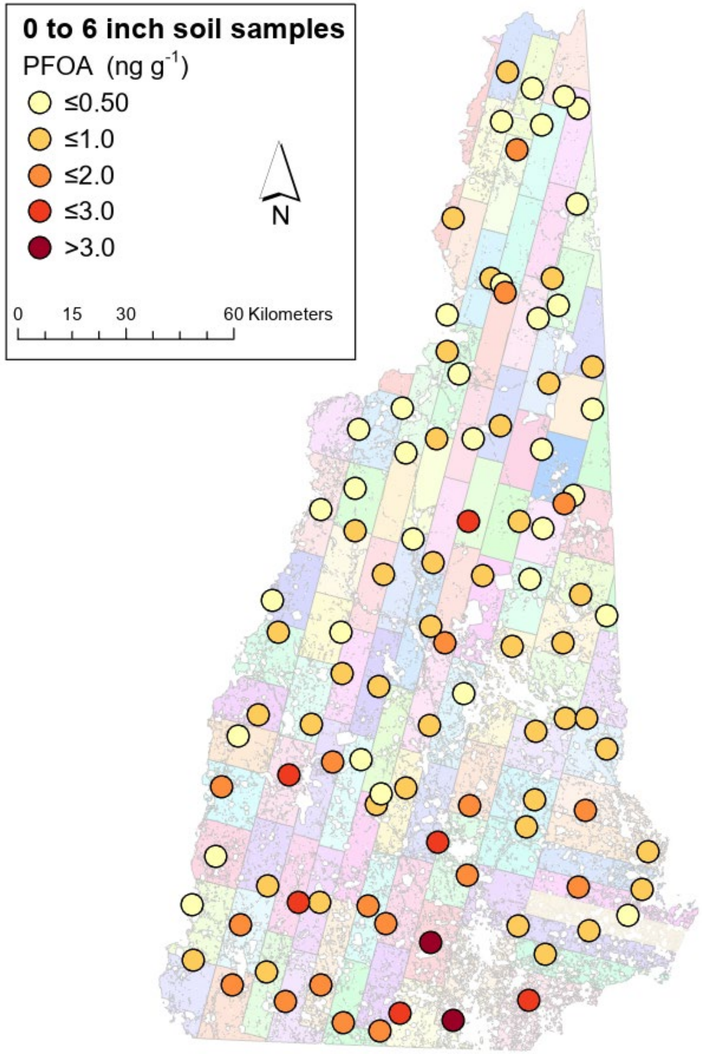
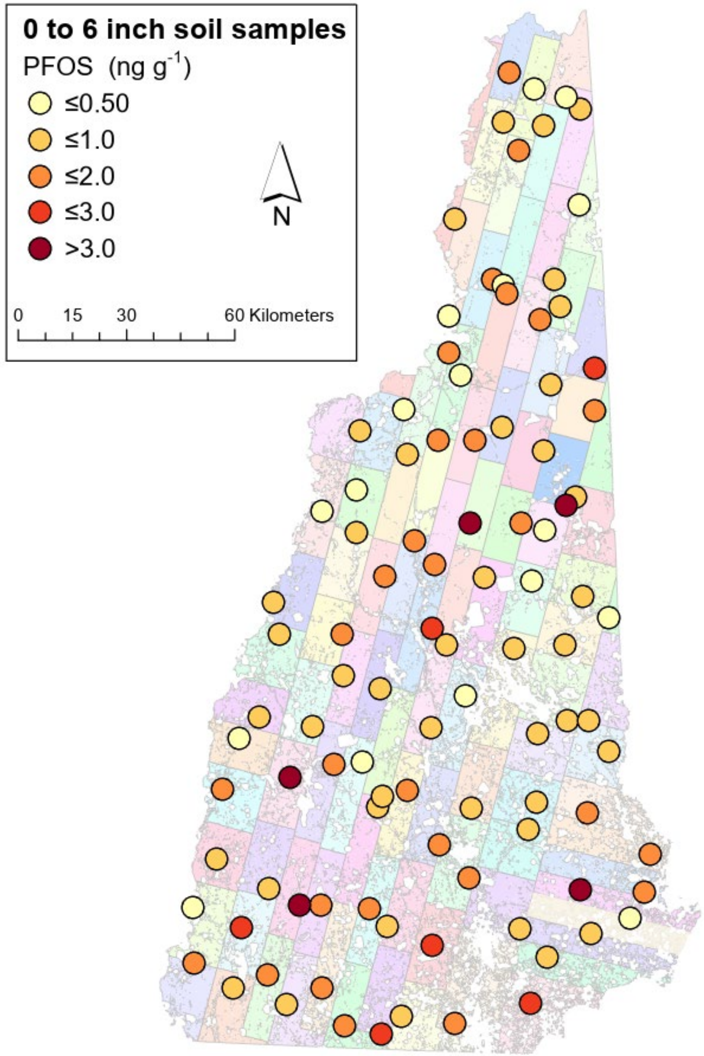
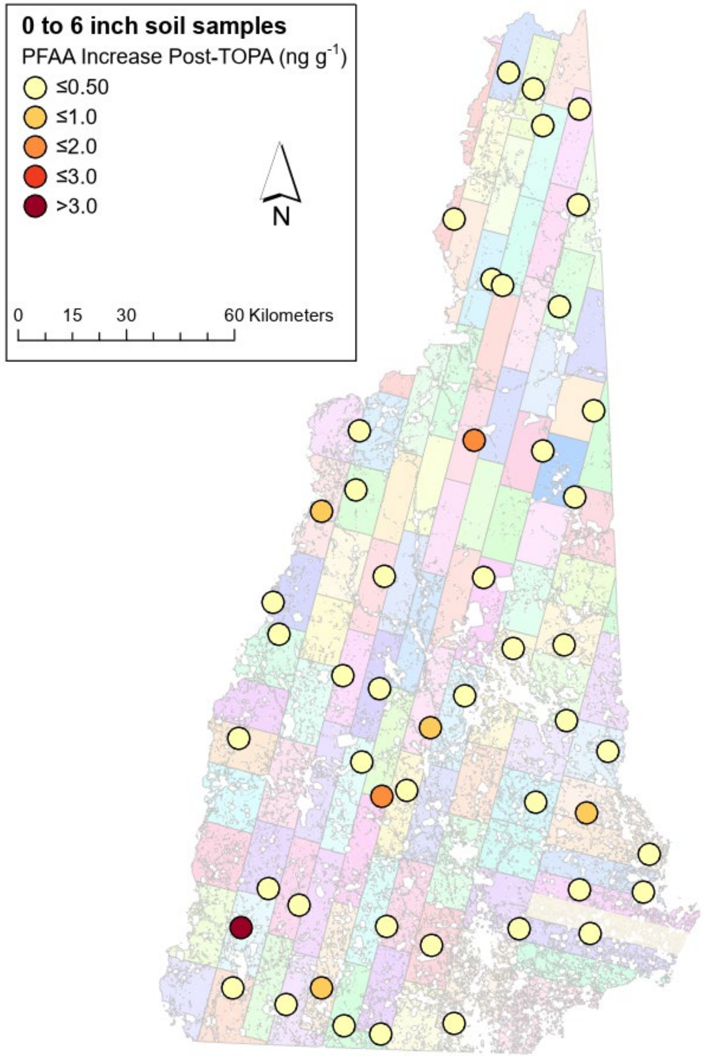
PFOA



