# Advanced fingerprint analysis of PFAS in groundwaters: the use of advanced multivariate statistics and machine learning techniques

Carlo Monti, Ph.D.
Nicholas Rose, M.S.
Tim Negley, M.S.

Paris, June 13, 2023

A Member of TheIntelligenceGroup
RESEARCH ▾ INVESTIGATIONS ▾ FORENSICS
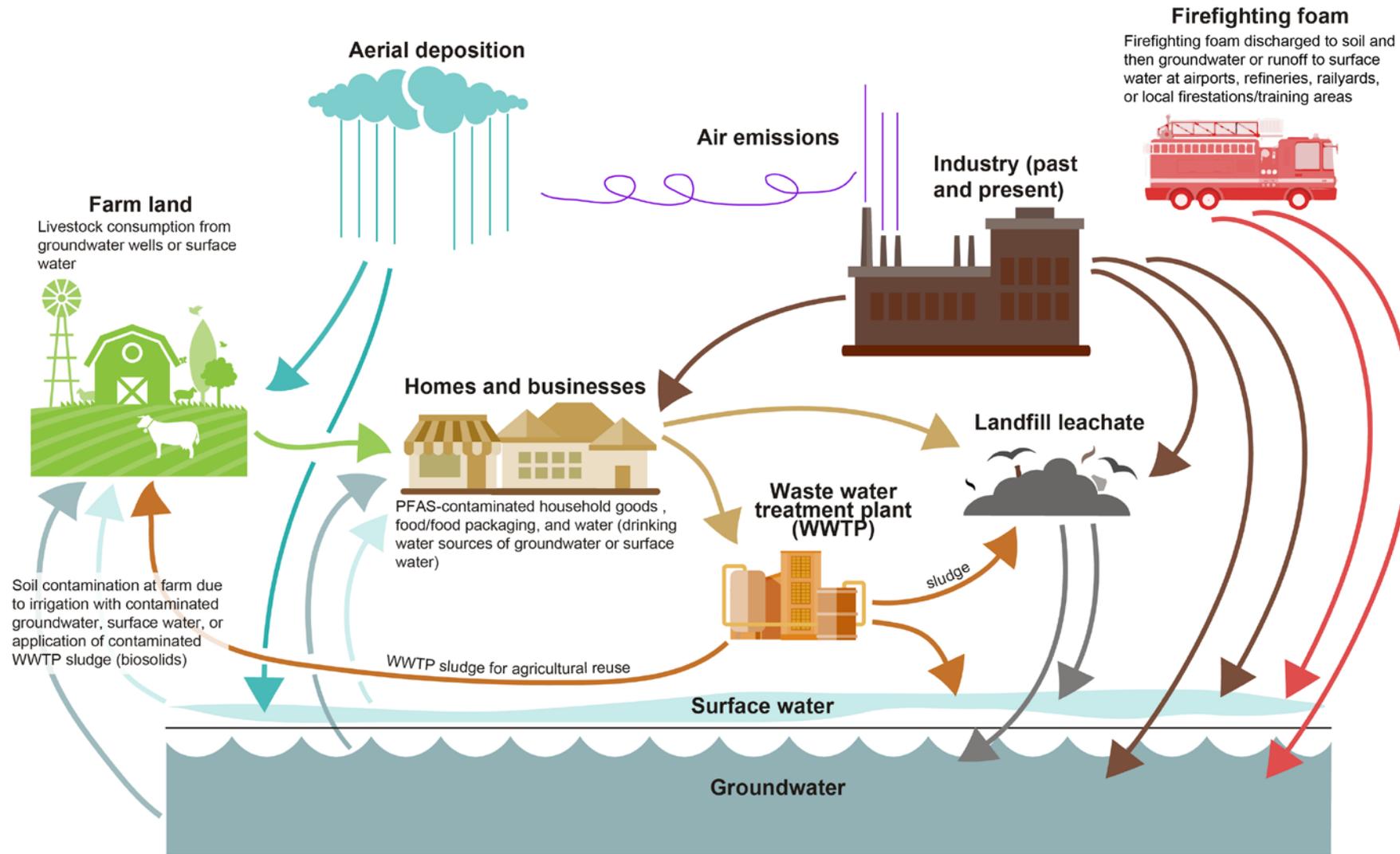
PFAS Fingerprintin Veneto Region, Italy

- The scope of this project is to demonstrate an approach to identify original PFAS sources using a multivariate method (PCA and cluster analysis) and PVA (polytopic vector analysis) algorithm developed in R by the authors. This case study is in the Veneto Region of Northern Italy.

- We analyzed data gathered by the Regional Environmental Protection Agency and available on-line.

- We cleaned the data and then we performed a PCA, a cluster analysis and a PVA.

- The PCA, cluster analysis, and PVA results indicate that in certain parts of the Veneto region groundwater and surface water contamination is associated with the nearby PFAS manufacturer and industrial sources, while other sources are responsible for PFAS contamination elsewhere in the Region. The results highlight the ability of the approach to differentiate original sources of PFAS contamination, particularly when source fingerprints can be derived.

