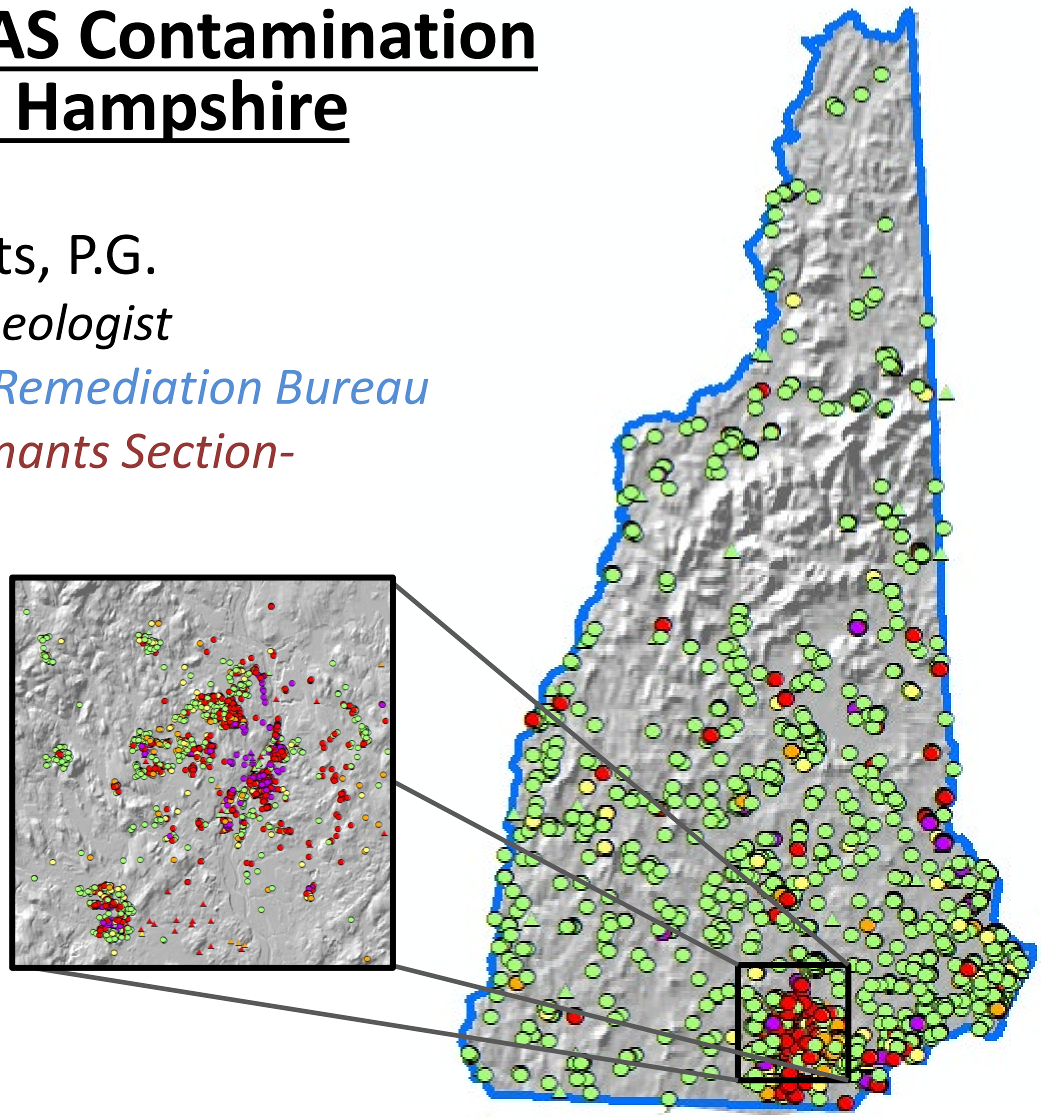
Evaluating Sources, Fate, and Transport in an Area of Regional PFAS Contamination in Southern New Hampshire

Jeffrey Marts, P.G.

Senior Hydrogeologist

NHDES Hazardous Waste Remediation Bureau

-Emerging Contaminants Section-



NEWMOA Northeast Conference

The Science of PFAS:

Public Health & The Environment

April 5, 2022

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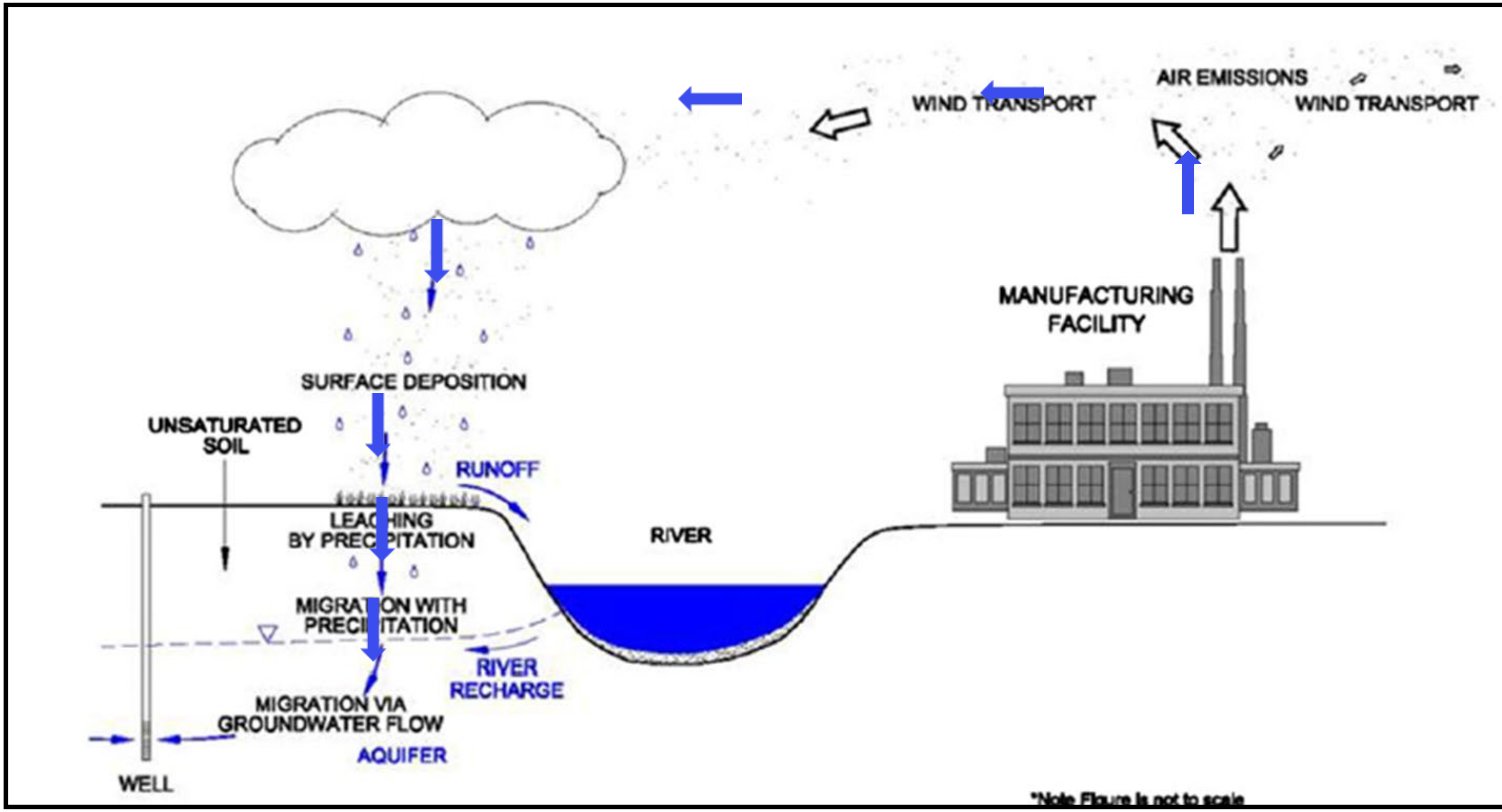
Air Release

Conceptual Pathway to Groundwater Contamination



Davis et al., 2007, *Chemoshpere*

Challenges Associated with the Investigation and Mitigation of PFAS Air Releases

- Wide geographic area involved
- Numerous impacted public and private wells
- Changes in PFAS composition released to the air over time spanning years to decades
- Multiple geologic settings
- Potential for co-mingled plumes
- Release/transformation of precursors
- Changes in target analytes and reporting limits