PFOS



TOPA



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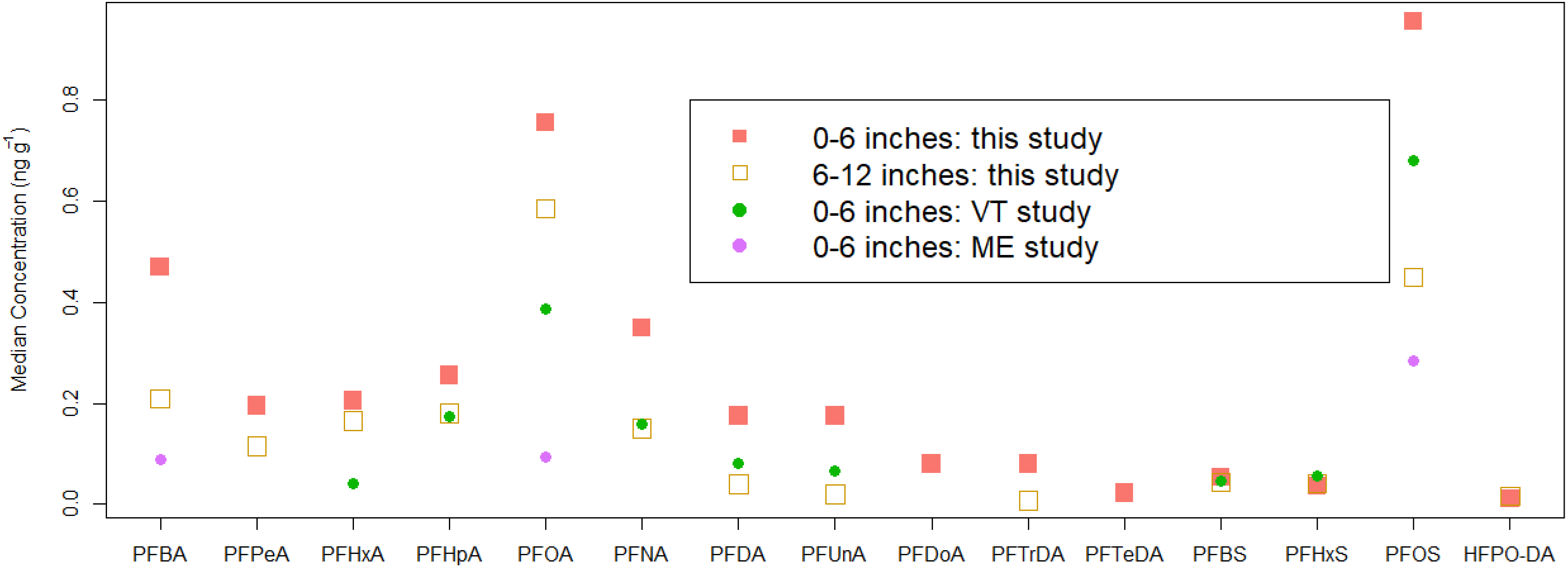
Median PFAS concentrations generally higher in NH compared to ME and VT