TIG
environmental®
INVESTIGATIONS • FORENSICS • REMEDIATION

PFAS Source Tracing
# Statistical Fingerprinting Methods

Existing Fingerprinting Methods

- Targeted Analysis (Typically < two dozen PFAS)
- Principal Component Analysis (PCA)
- Polytopic Vector Analysis (PVA)
- Multivariate Cluster Analysis

Forensic Laboratory Methods

- Branched Isomer Characterization for Forensics (additional separation of PFOS, PFOA, PFNA)

Evolving Methods

- Nontargeted Analysis - potential to identify thousands of PFAS
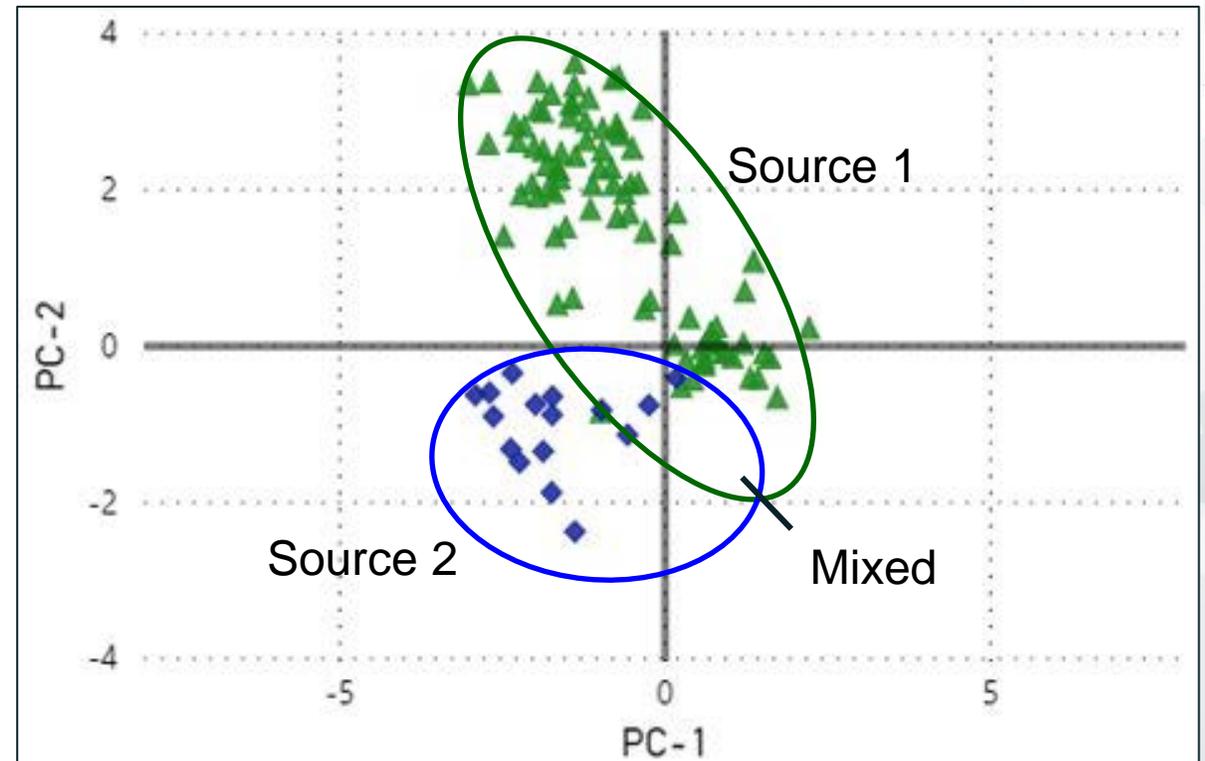
PFAS Fingerprinting
Veneto Region, Italy

- Of 8000+ samples, about 1,400 samples for eight (of 18) PFAS were deemed useable for fingerprinting
- Methodology: PCA, cluster analysis, and TIG's proprietary PVA algorithm

- Chemical plant was dissimilar to industrial waste water
- Chemical plant was dissimilar to many groundwater and freshwater samples
- Further evaluation of source contributions evaluated with PVA