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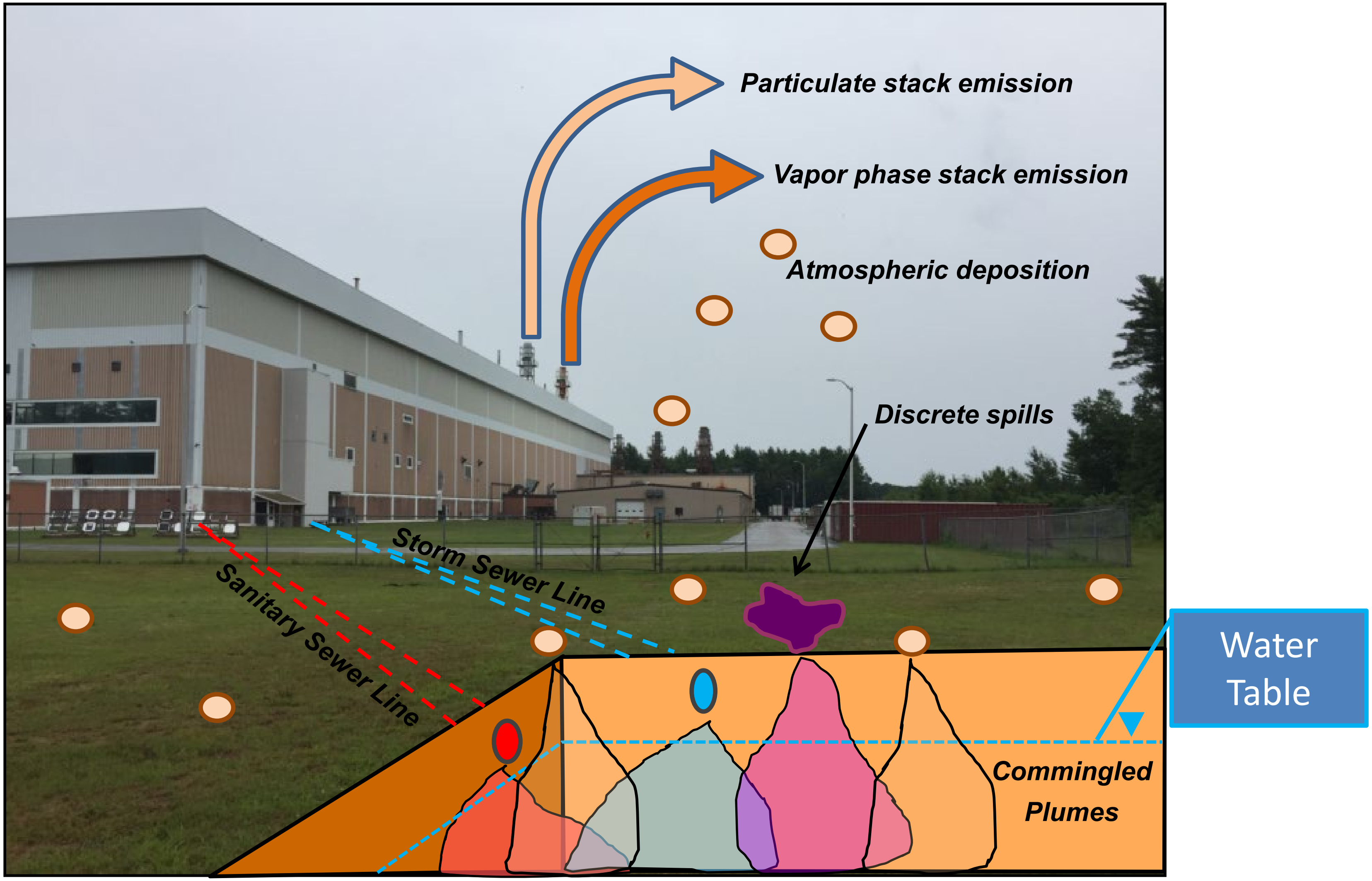
Potential Release Pathways and Commingling of PFAS Releases



Schematic representation of potential PFAS release pathways and commingled plumes for illustration purposes only (not intended to reflect actual site conditions).

Partial Timeline – 2016 to Present

- 2016 – PFAS discovered in water sample collected at a coating facility
  - *Prompts investigation that included sampling private water supply wells*
  - *USEPA Lifetime Health Advisory Issued / NH Adopted as AGQS (70 ng/L for PFOA and PFOS, combined)*
- September 30, 2019 – Effective date for four new PFAS AGQS/MCL
  - *PFOA – 12 ng/L (Parts per trillion – ppt)*
  - *PFOS – 15 ng/L*
  - *PFHxS – 18 ng/L*
  - *PFNA – 11 ng/L*
- July 2020–PFAS AGQS/MCL's adopted as a matter of law.

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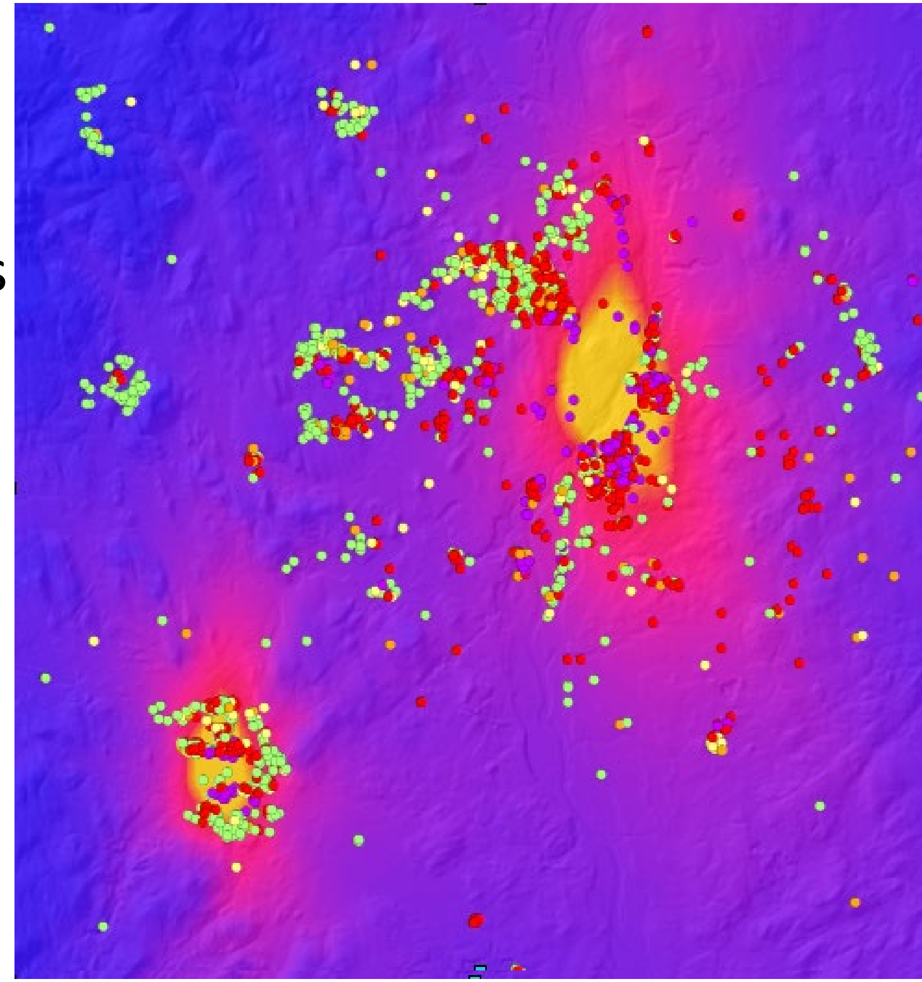
Potential PFAS Air-release Pathway(s)

NHDES used data provided by others to model historic PFOA-only air emissions from three textile coating facilities. Results of the PFOA air modeling are used as a tool to guide the groundwater investigation.

Modeled air deposition of PFOA decreases non-linearly from areas of high deposition(yellow to red) to areas of lower deposition (pink to blue).



The image on this slide was created by adding two model outputs using GIS raster math in 2019. The color scaling for PFOA deposition is based on a standard deviation 'stretch' to highlight minor differences in modeled deposition further from the source. The image covers an area approximately 14 miles wide.

Groundwater PFOA (ng/L)

- 0 - 6
- >6 - 9
- >9 - 12
- >12 - 70
- >70

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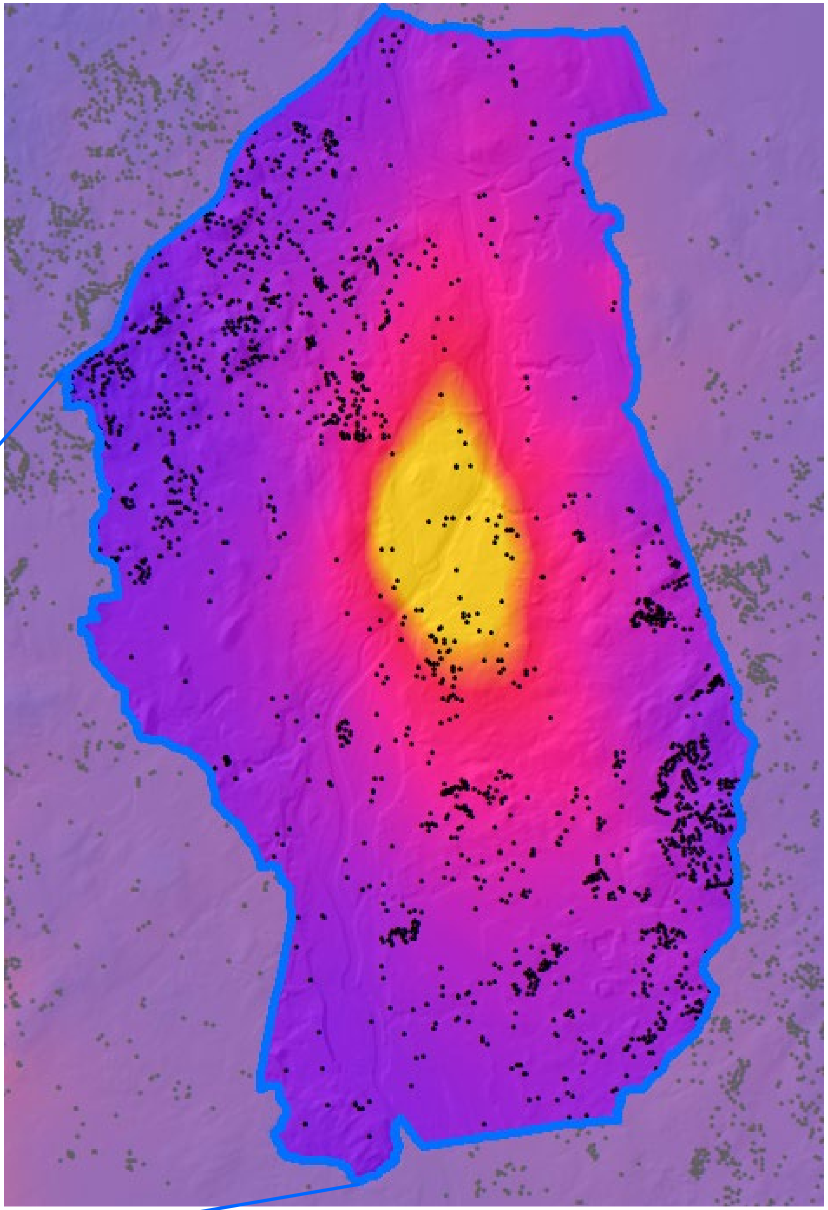
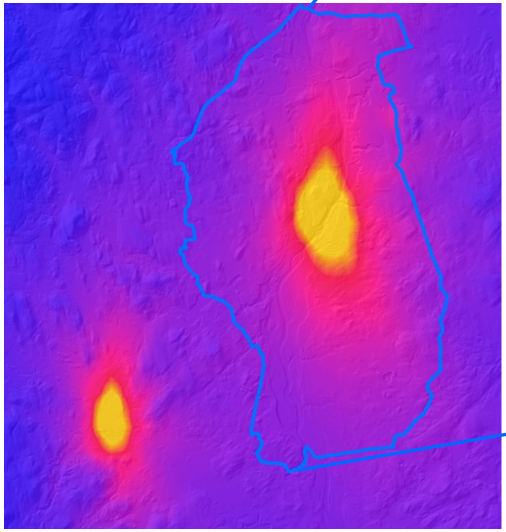
64 Square Mile Consent Decree Area

One textile coater entered into a 2018 Consent Decree with NHDES that defined a 64 square-mile area.