Wilcoxon Test: Paired 0 to 6 inch and 6 to12 inch soil samples were significantly different at $p<0.01$ for Σ_{35} PFAS (ng g^{-1})

VT Study: Zhu, W.; Roakes, H.; Zemba, S. G.; Badireddy, A. R., PFAS Background in Vermont Shallow Soils. 2019

ME Study: Roakes, H.; Zemba, S., Background levels of PFAS and PAHs in Maine Shallow Soils. 2022

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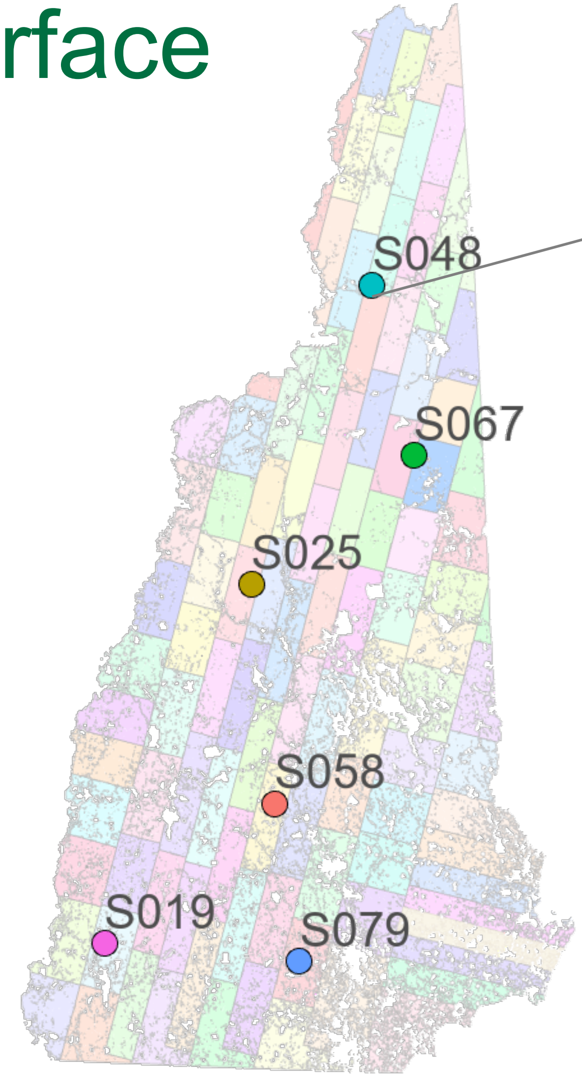
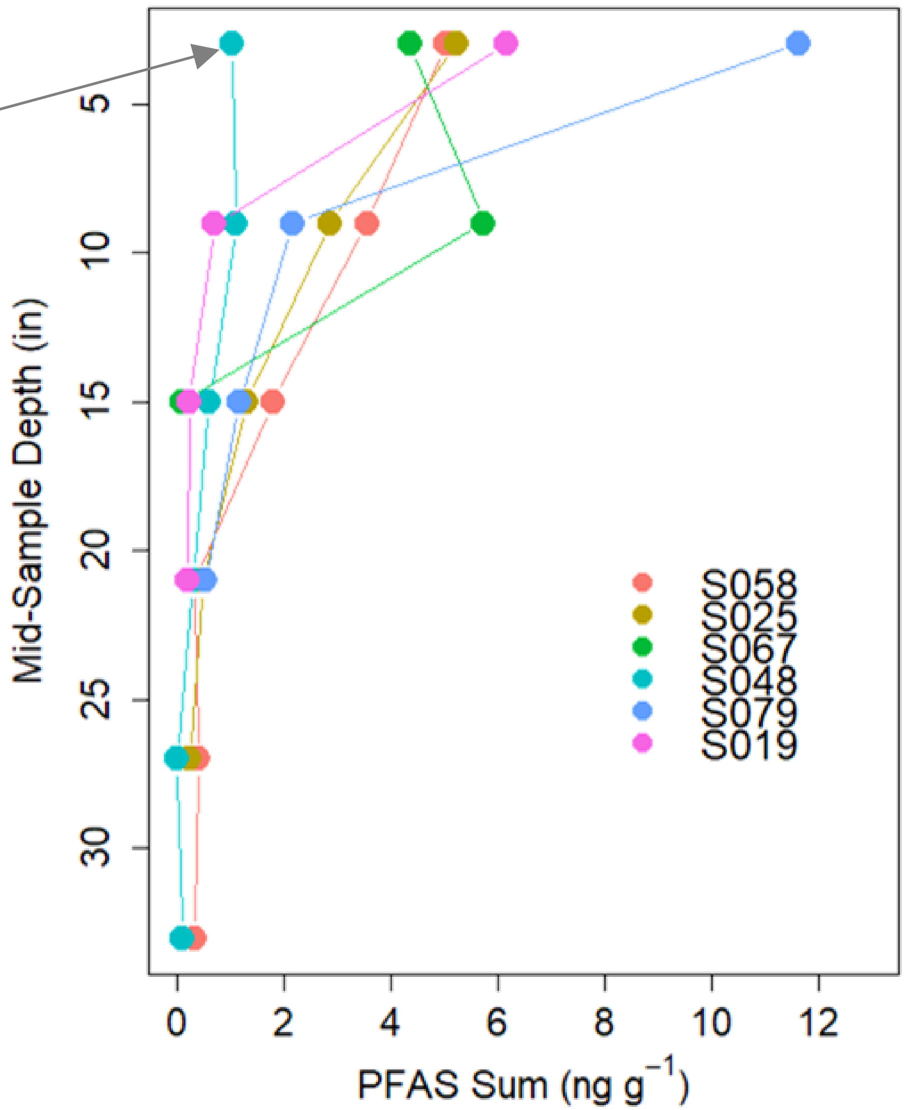
PFAS concentrations typically decrease with depth below land surface





