Considerations for PFAS Fingerprinting

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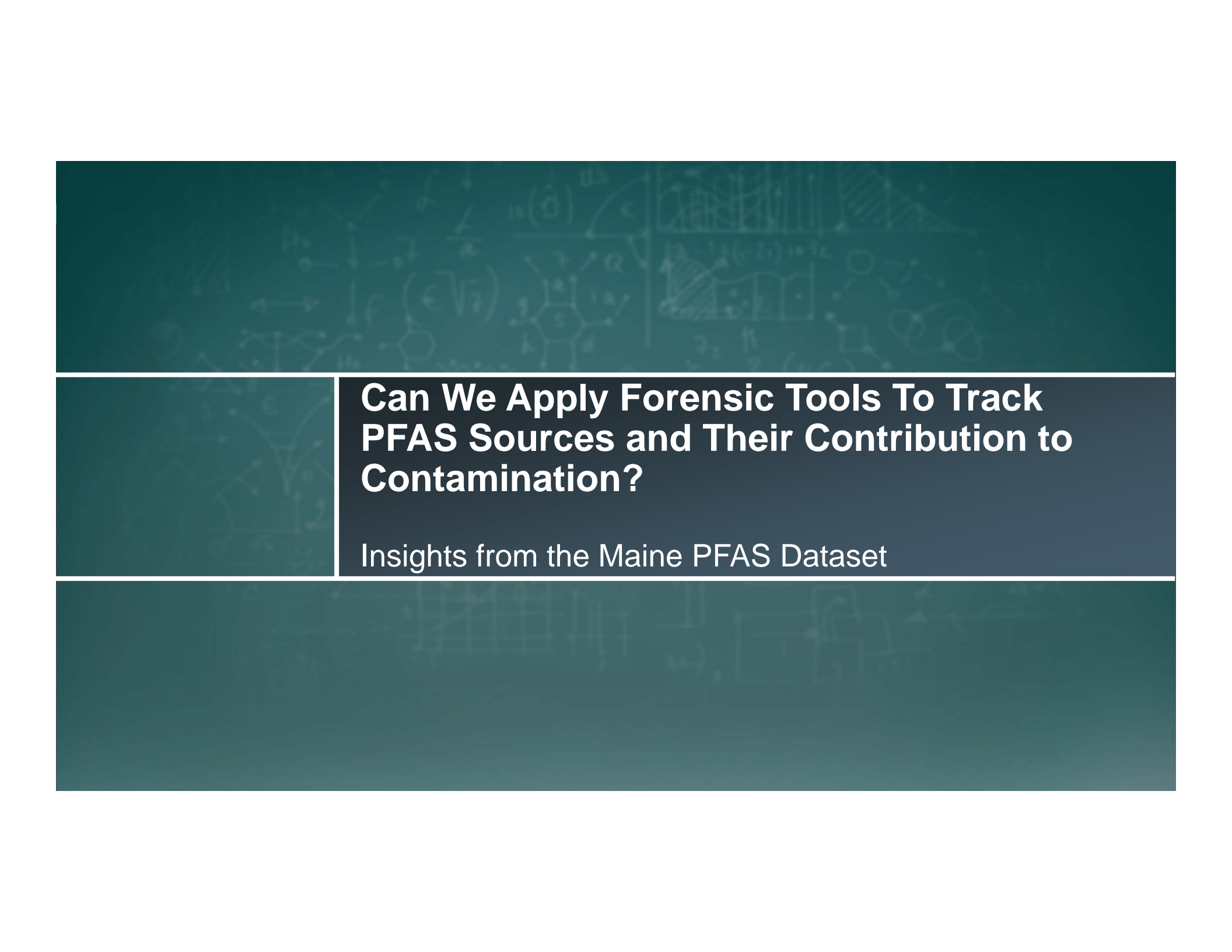# Abstract

With the long history and diverse array of perfluoroalky and polyfluoroalkyl substance (PFAS) uses and chemical compositions, forensic evaluation and fingerprinting PFAS sources in the environment is uniquely challenging. In addition to the complex chemical composition of products, some PFAS undergo chemical transformations and differential transport in the environmental which alter the chemical profiles. Forensic fingerprinting and allocation of PFAS contamination requires evaluation of many lines of evidence to determine likely sources. During this presentation, the types of evidence needed to evaluate sources of PFAS will be addressed. The first evaluates the chemical composition of the contamination with a focus on assessing the PFAS product process (electrochemical fluorination or telomerization), chain length distribution (long vs short chain), presence/absence of newer replacement substances, branched isomer profiles, and other non-PFAS chemical markers. Additional evidence includes review of historic site information, evaluation of known PFAS uses and products, assessment of parties in the area and their PFAS use, and local factors affecting fate and transport of contaminants at the site. Along with these multiple lines of evidence, forensic chemists can evaluate the fitness and limitations of the chemistry data. With assessment of all available evidence and evaluation of the fitness and comparability of available data, successful forensic evaluation of PFAS sources and allocations can be achieved.