Thousands of wells, both private and public, are located in this area.





Wells georeferenced in the NHDES water well inventory are shown as black dots (above).

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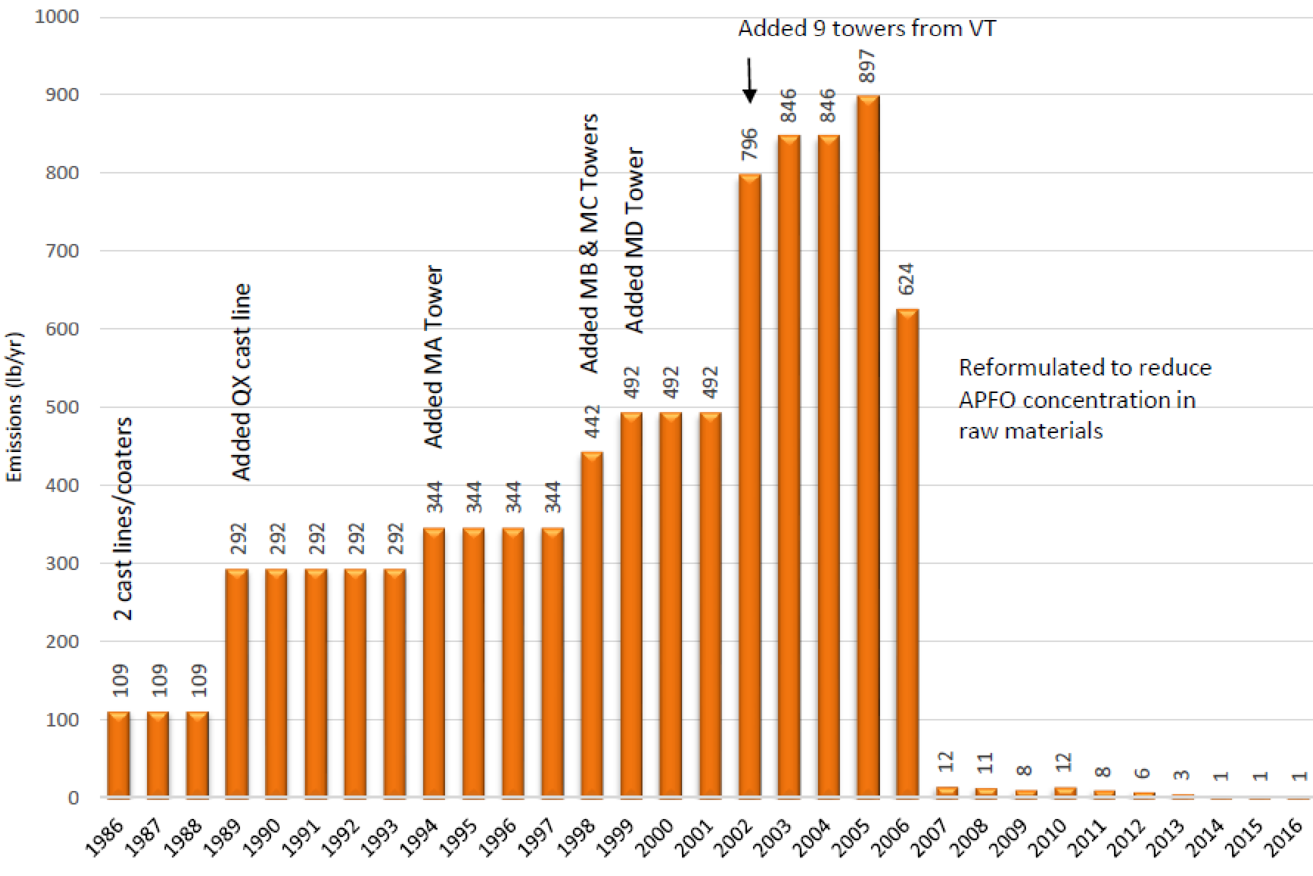
PFAS Emissions History
Variable Over Time

ESTIMATED HISTORICAL PFOA AIR EMISSIONS



Reformulation of ingredients in the mid-2000's reduced PFOA emissions, but the history of other of other PFAS emissions is not know.

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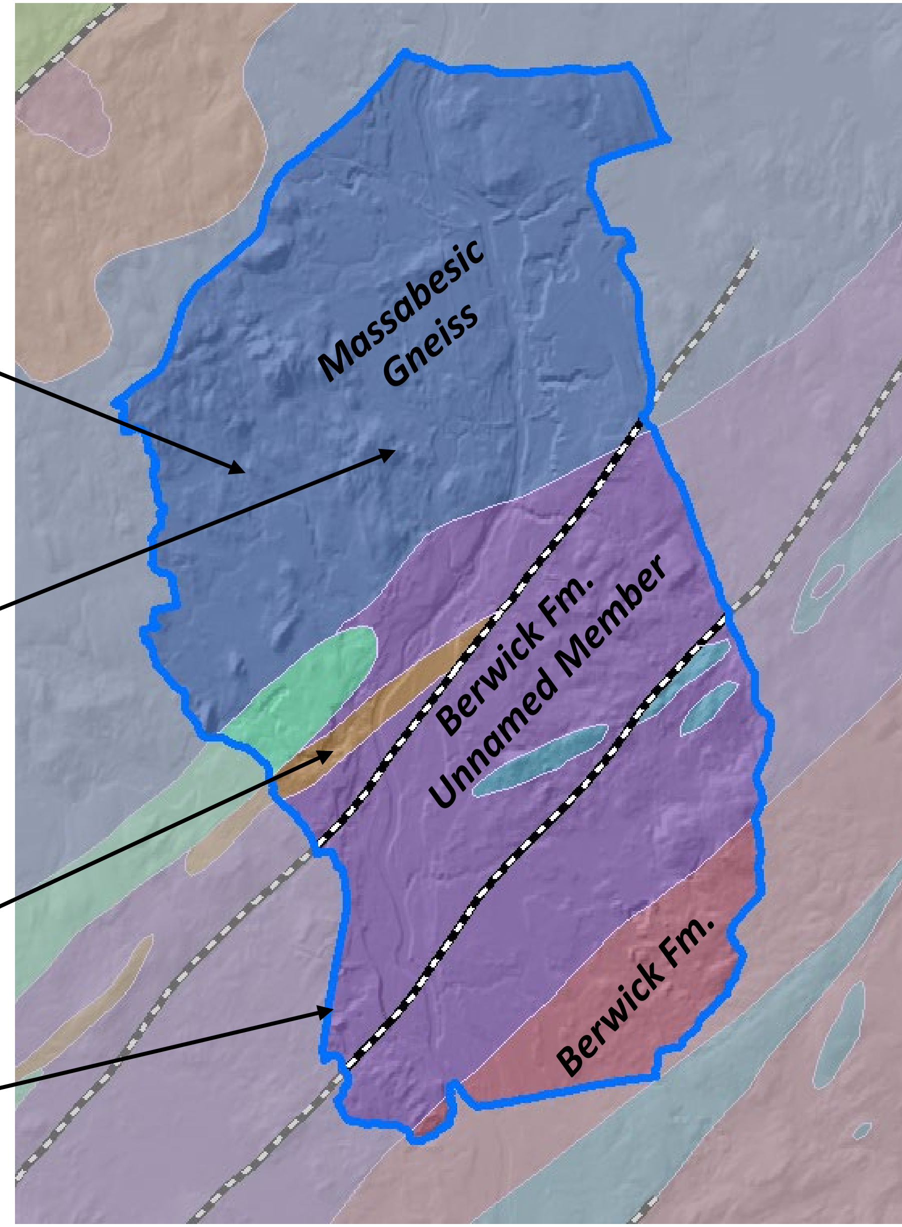
Bedrock Geology

Two outcrops of Massabesic Gneiss

Berwick Formation Gove Member.

Berwick Formation Unnamed Member.



Bedrock Geology Credit: Bennett, D.S., Lyons, J.B., Wittkop, C.A., and Dicken, C.L., 2006, Bedrock geologic map of New Hampshire, a digital representation of Lyons and others 1997 map and ancillary files: U.S. Geological Survey Data Series 215, 1 CD-ROM.