Chemical plant fingerprint

Industrial collector fingerprint
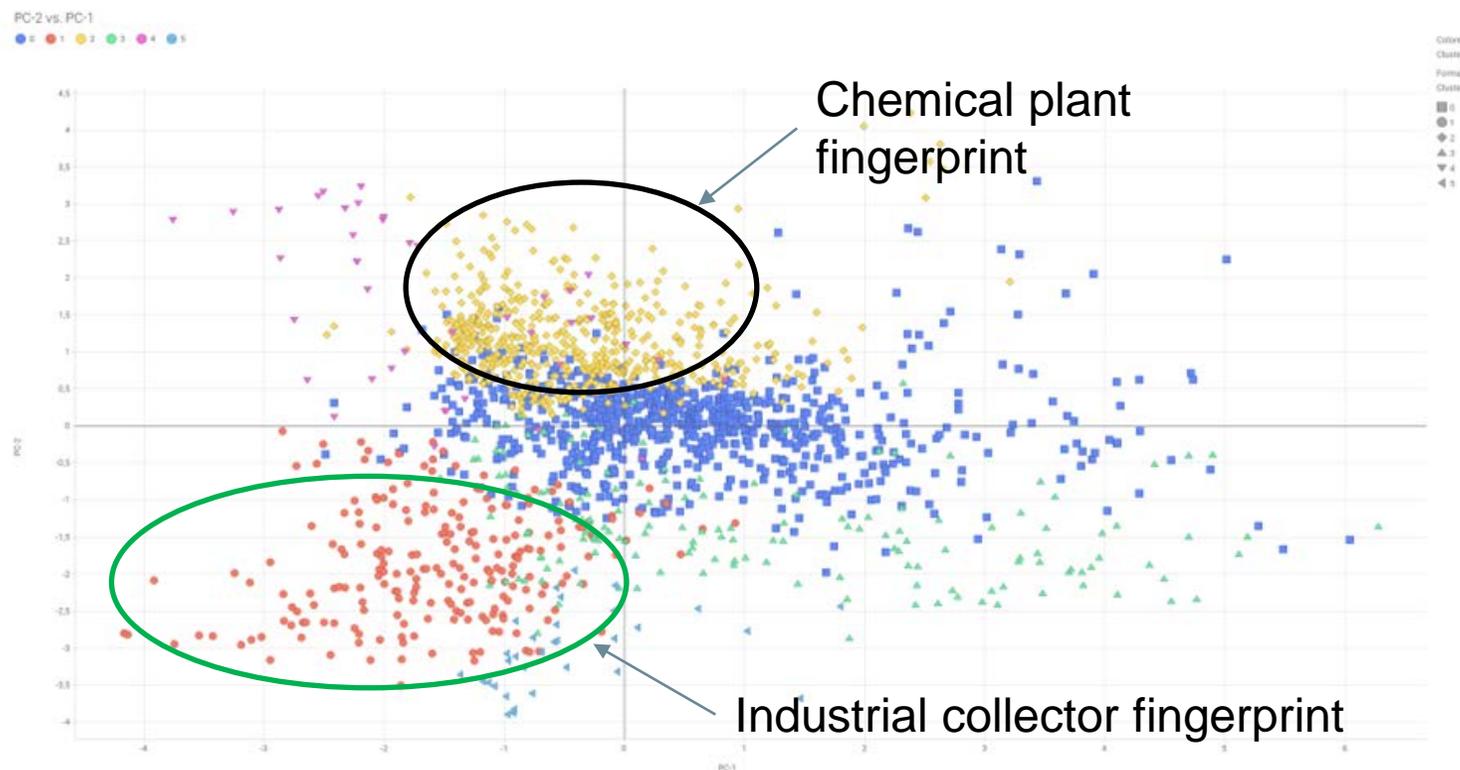
PFAS Fingerprinting
Veneto Region, Italy

- **PVA Results:** TIG's proprietary PVA algorithm suggested more than one source, each source dominated by specific PFAS, all of which exceeded the Veneto performance levels
  - PFBS (Source 1)
  - PFBA (Source 5)
  - PFOS (Source 4)
  - PFOA (Source 2)
  - Mixture (Source 3)

- The methodology demonstrated one source dominated, but other less dominant sources also appear to contribute.

Substance	Results	Exceedances	% Exceedance	Max Detect	Detect Unit
PFBS	7384	470	22.03%	17,300.00	ng/L
PFBA	7382	453	21.24%	11,900.00	ng/L
PFOS	3077	359	16.83%	4,610.00	ng/L
PFOA	3051	339	15.89%	28,667.00	ng/L
PFHxA	7388	229	10.74%	6,310.00	ng/L
PFPeA	7388	202	9.47%	7,950.00	ng/L
PFHpA	7388	66	3.09%	3,240.00	ng/L
PFHxS	7388	7	0.33%	3,437.00	ng/L
HFPO-DA	2488	4	0.19%	1,190.00	ng/L
PMHpA	5	2	0.09%	2,809.00	ng/L
PFNA	7388	1	0.05%	885.00	ng/L
PFUnA	7383	1	0.05%	640.00	ng/L
PFDeA	7388	0	0.00%	232.00	ng/L
PFDoA	7382	0	0.00%	22.00	ng/L
PFHpS	2521	0	0.00%	59.00	ng/L
PMHpS	7	0	0.00%	94.00	ng/L

- The fingerprint of each cluster is represented in the first figure. Each cluster have a well defined fingerprint;
- Clearly cluster 2 (the Manufacturer's one) and 4 (Industrial wastewater one) show a completely different fingerprint. The first is dominated by PFOA while the second by PFOS;
- Cluster 1 is dominated by PFBS and cluster 5 and 3 by PFBA. Different dominant PFAS compounds indicate, very often, a different origin of the contaminant.
- The larger part of Groundwater and freshwater samples belong to Cluster 1 which is the cluster containing more than 80% of the samples of the industrial discharges collected and treated in the Vicenza province.