A Trend of Increasing Number of PFAS Compounds Analyzed For in Public Data Bases

- With increasing number of PFAS compounds analyzed for, chemical fingerprinting techniques become more promising
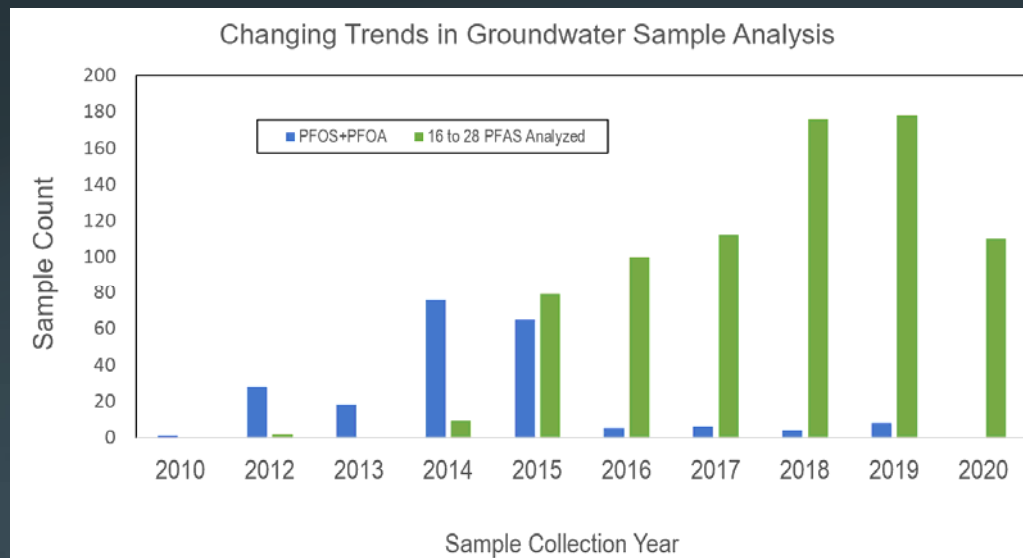
Data from Maine Department of Environmental Protection (https://www.maine.gov/dep/maps-data/egad/

Can We Apply Forensic Tools To Track PFAS Sources and Their Contribution to Contamination?

Insights from the Maine PFAS Dataset

Naval Air Station – Brunswick PFAS Data

- "Eastern Plume" and "Site 11"

- Sampled for PFAS between 2012 and 2018

  – PFOA and PFOS found in groundwater

  – PFAS data used at its face value
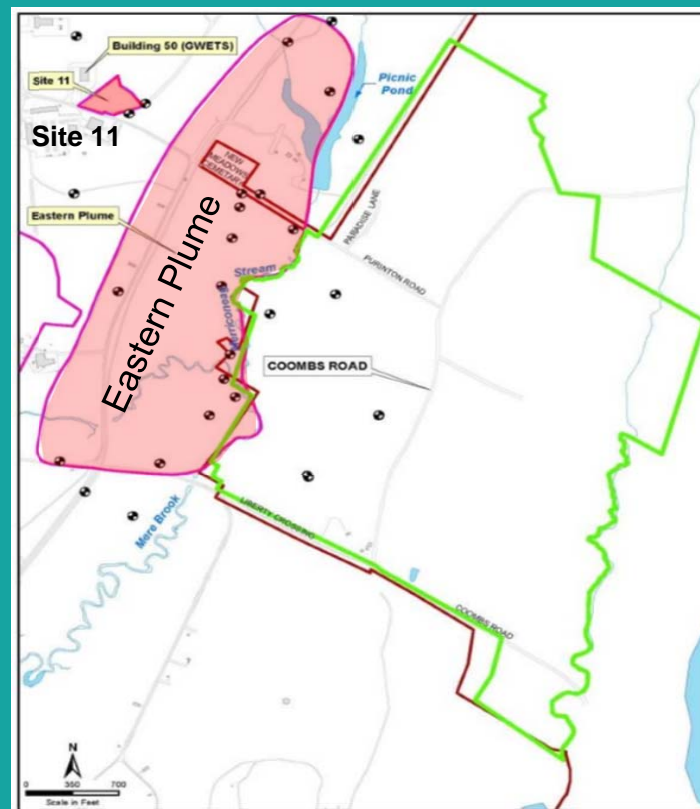
Figure 1 – Approximate Extent of Eastern Sampling Area

https://www.maine.gov/dep/spills/topics/pfas/NASB_ResWell_PFC_FactSheet_April2016.pdf