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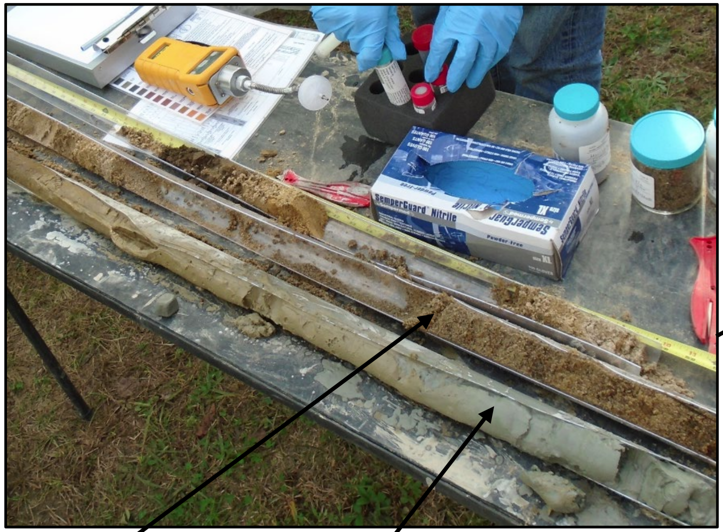
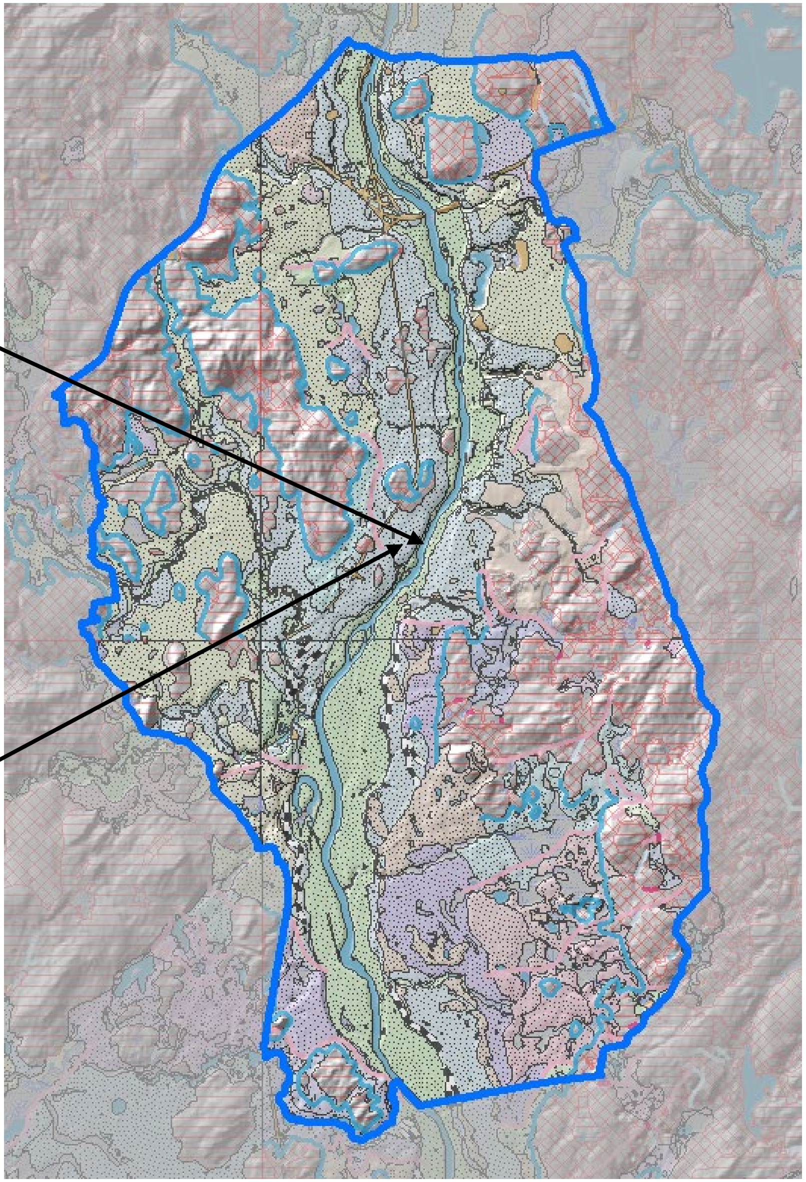
Surficial Geology

Glacial till and alluvial deposits.



Fluvial and Glaciolacustrine deposits from a drilling core.



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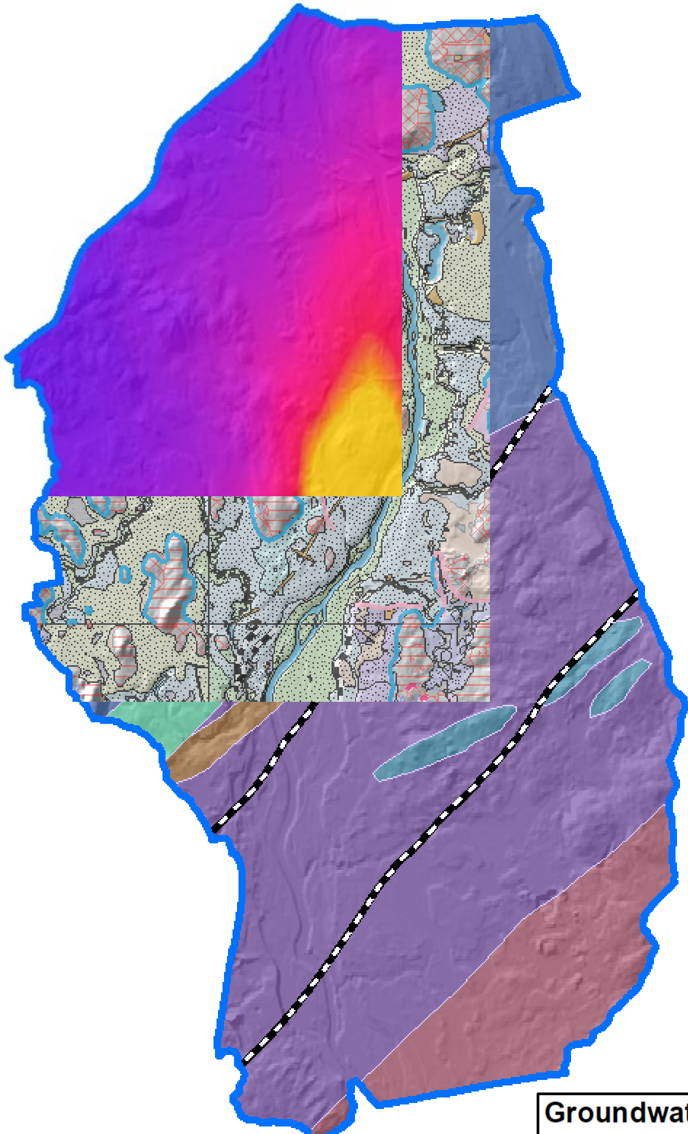
Surficial Geology Digital GIS Compilation of: Koteff, Carl, 2001, Surficial geologic map of the Pinardville 7.5 minute quadrangle, New Hampshire: New Hampshire Department of Environmental Services, Open-File Reports, scale 1:24,000. Koteff, Carl, 2001, Surficial geologic map of the South Merrimack quadrangle, Hillsborough County, New Hampshire: New Hampshire Department of Environmental Services, Open-File Reports, scale 1:24,000. Koteff, Carl, and Stone, B.D., 2000, Surficial geologic map of the Manchester South quadrangle, Hillsborough and Rockingham Counties, New Hampshire: New Hampshire Department of Environmental Services, Open-File Reports, scale 1:24,000. Koteff, Carl, 1976, Surficial geologic map of the Nashua North quadrangle, Hillsborough and Rockingham Counties, New Hampshire: U.S. Geological Survey, Geologic Quadrangle Map GQ-1290, scale 1:24,000.



Air Deposition +

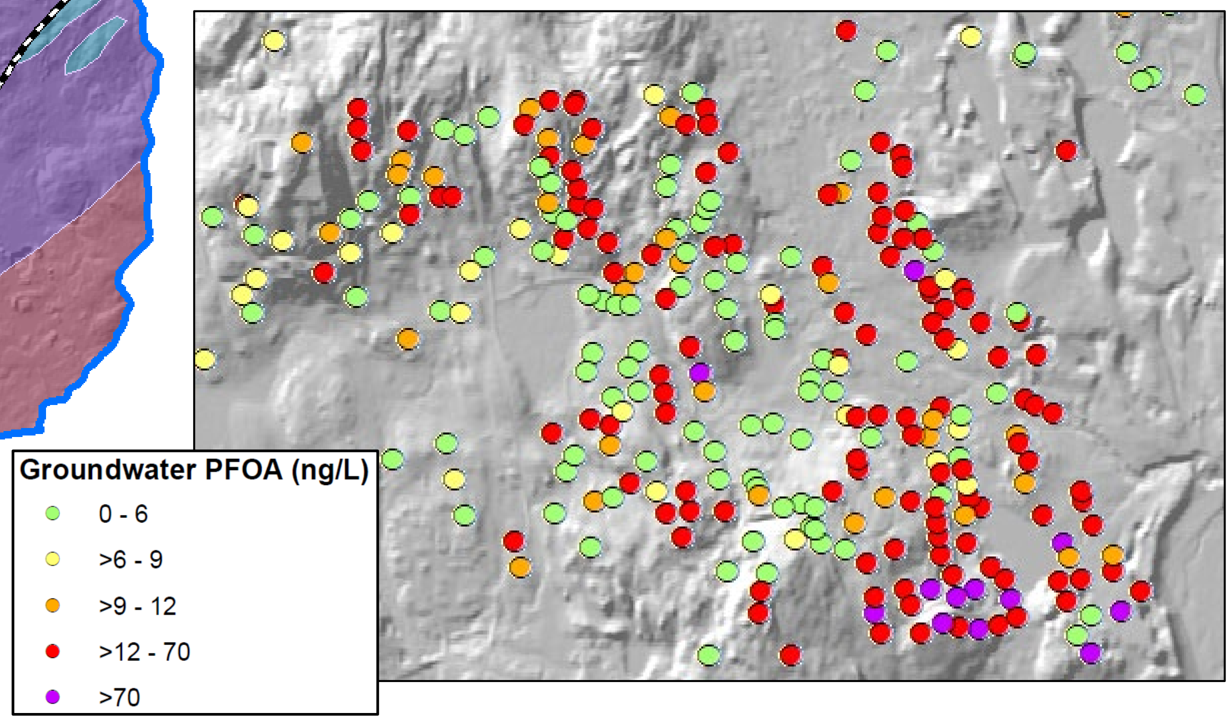
Surficial Geology +

Bedrock Geology +

Time-related factors =

(e.g., changes in chemicals released, precursor transformations, seasonal variation, etc.)