Cluster composition by PFAS compound

Legend: PFBA, PFPeA, PFBS, PFHxA, PFHpA, PFHxS, PFOA, PFOS
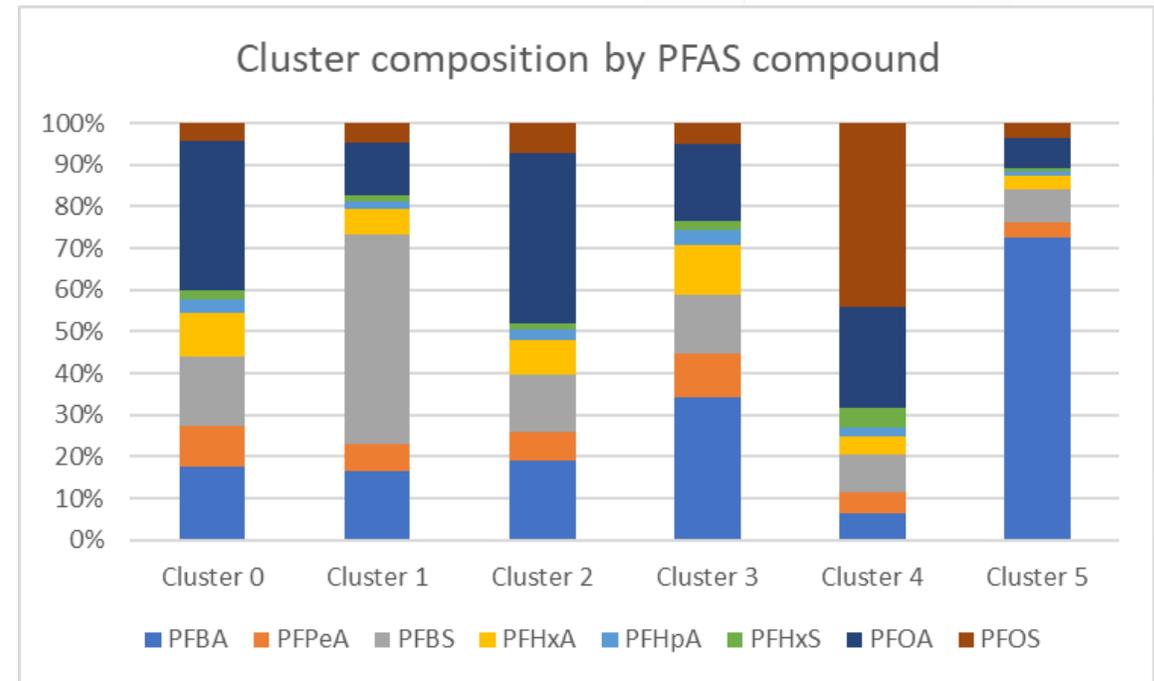
Confounding Factors:
Detection Limit Issues Can Obscure Profiles


Lower concentrations

ng/L
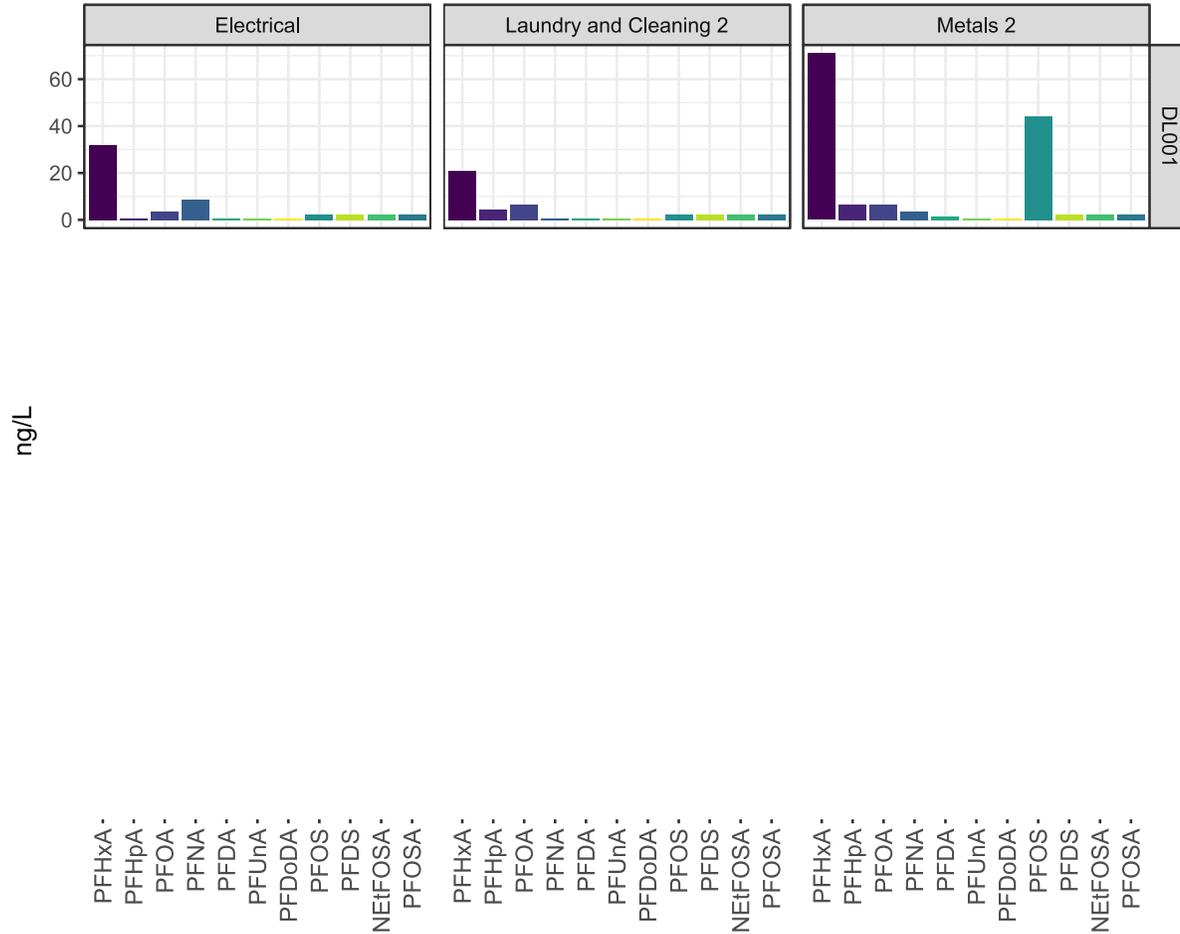
As the PFAS concentrations fall, the number of PFAS compounds detectable by the laboratory also falls