Stable PFAS Fingerprints With Time at a Receptor Location

- From the Maine PFAS dataset, PFAS fingerprints remained consistent over a one year period at a receptor location
  - Sampled monthly between July 2017 and July 2018

Analysis of the Eastern Plume And Site 11 To Identify Groups of Fingerprints

- Principal Component Analysis (PCA)
  - 11 Analytes

- Different groups of fingerprints
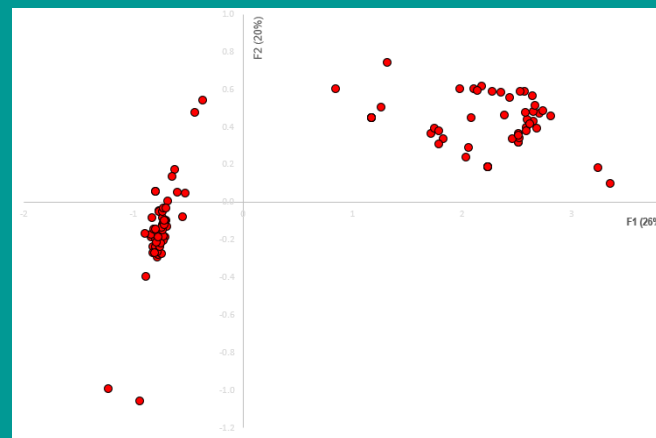
Scores Plot

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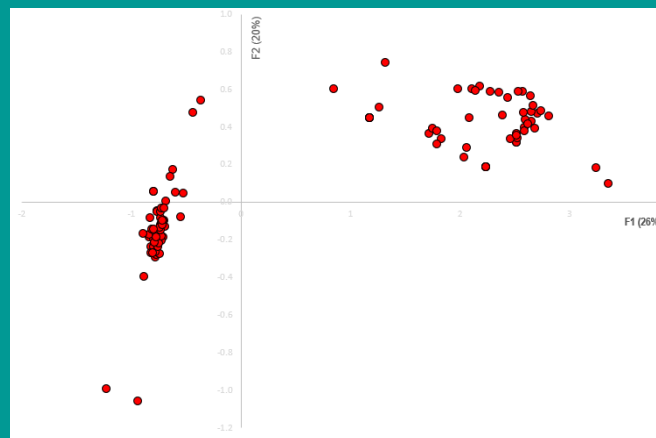
Scores Plot