Complex Spatial Distribution of PFAS in Groundwater



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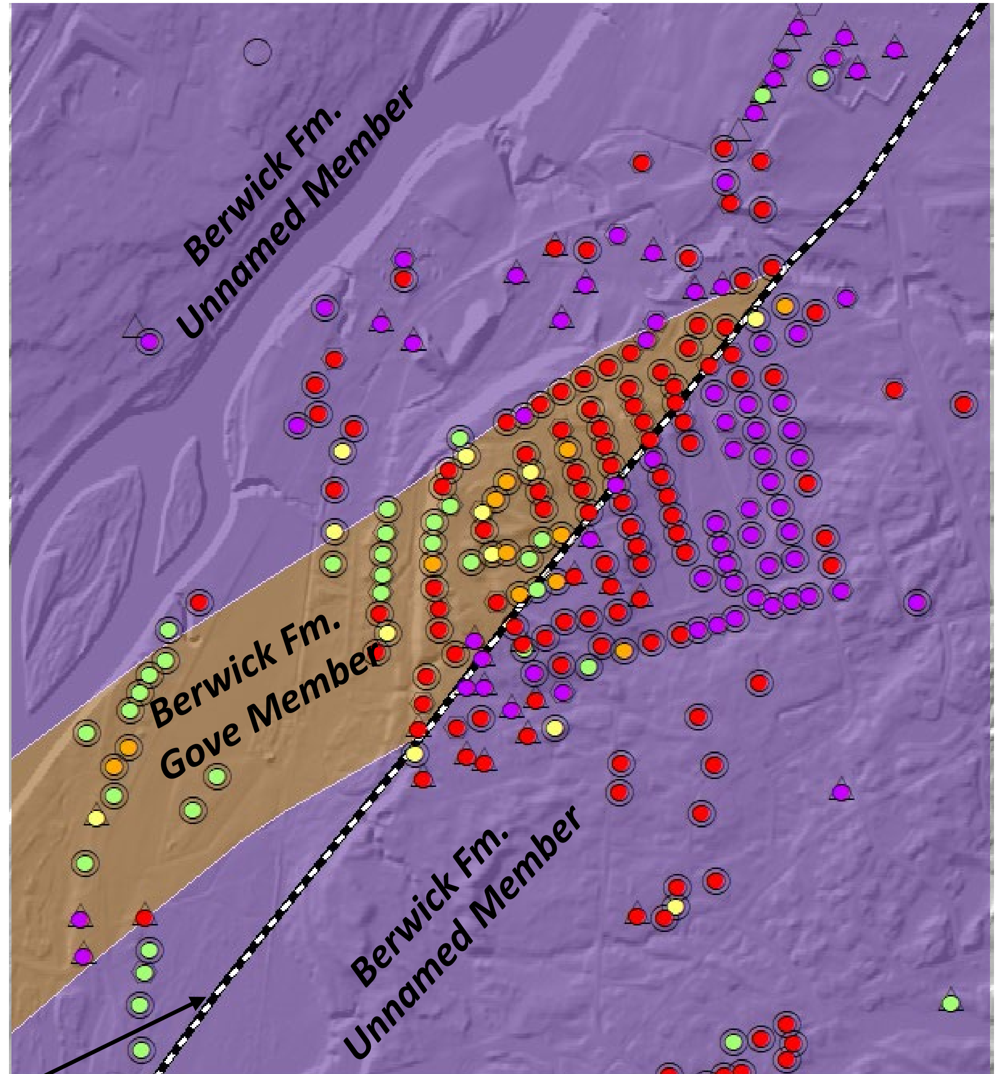
Geologic Factors: Bedrock?

The PFOA concentration in groundwater samples from bedrock wells shown on the map (right) tend to be lower in wells drilled in the Gove Member compared to wells drilled in areas mapped as the Unnamed Member of the Berwick Formation. Similarly, bedrock wells drilled west of the fault zone tend to have lower concentrations of PFOA. A USGS study (Flanagan, et. al., 2016) found the decontamination rate of MtBE was 1.5 times slower in the Berwick Formation compared to other rock units studied, suggesting inherent properties of the rocks influence fate and transport of contaminants.



Groundwater PFOA (ng/L)
- 0 - 6
- >6 - 9
- >9 - 12
- >12 - 70
- >70

Well Type
- BEDROCK
- OVERBURDEN
- CROSSOVER
- UNKNOWN

Silicified? Fault Zone

Bedrock Geology Credit: Bennett, D.S., Lyons, J.B., Wittkop, C.A., and Dicken, C.L., 2006, Bedrock geologic map of New Hampshire, a digital representation of Lyons and others 1997 map and ancillary files: U.S. Geological Survey Data Series 215, 1 CD-ROM.

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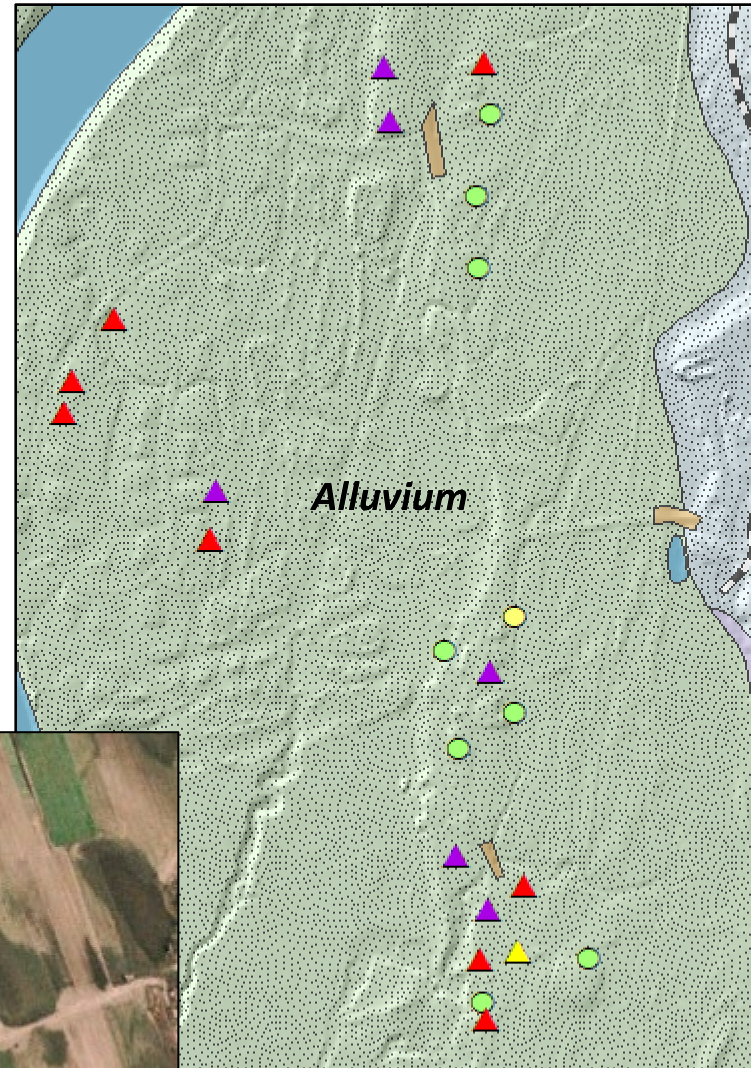
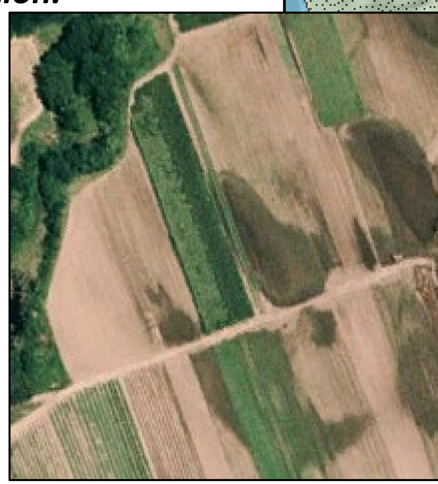
Geologic Factors: Overburden vs. Bedrock

PFOA concentrations in groundwater samples from all nine bedrock wells shown on this slide were less than or equal to 12 ng/L, while 14 out of 15 overburden wells exceeded 12 ng/L. The alluvial deposit in this area consists of fine sand with silt and localized ponding occurs after precipitation (dark patches on the aerial photo). Water well records suggest the alluvial deposit is generally thicker than 20 feet in the vicinity of this terrace. ***One possible explanation for the disparity between the overburden and bedrock PFAS concentrations is that PFAS sorb to the fine-grained alluvial deposits, which "shield" the underlying fractured rock from greater levels of contamination.***





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Well Type
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- OVERBURDEN

Surficial Geology Credit: Koteff, Carl, 1976, Surficial geologic map of the Nashua North quadrangle, Hillsborough and Rockingham Counties, New Hampshire: U.S. Geological Survey, Geologic Quadrangle Map GQ-1290, scale 1:24,000.