We assumed modest reduction in the concentrations (1/5, 1/10 and 1/50)

- Non-detects plotted as the detection limit
- As concentrations fall, our ability to distinguish between PFAS profiles falls
- Profiles can become uninterpretable as they are diluted
- More complicated if the compounds have different detection limits

Confounding Factors:
Alteration of Profiles in Plumes


Direction of Groundwater Flow
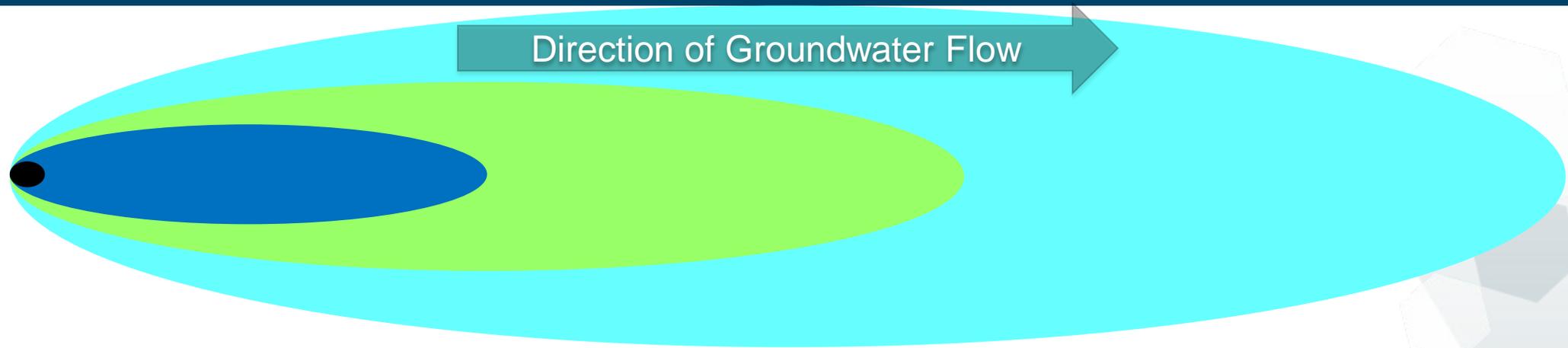
As PFAS move through the subsurface with groundwater

- Lighter, less hydrophobic compounds move more quickly

- Heavier, more hydrophobic compounds move more slowly

- The PFAS profile could be altered as the plume propagates, alterations in chemical profiles have been noted for PCBs and other chemicals