Loadings Plot

Example PFAS Fingerprints
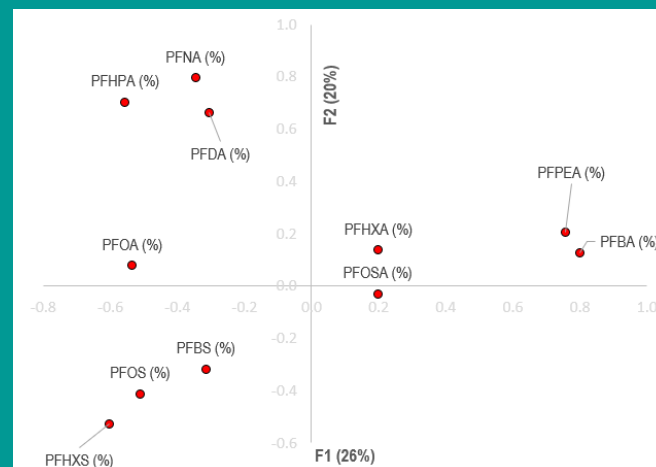
Scores Plot

Generally higher concentrations

Example Fingerprint (PFOA dominant)
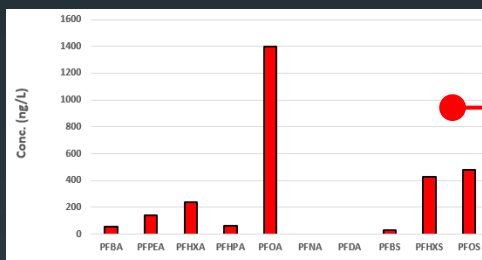
Example Fingerprint (PFPEA dominant)
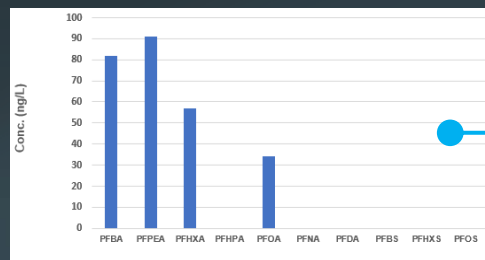
Example Fingerprint (PFBA dominant)
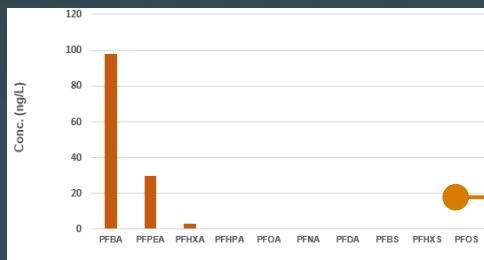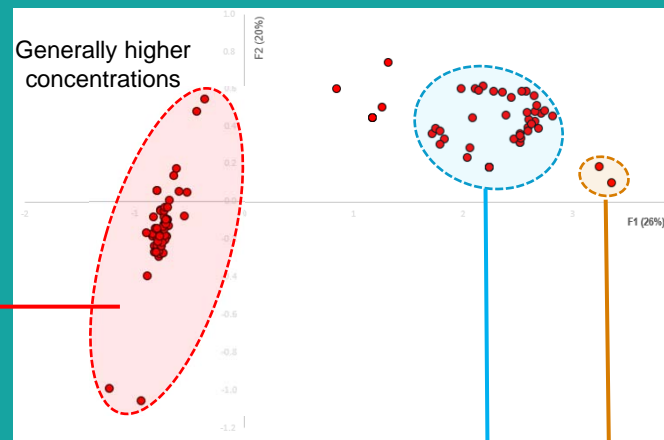
Example Source Area Fingerprints From the Maine PFAS Database

- PCA
  - 17 PFAS Compounds
  - Concentrations > 70 ng/L

- Sources
  - Landfill (Corinna)
  - Landfill (other)
  - Military (LAFB)
  - Tannery
  - Metal Finishing

Scores Plot

Legend:
- Landfill (Corinna)
- Landfill (Other)
- Military (LAFB)
- Tannery
- Metal Finishing

F2 (13%), F1 (20%)

Loadings Plot

PFPEA (%), PFHXA (%), PFBA (%), PFTEA (%), PFHXS (%), PFUNDA (%), 6:2 FTS (%), PFBS (%), PFDA (%), PFDOA (%), 8:2 FTS (%), PFHPA (%), PFNA (%), PFOS (%), N-MeFOSAA (%), N-EtFOSAA (%), PFOA (%)
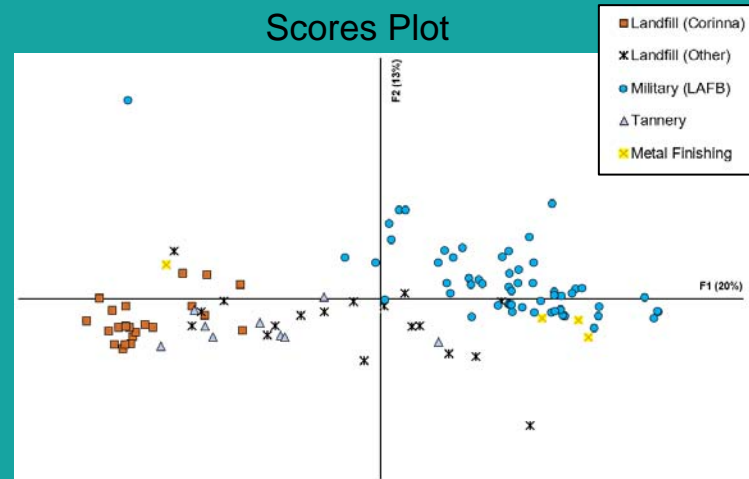
Scores Plot

Landfill (Corinna)