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PFAS soil reservoir

Mass of PFOS in 0-6 inch soil layer across NH: **~3,400 kg PFOS**

Assumptions:

- *Median concentration of PFOS: 0.96 ng/g*
- *Assume soil dry bulk density = 1 g/cm^3*
- *NH land area (includes all land uses types): 23,380 km^2*

To put that into context, it is enough PFOS to contaminate **>7,000 years** of domestic water use in NH at a concentration of 4 ng/L. *Note that this is an unrealistic scenario, but provides some context on the mass of PFOS being discussed.*

Assumptions:

- *79.7 million gallons/day used in NH for domestic uses (drinking, food prep, washing, bathing, etc.) – Dieter et al., 2015*

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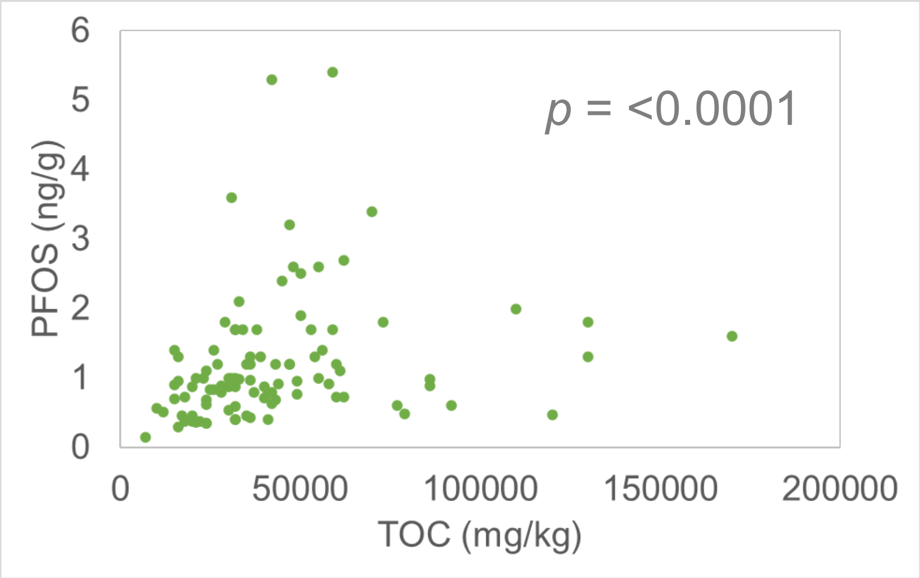
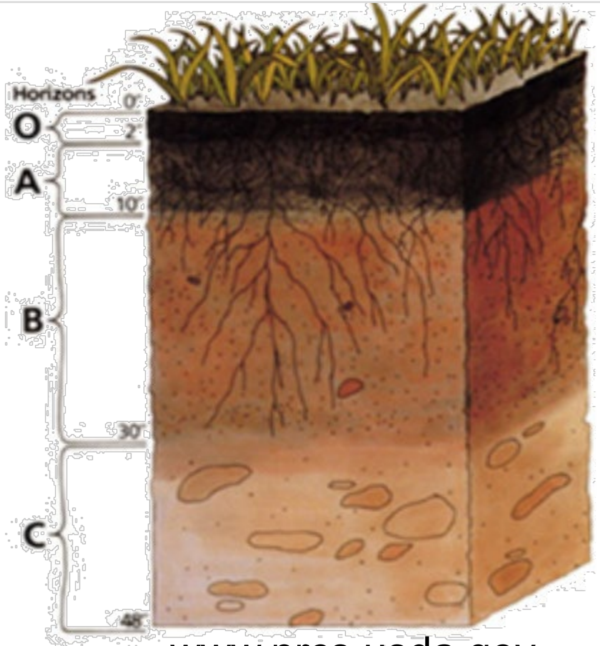
Correlations