Identifying, segregating, and tracking sources early in the investigation can result in more targeted risk assessments and remedial actions
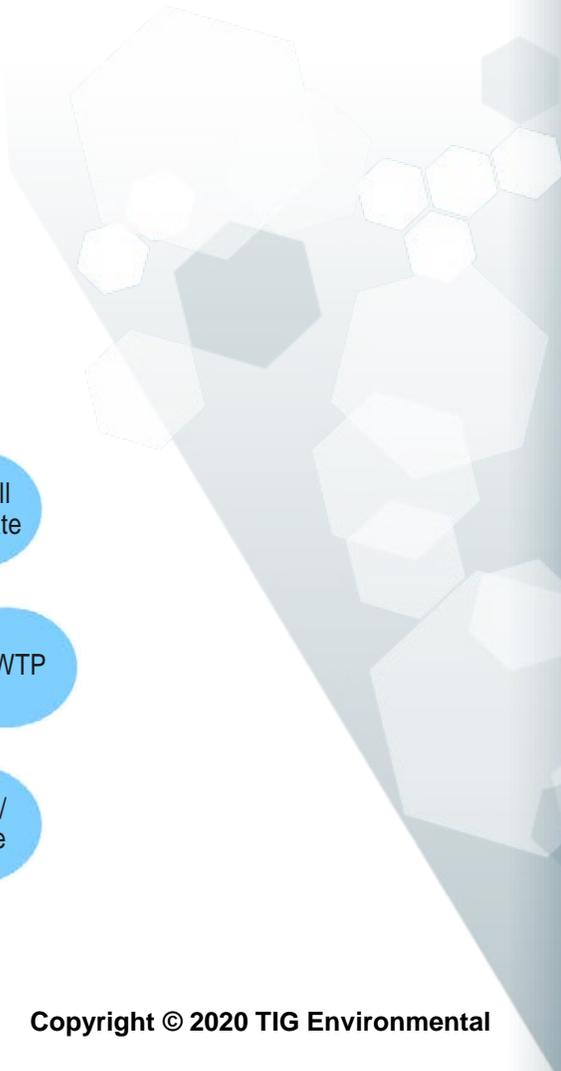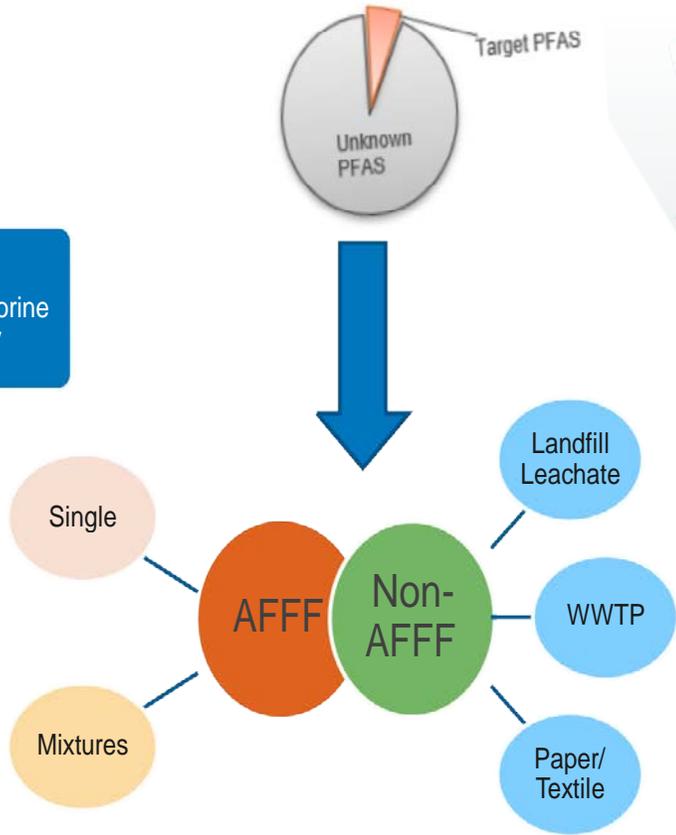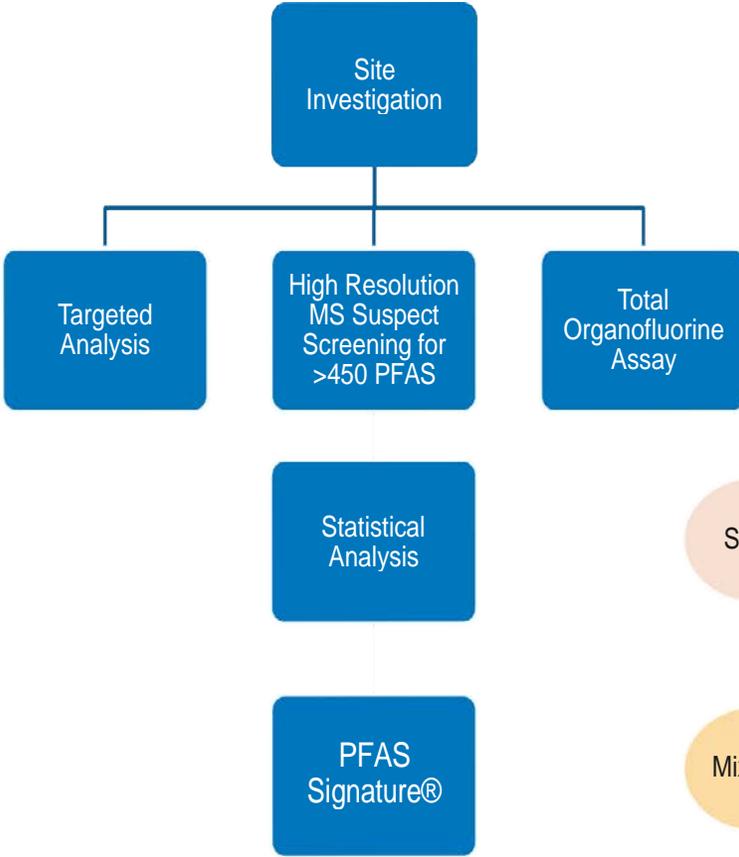
PFAS Signature®

Challenge: Limited number of target analytes that are commonly found across different sources provides incomplete understanding of PFAS source characteristics.

Solution: PFAS Signature® Source Discrimination Tool, a first-to-market technology for identifying PFAS sources.