Landfill (Other) Has Different Fingerprints
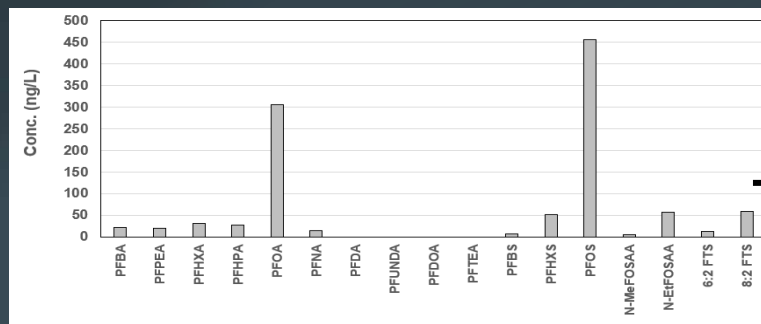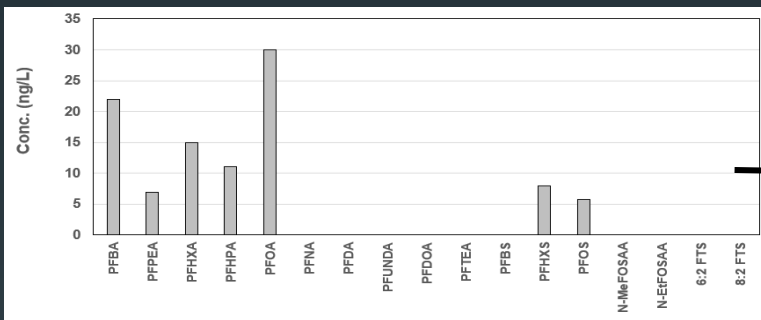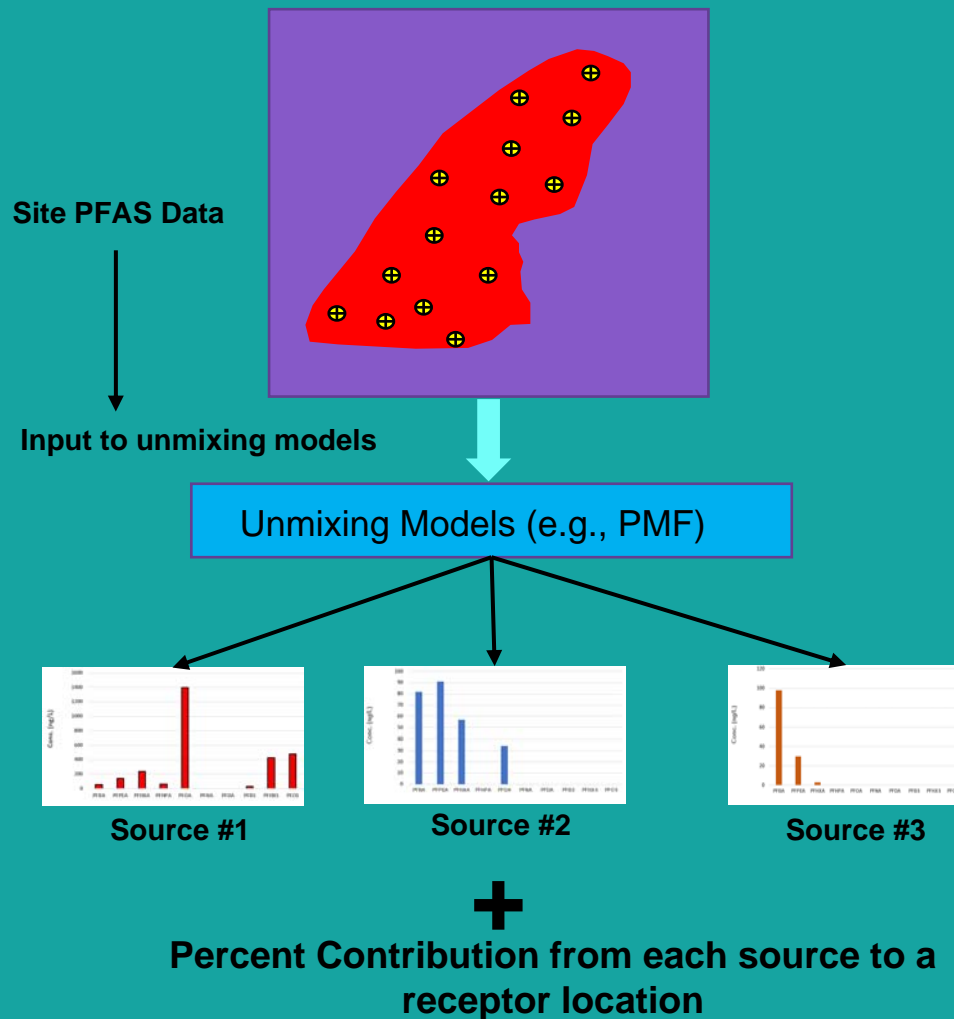
Scores Plot
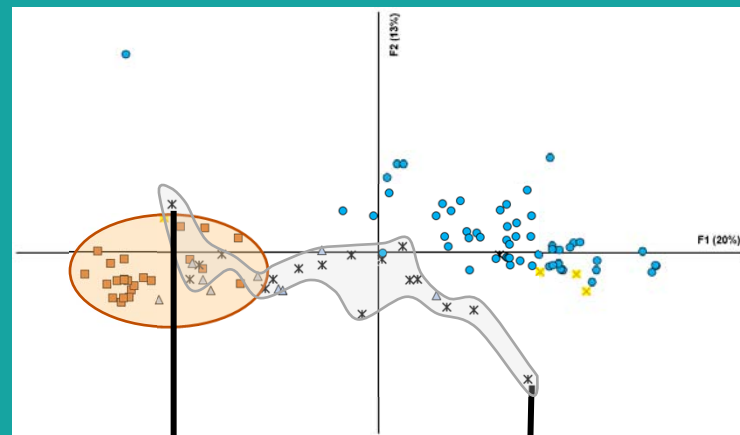
Loring Air Force Base