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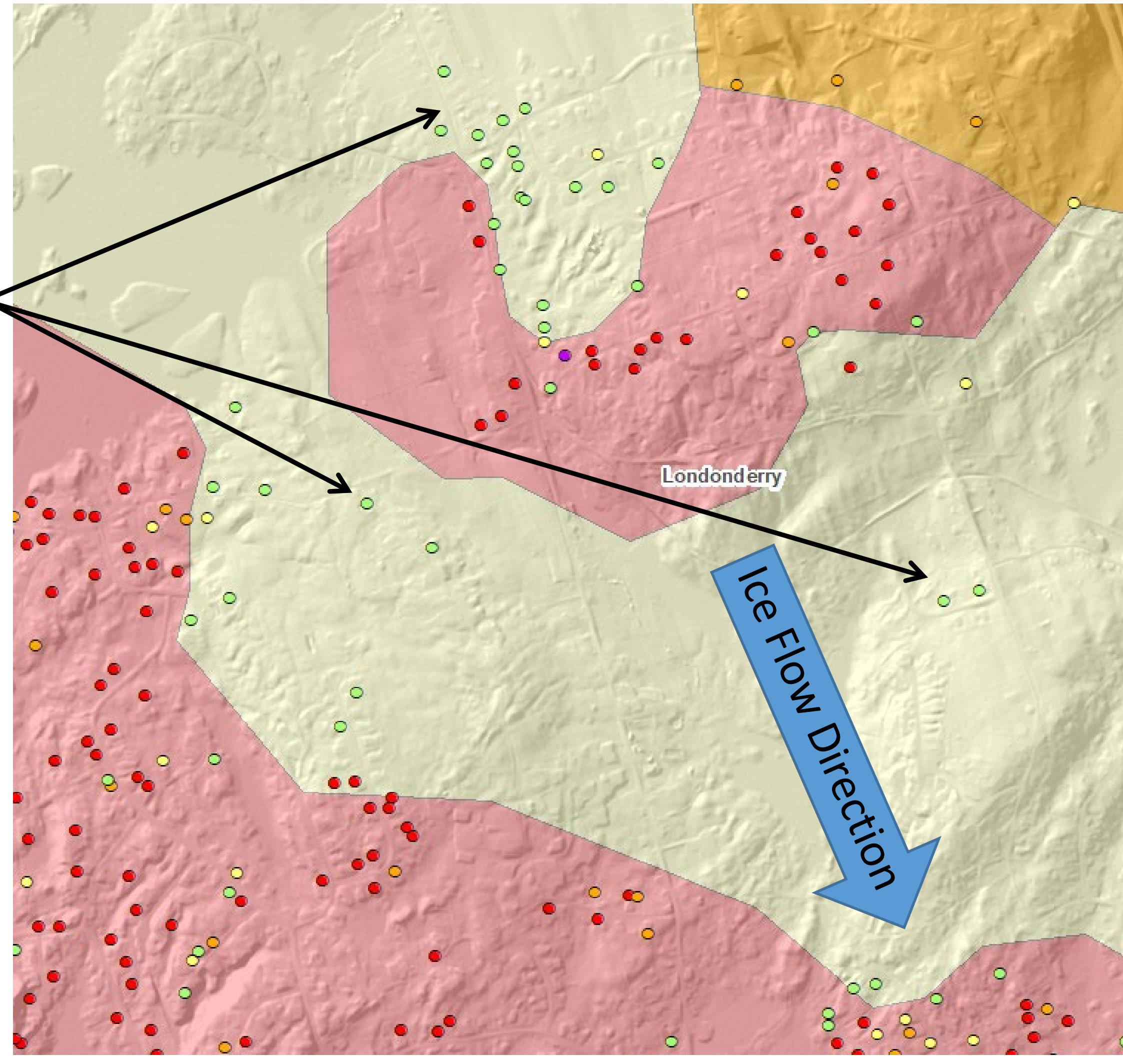
Spatial Patterns Till Deposits

PFOA concentrations in groundwater samples tend to be less than or equal to 12 ng/L in the portions of this figure exhibiting a smooth, fluted texture in the LiDAR imagery. Presumably, the smooth fluted texture is indicative of basal till that was deposited at the base of flowing glaciers. ***One possible explanation for the variable spatial distribution of PFOA is that PFAS sorb to the (thicker?) basal till deposits preventing migration of greater levels of contamination into the underlying fractured rock.***



Groundwater PFOA (ng/L)

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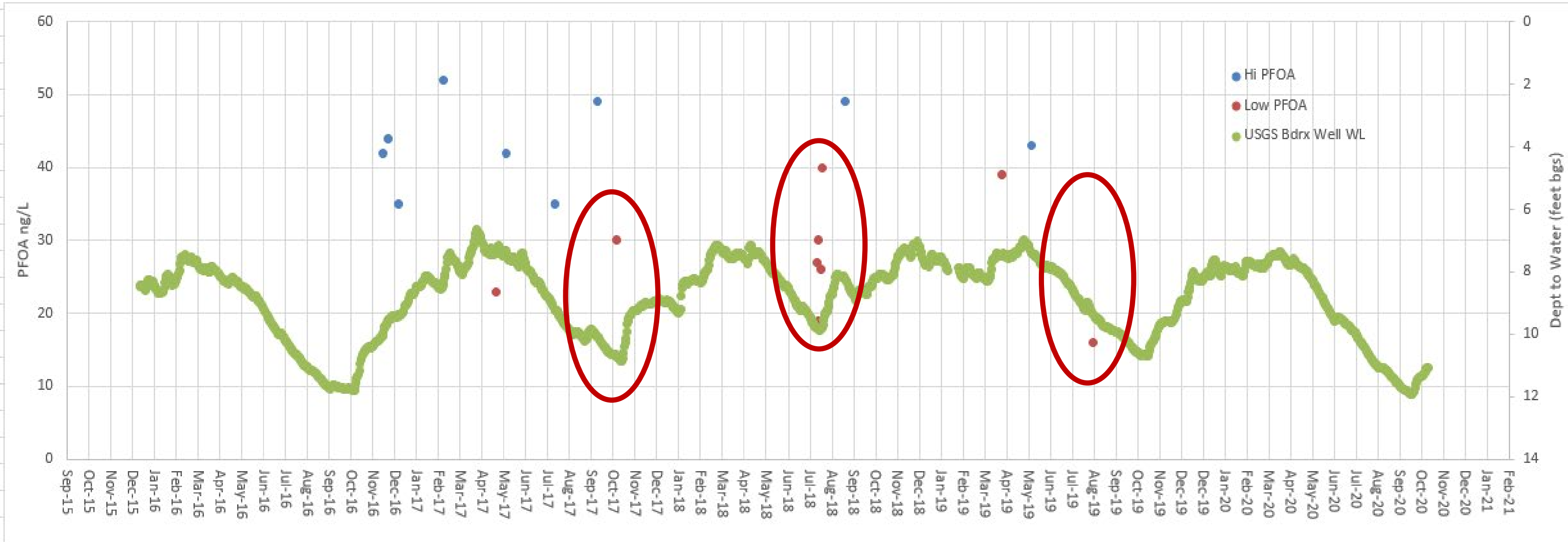
Temporal Variability in Bedrock Water Supply Wells



In a project dataset, nine bedrock water supply wells have four or more samples collected through time. This plot shows the highest concentration (blue) and the lowest (red) concentration of PFOA plotted through time. Water level data from a USGS bedrock monitoring well in Pembroke is plotted on the right Y-axis as a proxy for climatic factors influencing groundwater fluctuations in the bedrock aquifer in the Southern New Hampshire area. Seven of the nine samples with the lowest PFOA concentrations (red ovals) were collected when the groundwater levels were receding or at the lowest seasonal point in the Pembroke well, suggesting seasonal factors influence PFAS concentration in some bedrock wells.

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Water level Data from USGS Well NH-PWB 148:
https://groundwaterwatch.usgs.gov/AWLSites.asp?mt=g&S=431120071284201&ncd=awl

WHY DO NEIGHBORING WELLS HAVE DIFFERENT CONCENTRATIONS OF PFOA?

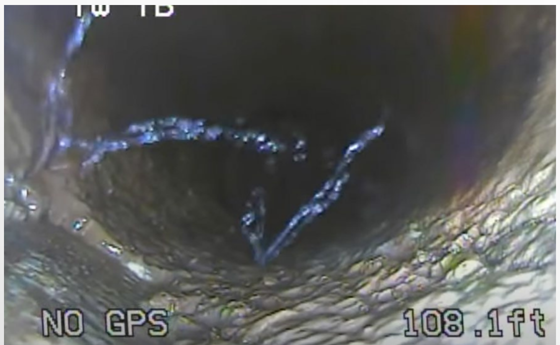
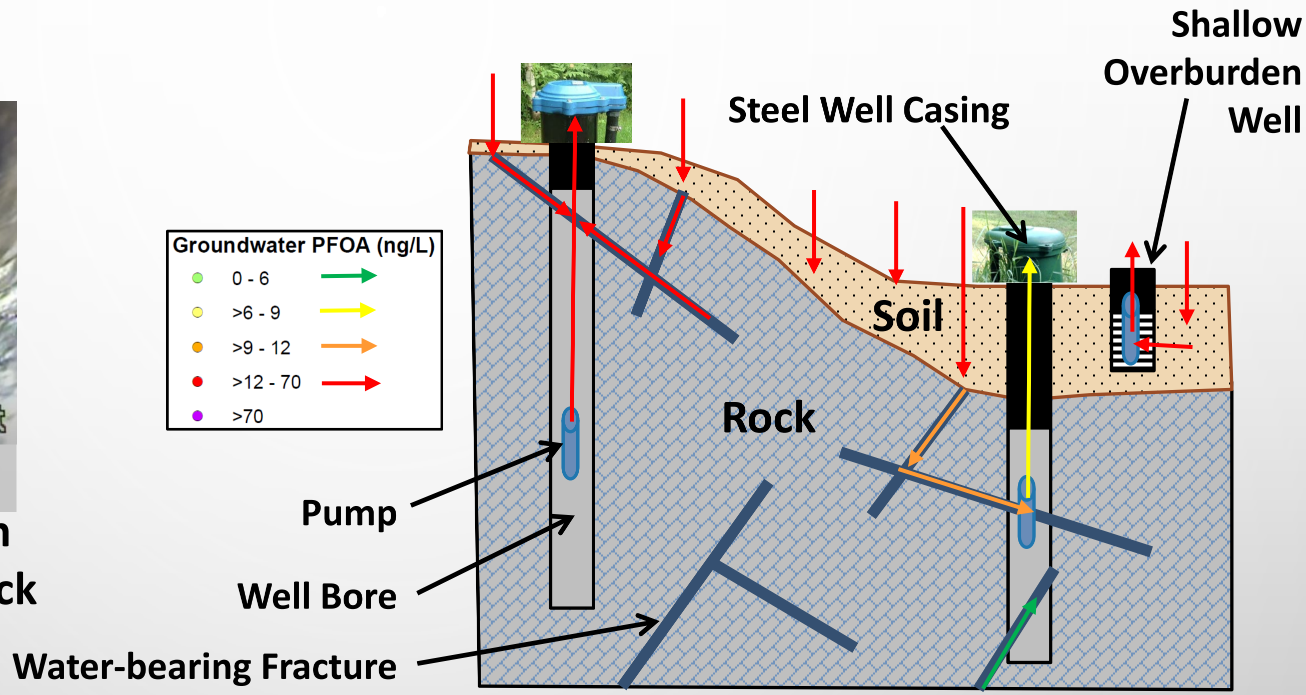


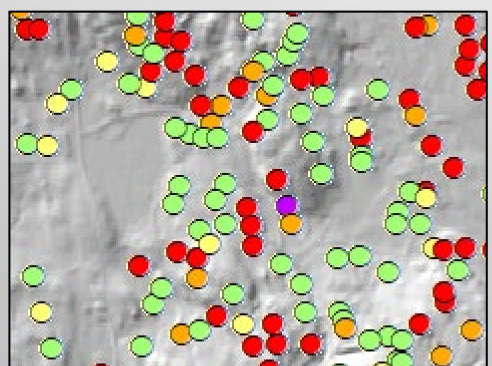
Photo from Youtube Video posted by Ohio EPA: https://www.youtube.com/watch?v=Y_4aTJlcGuI

Water entering a well from fractures (cracks) in the rock



Cross Section (Profile)View

This diagram illustrates a hypothetical cross section showing potential groundwater flow pathways to water supply wells that are depicted by color-coded arrows that correspond to PFOA concentration. The downward red arrows into the soil layer represent aerial deposition of PFOA that infiltrates into the soil above bedrock.