Σ_{35}PFAS significantly correlated (spearman rho, $p<0.05$):

- Protein (positive)
- pH (negative)
- Latitude (negative) → particularly for PFCAs
- TOC concentration (positive)
- Percent O horizon in sample (positive)
- Percent B horizon in sample (negative)





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Summary

Soil Occurrence Study

- Equal area grid approach minimized sampling bias and provided equal state-wide coverage
- PFAS detected in every 0 to 6 inch and 6 to 12 inch soil sample
- The soil represents a “reservoir” of PFAS
- PFAS concentrations typically decreased with depth in the soil, suggesting PFAS are, to some extent, retained by the soil
- TOPA results indicate low concentrations of precursors in shallow soil in NH
- Many variables correlate with PFAS: full analysis of data ongoing

Other studies supporting NH regulations

1. **Characterize concentrations of PFAS in shallow soil throughout NH in areas NOT known to be impacted by local PFAS sources.**
   - https://doi.org/10.5066/P9KG38B5
     - Additional confirmatory study targeting 15 locations
       - https://doi.org/10.5066/P9C0FAHD

2. Conduct extensive laboratory experiments to understand how PFAS move from soil and biosolids to water under a variety of environmentally relevant conditions.
   - https://doi.org/10.5066/P9TKSM8S

3. Investigate PFAS groundwater and soil concentrations at two selected sites in NH to compare field observations with soil-to-water transport properties measured in the laboratory.
   - https://doi.org/10.5066/P92C21F6

4. Pilot study to better understand leaching from soils to groundwater in locations sampled as part of (1) above. Do pervasive low concentrations in soil result in groundwater PFAS contamination?