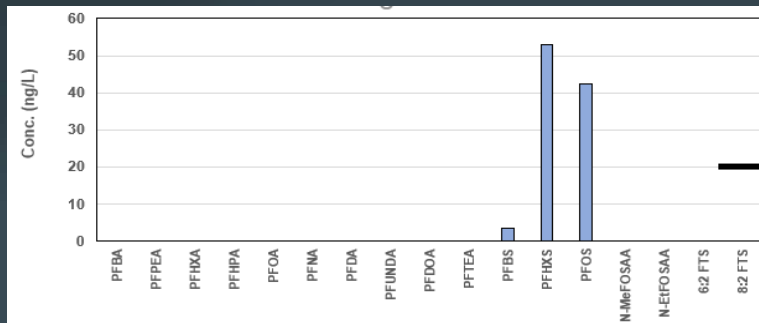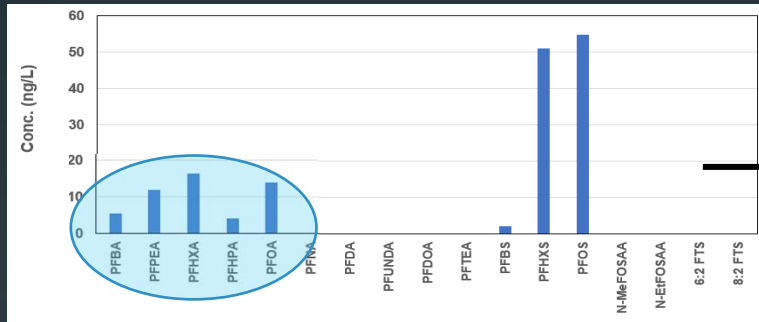
Scores Plot
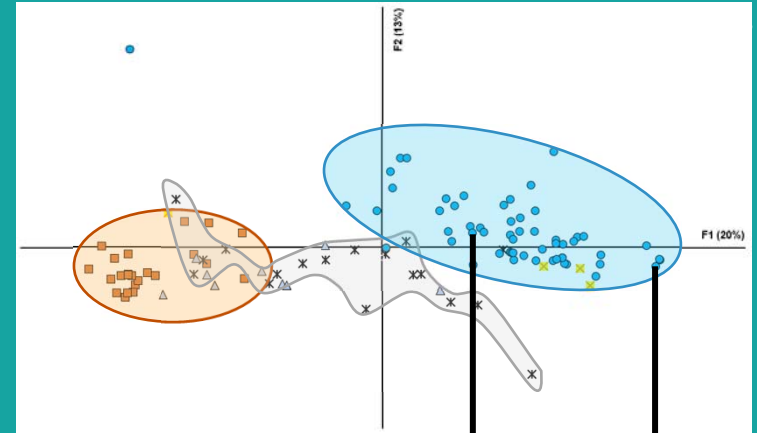
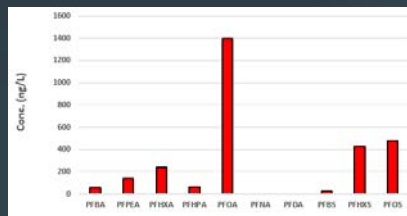# Unmixing Models to Apportion Contribution From Different Sources –Concept