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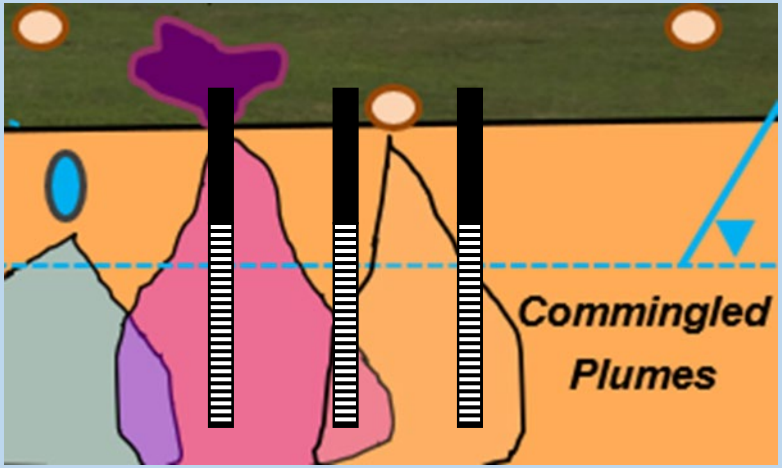
Untangling Commingled Plumes

Investigation Approaches / Tools

1. Explore the data (Qualitative to Quantitative)
   a) Geospatial (3-D)
   b) Temporal (4^{th} D)
   c) PFAS Assemblages (consider variable analyte lists and detection limits)
2. Develop Multiple Working Hypotheses
3. Hypothesis Testing
4. Refine Conceptual Site Model (Supported by multiple lines of evidence)



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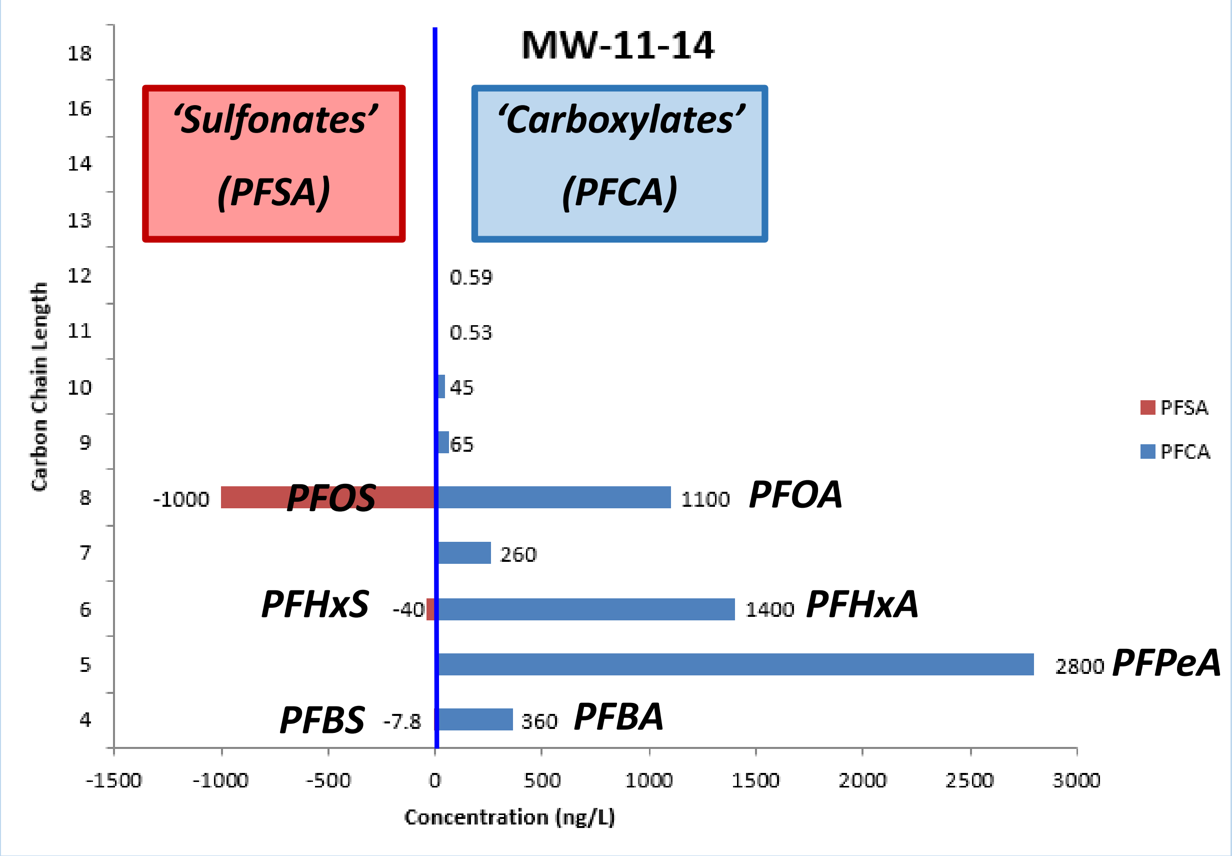
PFAS Data Visualization

Mobility of PFAAs generally increase with decreasing chain length and PFCA are more mobile than the corresponding PFSA of equal carbons.

By plotting PFAAs as a function of carbon atoms and PFSAs & PFCAs of equal number of carbons side-by-side, the compounds are organized by mobility in the subsurface. This plot shows the relative and absolute amounts of each compound.



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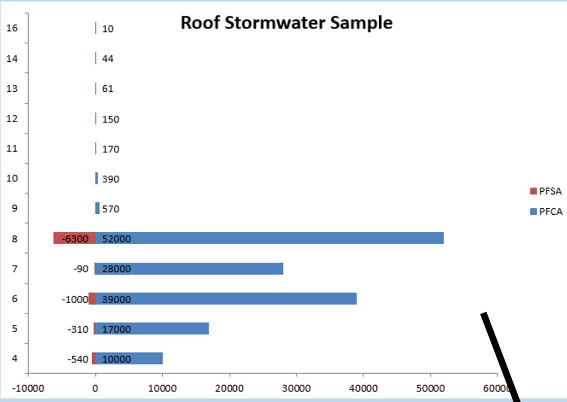
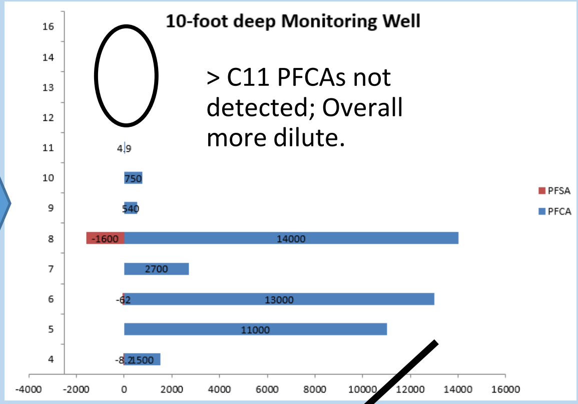
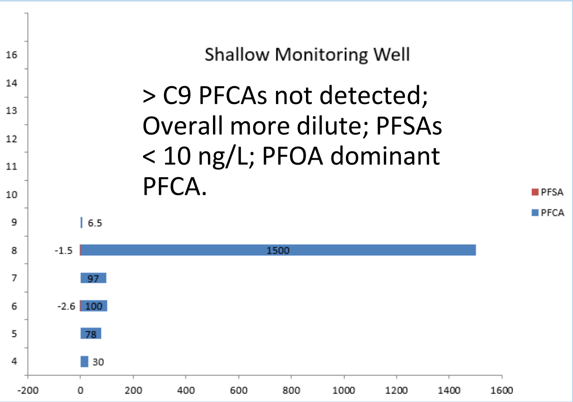
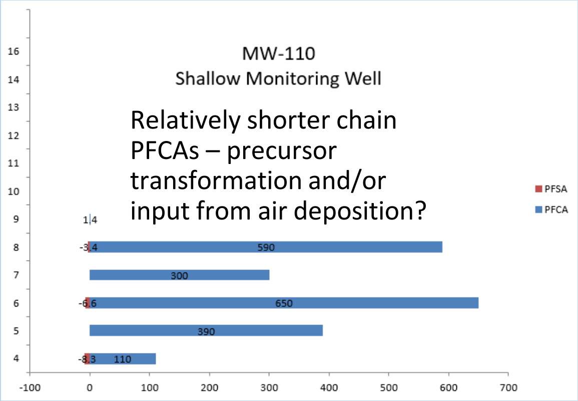
PFAS Fingerprint? or Evolution Along a Flowpath(s)?