- High Resolution MS Analysis considers the extended list of **495 PFAS analytes**
- PFAS-focused data filtering tools allows for informed data reduction
- PFAS Source Signature Trained AI/ML tools allows for the identification and discrimination of PFAS Sources
- High throughput/limited analyst time to process

Sample Preparation
- SPE Extraction
- Direct Injection

Sample Analysis
- Targeted Analysis
- High Resolution

Data Processing
- Data Filtering
- Machine Learning Tool

**Data Interpretation**
- Other Lines of Evidence
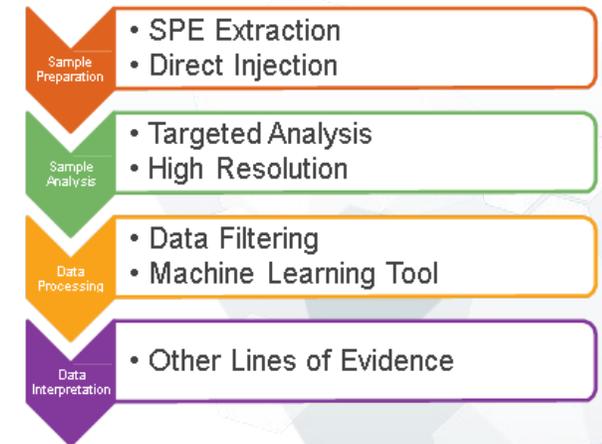
Tool Components
- Targeted Analysis
- High Resolution MS Analysis
- Data filtering
- PFAS Suspect Screening Library
- PFAS Source Library
- Statistical Analysis

TIG environmental®
INVESTIGATIONS • FORENSICS • REMEDIATION

PFAS Signature®

Includes Database of Source Specific Signature Library

Library is continually populated as more source data is generated

- AFFF formulations
  - More than 10 sources of different AFFFs

- AFFF-Impacted Sites (Multiple Matrices)
  - WWTP located within AFFF impacted site
  - AFFF impacted biosolids applied soil
  - AFFF used for emergency response

- Waste Sector
  - Landfill Leachates
  - Municipal WWTP related samples and additives
  - Paper Mill related WWTP samples

- Metal plating
- Commercial products
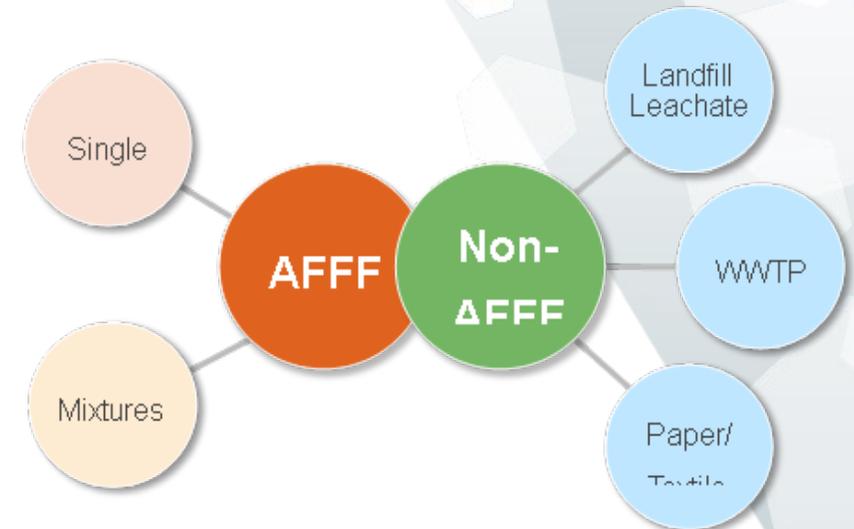
Example High Resolution MS Data

FT Based Precursors/Metabolites

ECF Based Precursors/Metabolites

Perfluoroalkyl acids (PFAAs)
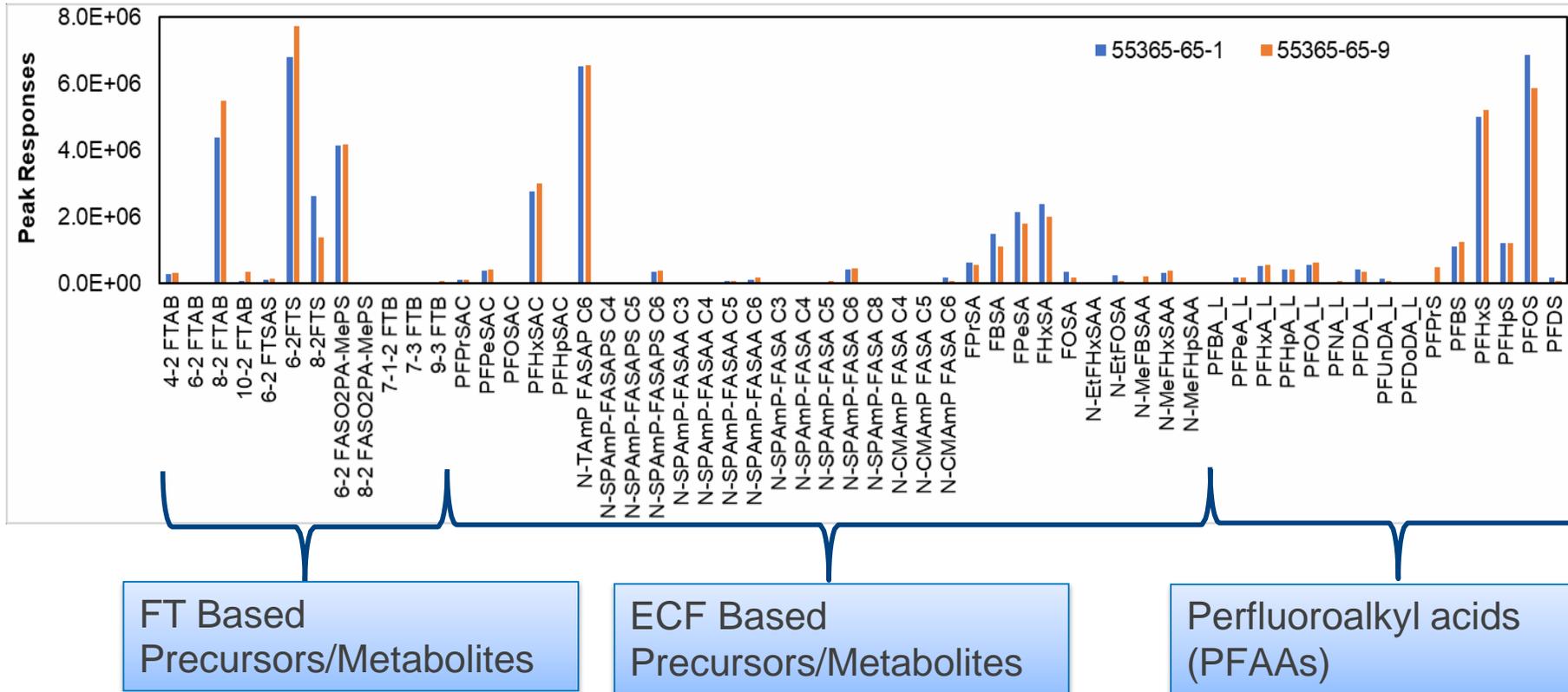
More than 100 analytes detected with both branched and linear isomers - Mix of both FT and ECF chemistries