- Applicability depends on the case details

Site PFAS Data

Input to unmixing models

Unmixing Models (e.g., PMF)

Source #1   Source #2   Source #3

+

Percent Contribution from each source to a receptor location

Application of Unmixing Models to a Training PFAS Data Set – Hypothetical Scenario

Source Profile from unmixing model

Percent contribution of the source profile to samples

Hypothetical Example
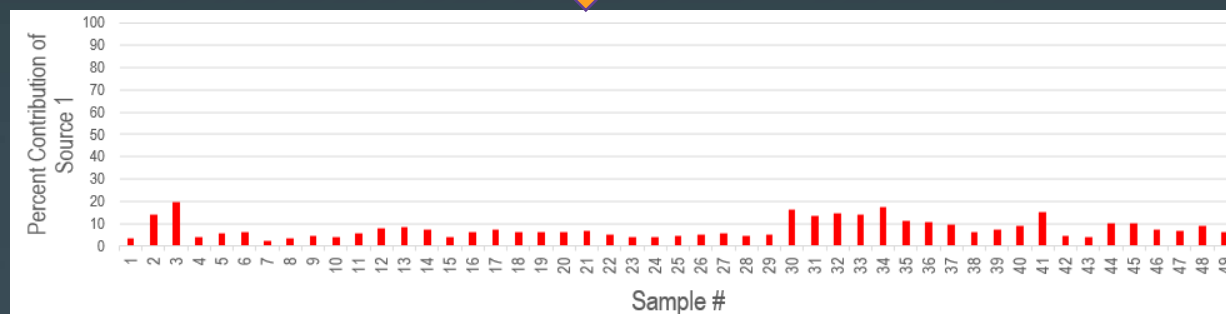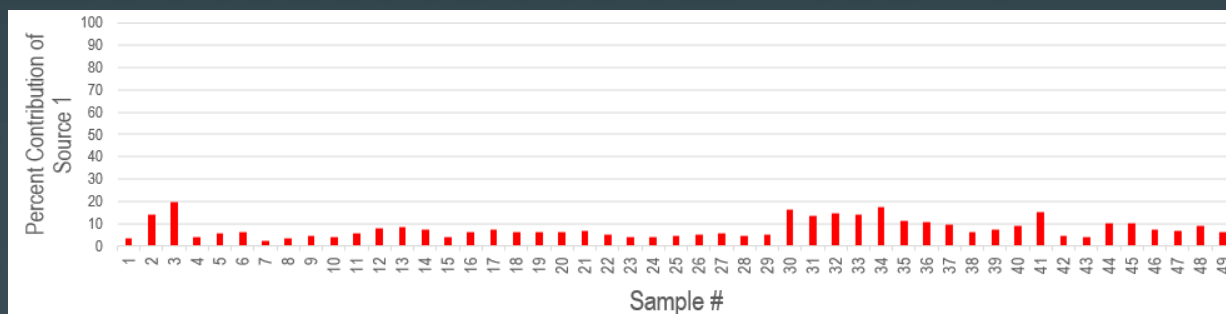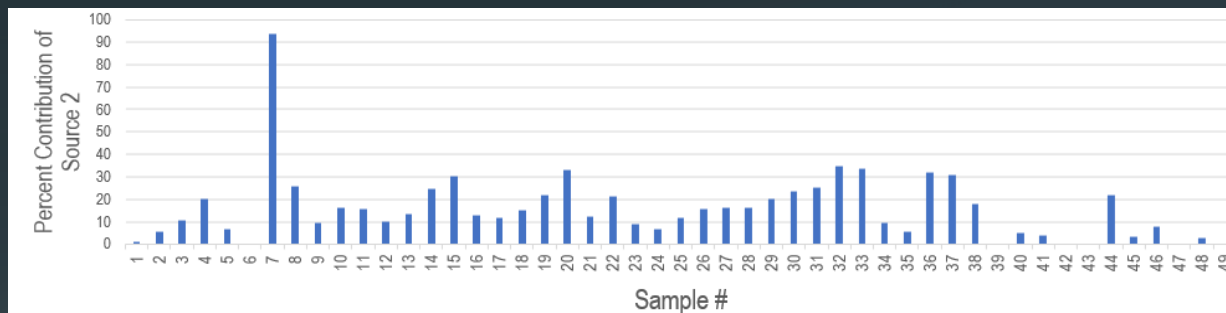