Other relevant national USGS Studies…

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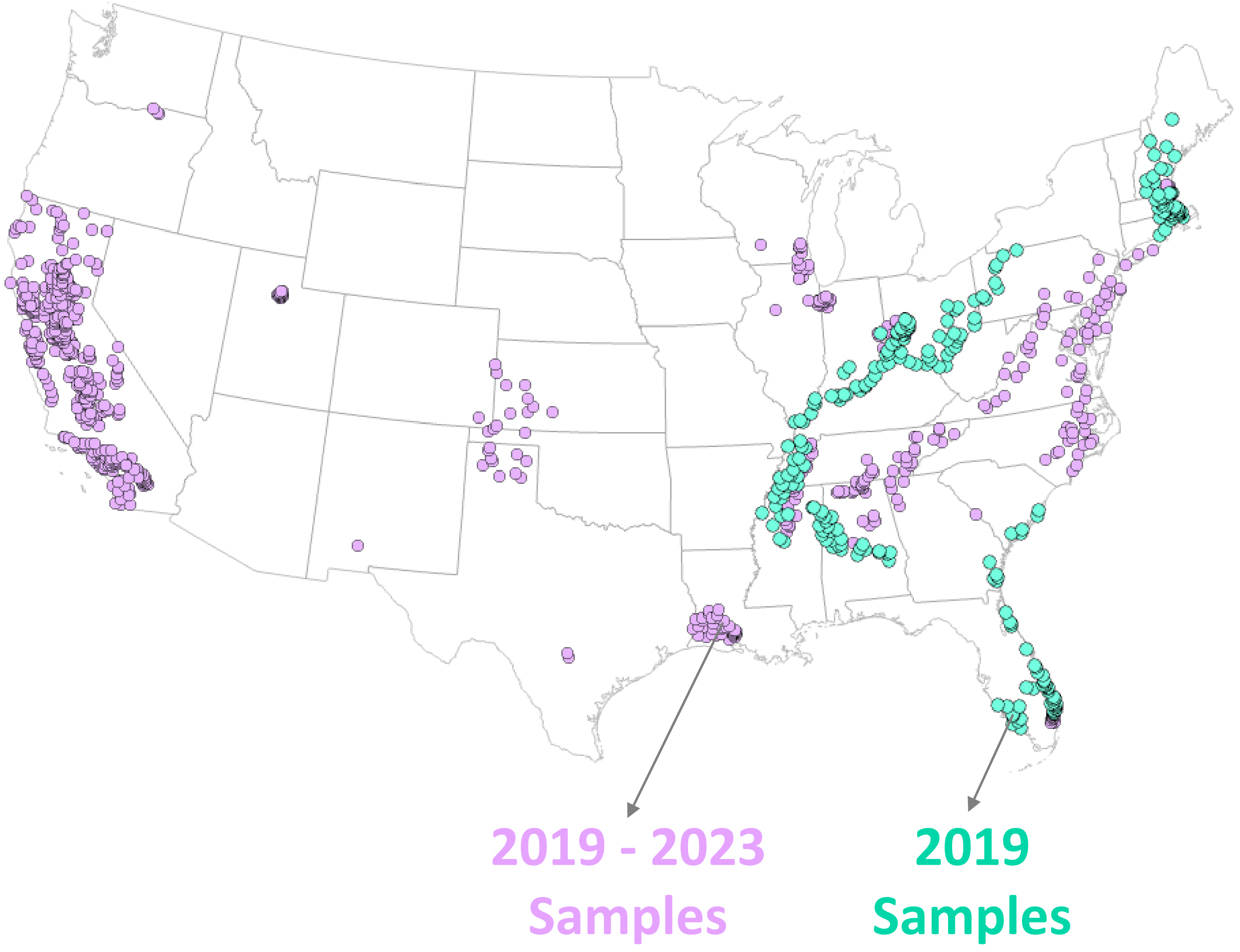
PFAS in groundwater of the United States

- Since 2019, PFAS sampling was included in the National Water Quality Network groundwater (NWQN-GW) and the California Groundwater Ambient Monitoring and Assessment Program – Priority Basin Project (GAMA-PBP), which provides:
  - Long-term, consistent, and comparable information on groundwater quality
  - Information on groundwater quality trends
  - Assessments of natural and human impacts



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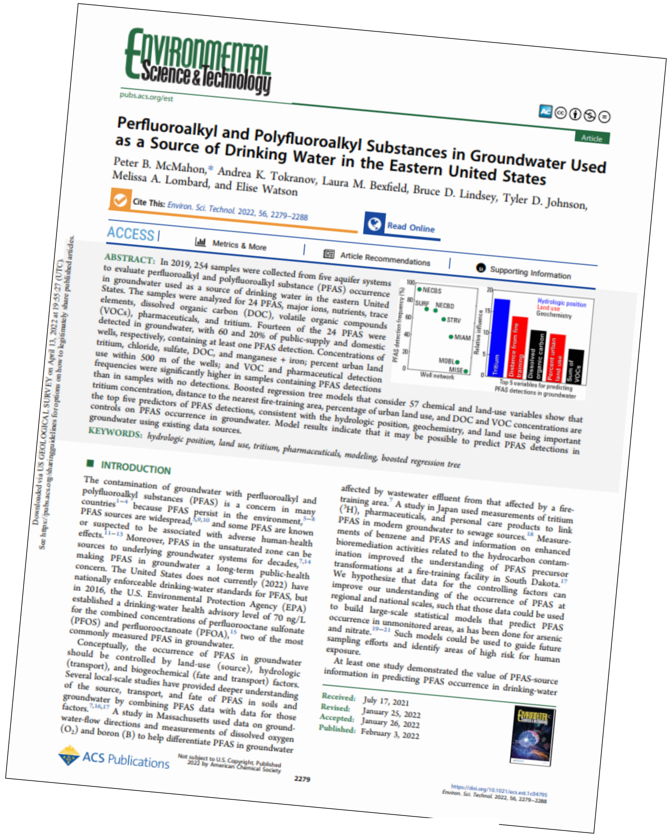
PFAS in groundwater of the United States

National Water Quality Network - groundwater :

- Composed of 82 networks of 20-30 wells each
- Well depths typically represent the depth zone used for drinking water, or target specific land uses
- Sampled on a 10-year cycle to evaluate decadal-scale trends