13

- Discriminates AFFF sources through development of source libraries with known samples

- Source discrimination of AFFF vs Non-AFFF in environmental samples

- Provides Delineation of distinct PFAS Sources and Co-Occurrence
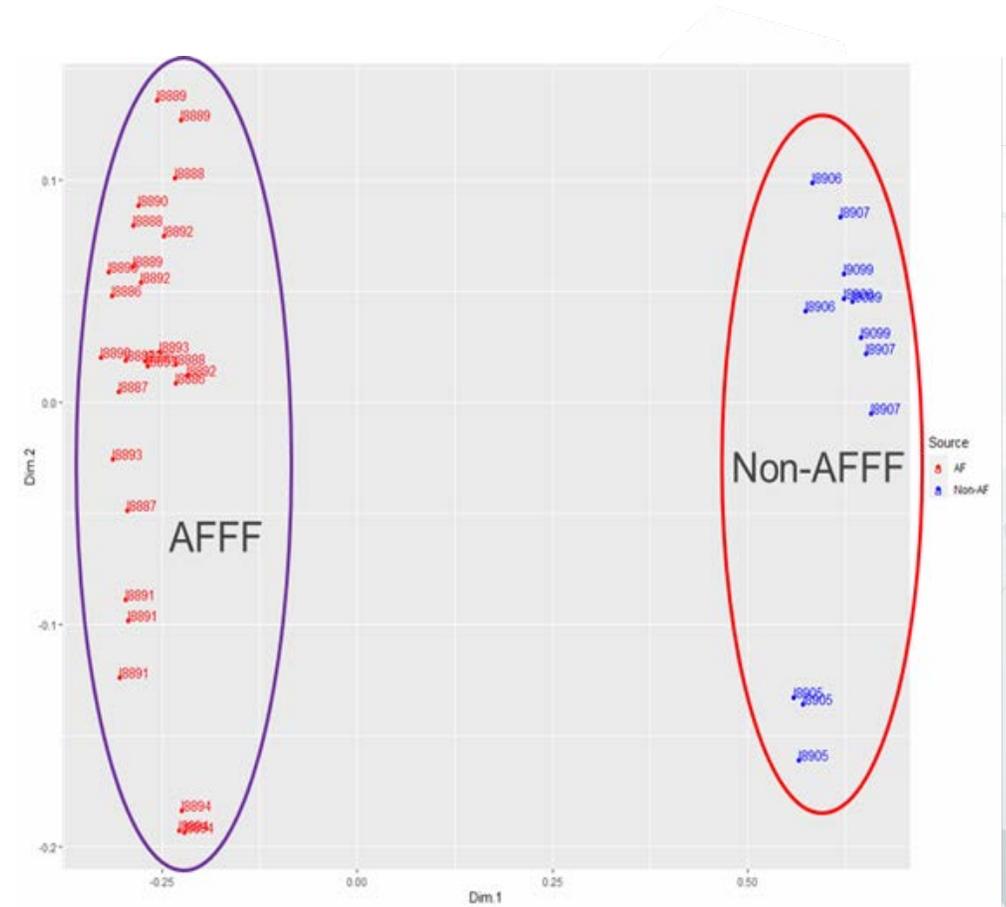
Contact

Carlo Monti, Ph.D.

Managing Director

Crocicchio Cortogna 6
CH-6900 Lugano
Switzerland

✉ cmonti@intell-group.com

☎ +39 (329) 917-3066

🖥 www.intell-group.com