PFAS Source Profile #1

Application of Unmixing Models to a Training PFAS Data Set
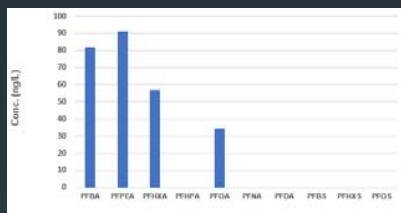
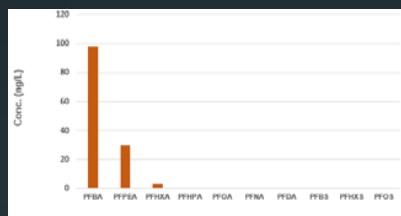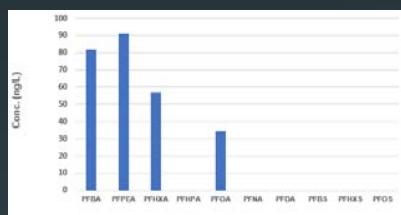
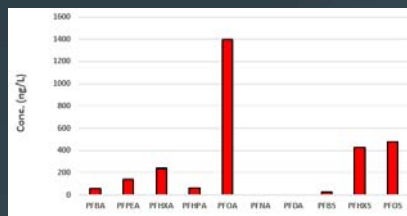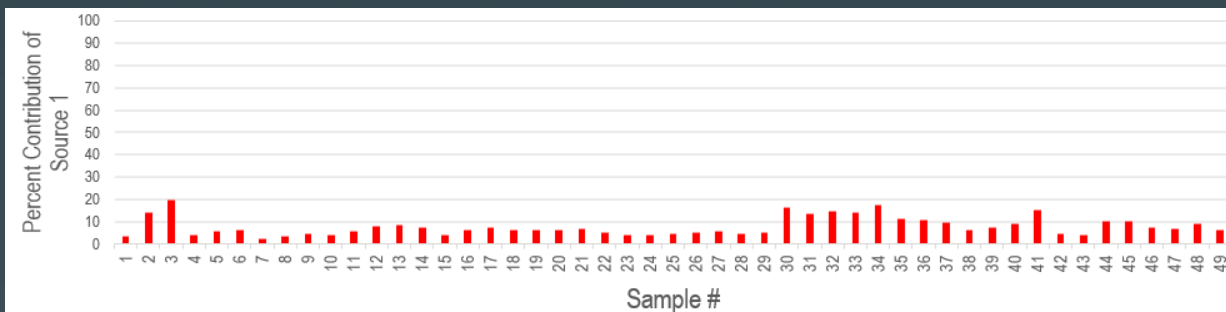PFAS Source Profile #2
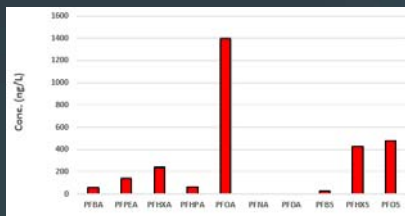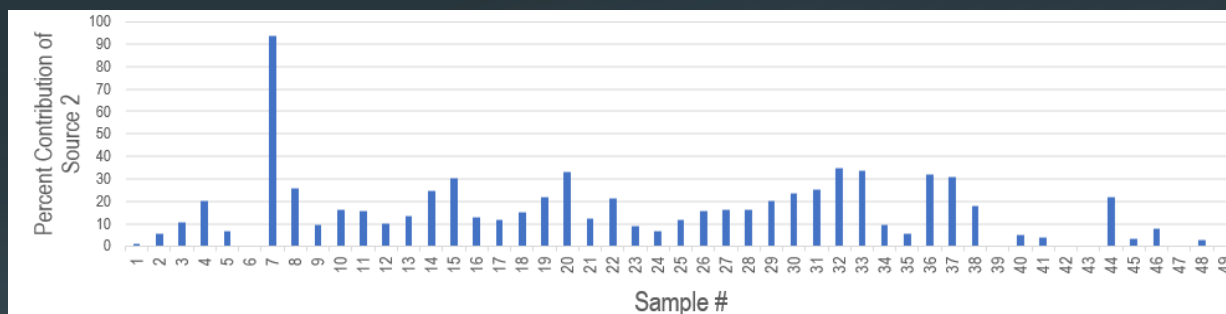

PFAS Source Profile #1

Hypothetical Example

PFAS Source Profile #3

PFAS Source Profile #2

PFAS Source Profile #1

Hypothetical Example

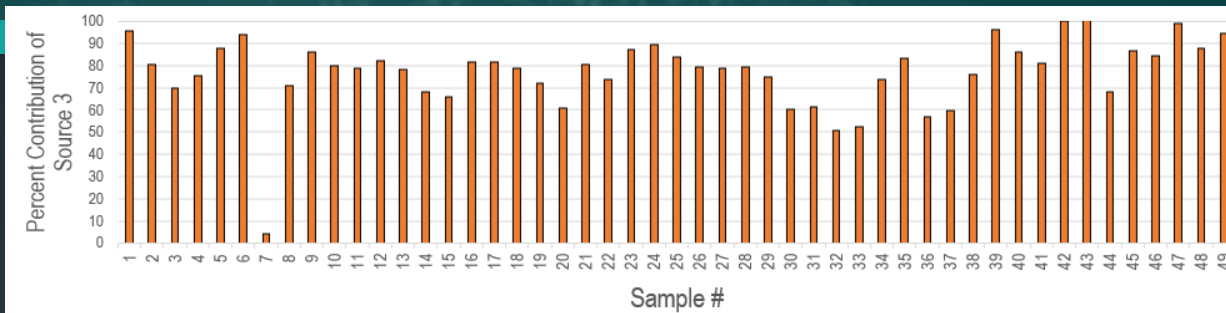# PFAS Forensics – Multi Lines of Evidence

- Reconstruct historical operations and operational changes
- PFAS uses and sources
- Transport pathways
- Additional evidence
  - Source marker chemicals
  - Water chemistry profiles