California Groundwater Ambient Monitoring and Assessment Program

- Cooperative program with the California State Water Boards
- Similar design to NWQN-GW for assessing water quality and monitoring trends
- Networks in areas used for drinking water supply statewide


Environmental Science & Technology

Perfluoroalkyl and Polyfluoroalkyl Substances in Groundwater Used as a Source of Drinking Water in the Eastern United States

Peter B. McMahon,* Andrea K. Tokranov, Laura M. Bexfield, Bruce D. Lindsey, Tyler D. Johnson, Melissa A. Lombard, and Elise Watson

Cite This: Environ. Sci. Technol. 2022, 56, 2279−2288

https://doi.org/10.1021/acs.est.1c04795

Boosted regression tree model

57 Potential Predictor Variables Considered

Hydrologic Position

Tritium
Well depth

Geochemical Conditions

pH
Dissolved oxygen
Turbidity
Total dissolved solids
Specific conductance
DOC
Volatile organic compounds
Pharmaceuticals

Total nitrogen
Organic nitrogen
Orthophosphate
Sulfate
Chloride
Vanadium
Magnesium
And others…

Potential Landscape Sources

Fire training
Petroleum
Plastics, resins
Textile, leather
Fire stations
Public use airport

Oil refinery
Paints, coatings
Metal coating
National defense
Wastewater treatment plant
And others…

Urban Land Use/N2 Loading

Natural land (%)
Agricultural land (%)
Urban land (%)
Nitrogen loading to septic systems