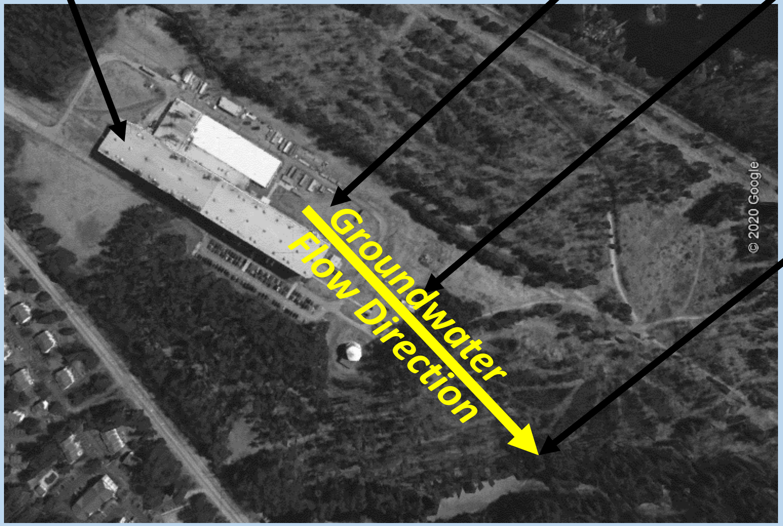








Near-source shallow groundwater PFAS detections are similar to PFAS detected in stormwater from the roof. Profiles of detected PFAS change along the groundwater flow path.



The groundwater "flow path" for the three monitoring wells (yellow arrow) is approximately 1,200 feet long. This flow path analysis does not account for potential vertical flow components.

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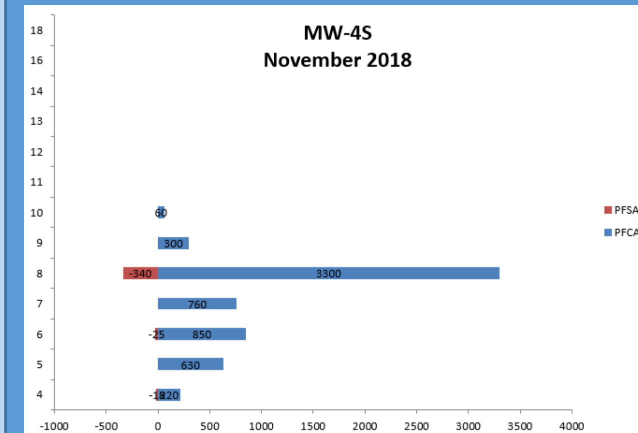
PFAS Fingerprint?

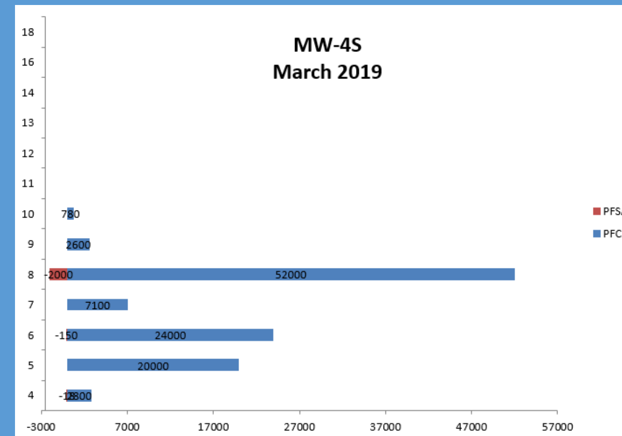
It is important to consider how relative amounts of individual PFAS will vary along the length of a groundwater plume:

Sulfonates are more sorptive than carboxylates.

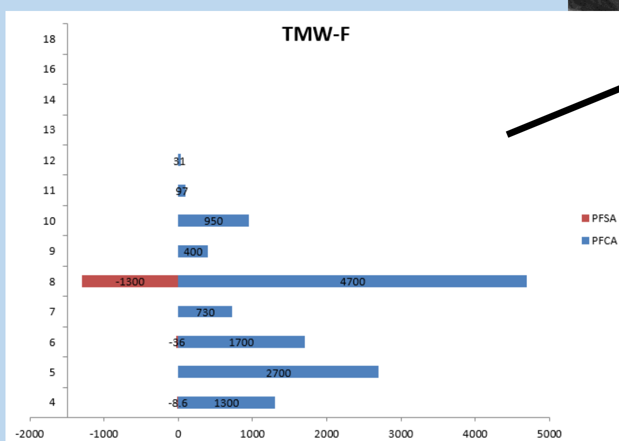
Within a functional group, short chain compounds are generally more mobile than longer chain compounds.

Precursors can be more (or less) mobile than terminal PFAAs – degradation of precursors can alter ratios of terminal PFAAs.





PFAS ratios change with time/season.



PFAS in well near a potential discrete release. Precursors to PFOS were detected in soil and groundwater samples near this well.

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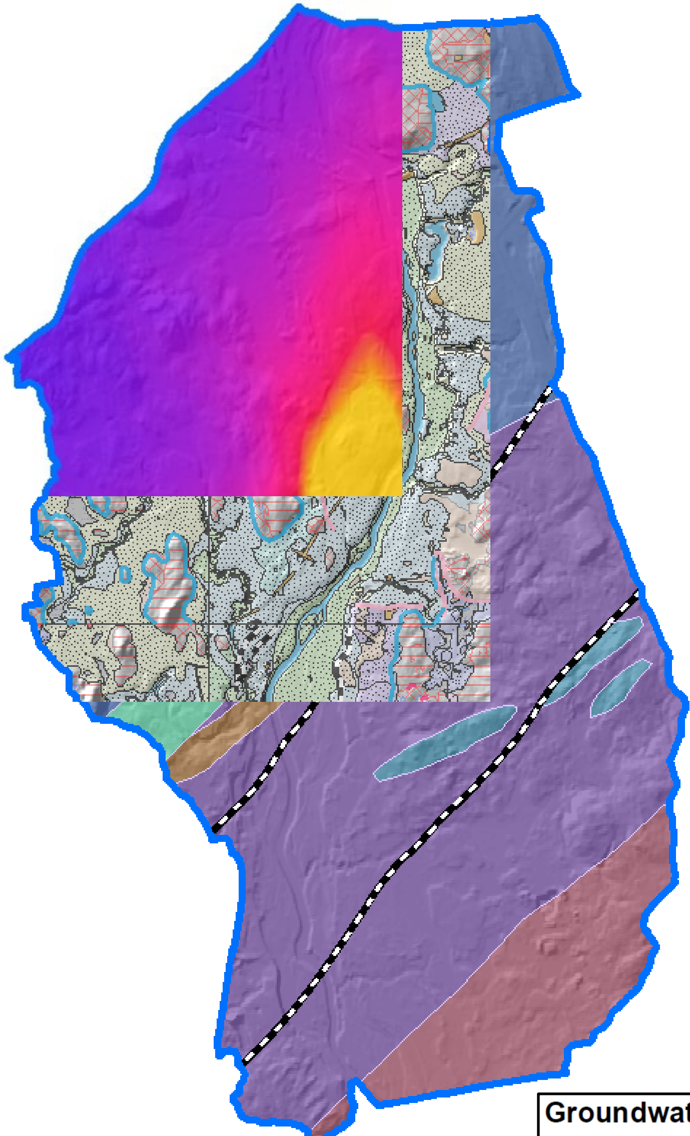
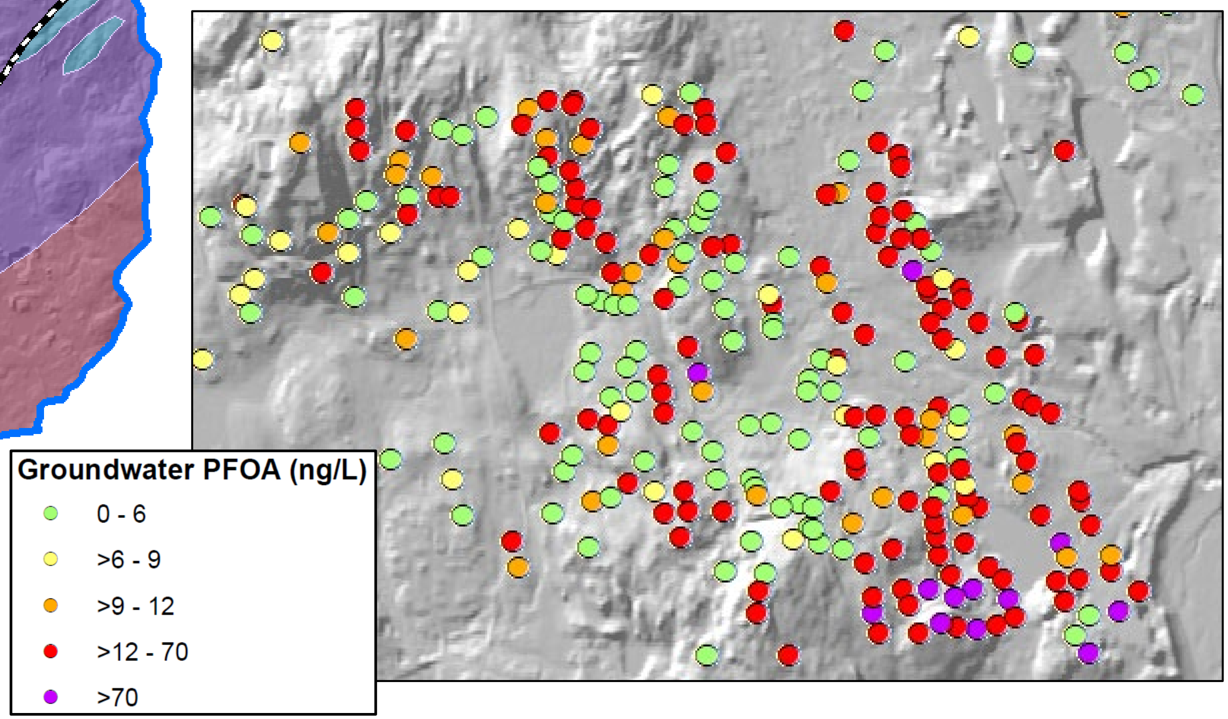


Thank You

Questions?



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