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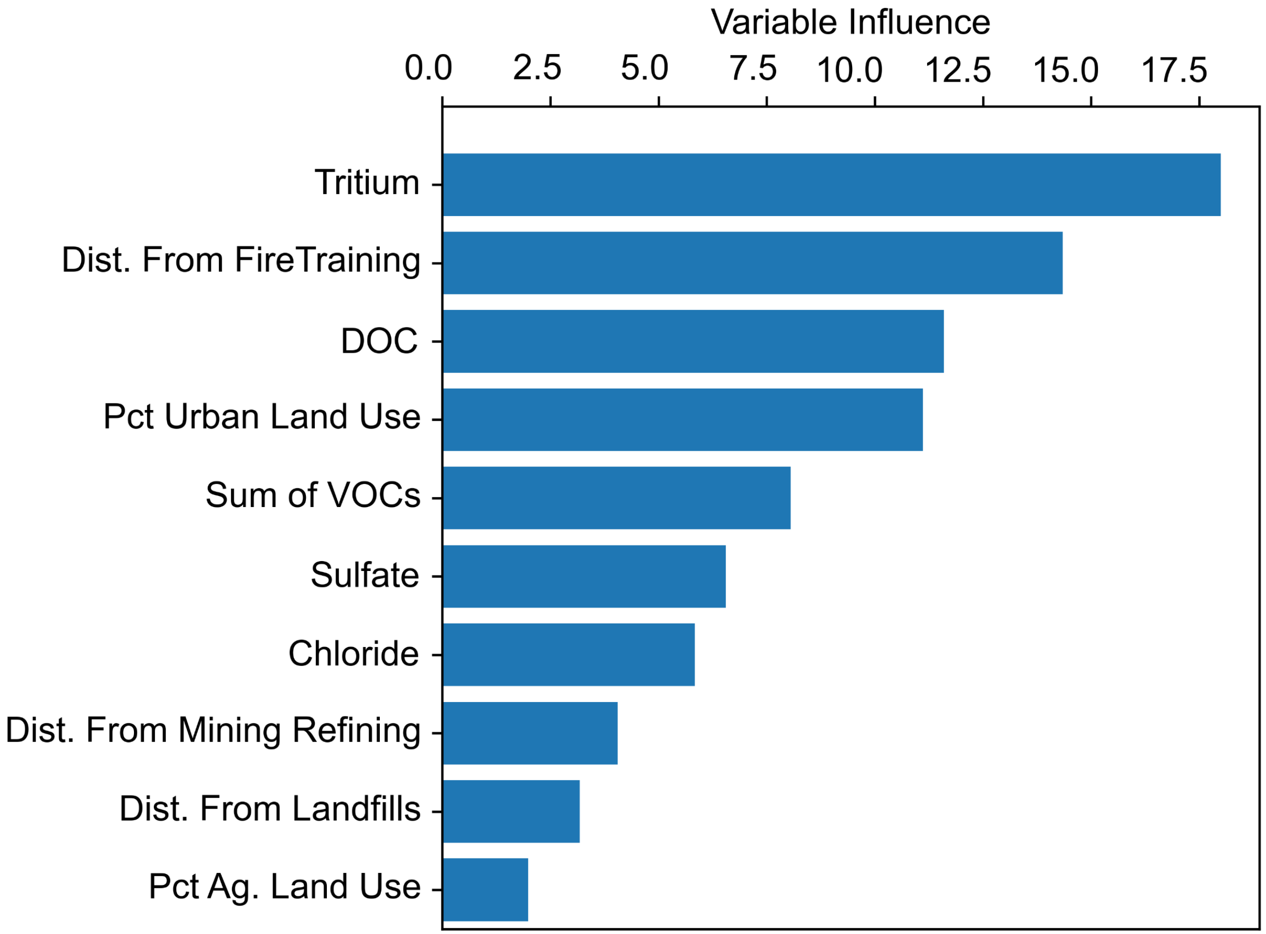
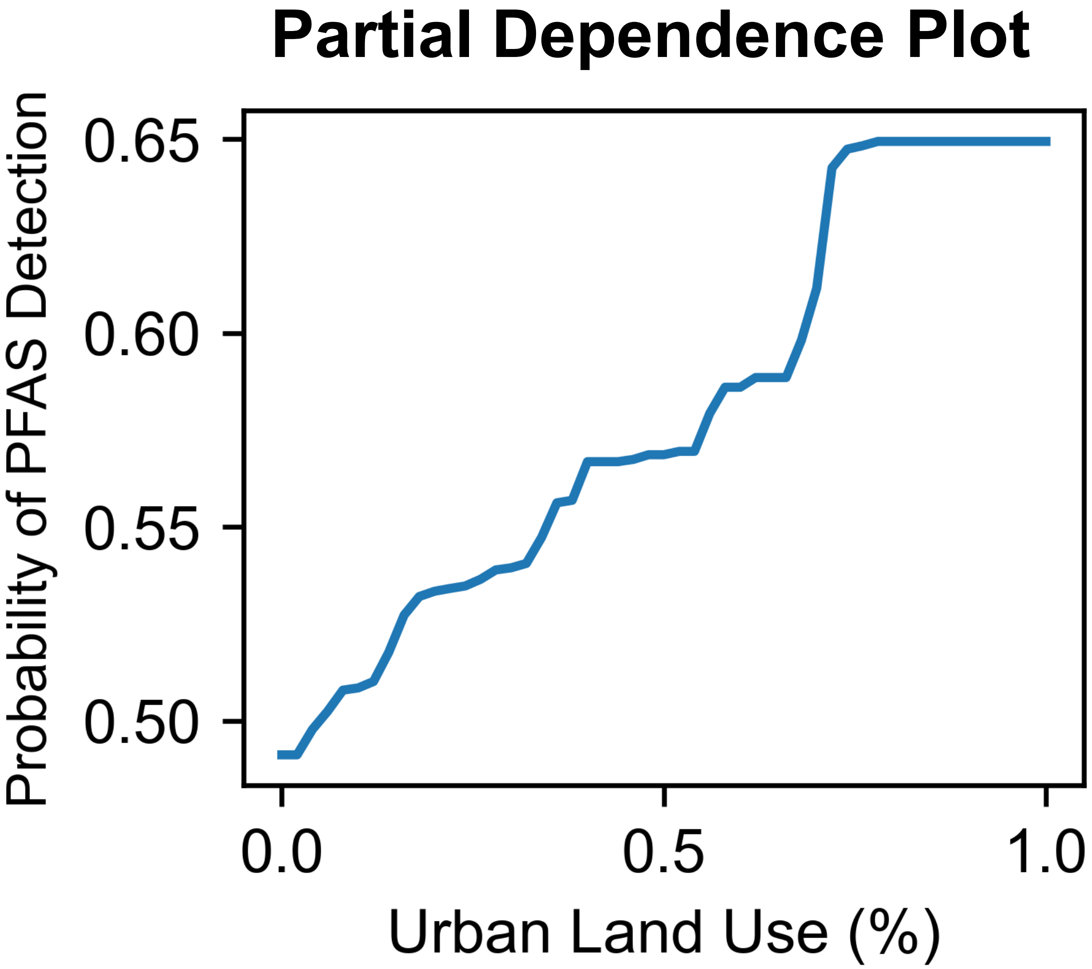
https://doi.org/10.1021/acs.est.1c04795

Model results





https://doi.org/10.1021/acs.est.1c04795

PFAS laboratory

Location: Eastern Ecological Science Center, Kearneysville, WV

Purpose: Research laboratory

High Resolution Mass Spectrometer:

- Targeted & non-targeted analysis
- Variety of matrices
- Can work with very small sample volumes

https://www.usgs.gov/media/videos/usgs-laboratory-analysis-and-polyfluoroalkyl-substances-pfas

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Thank you!

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