



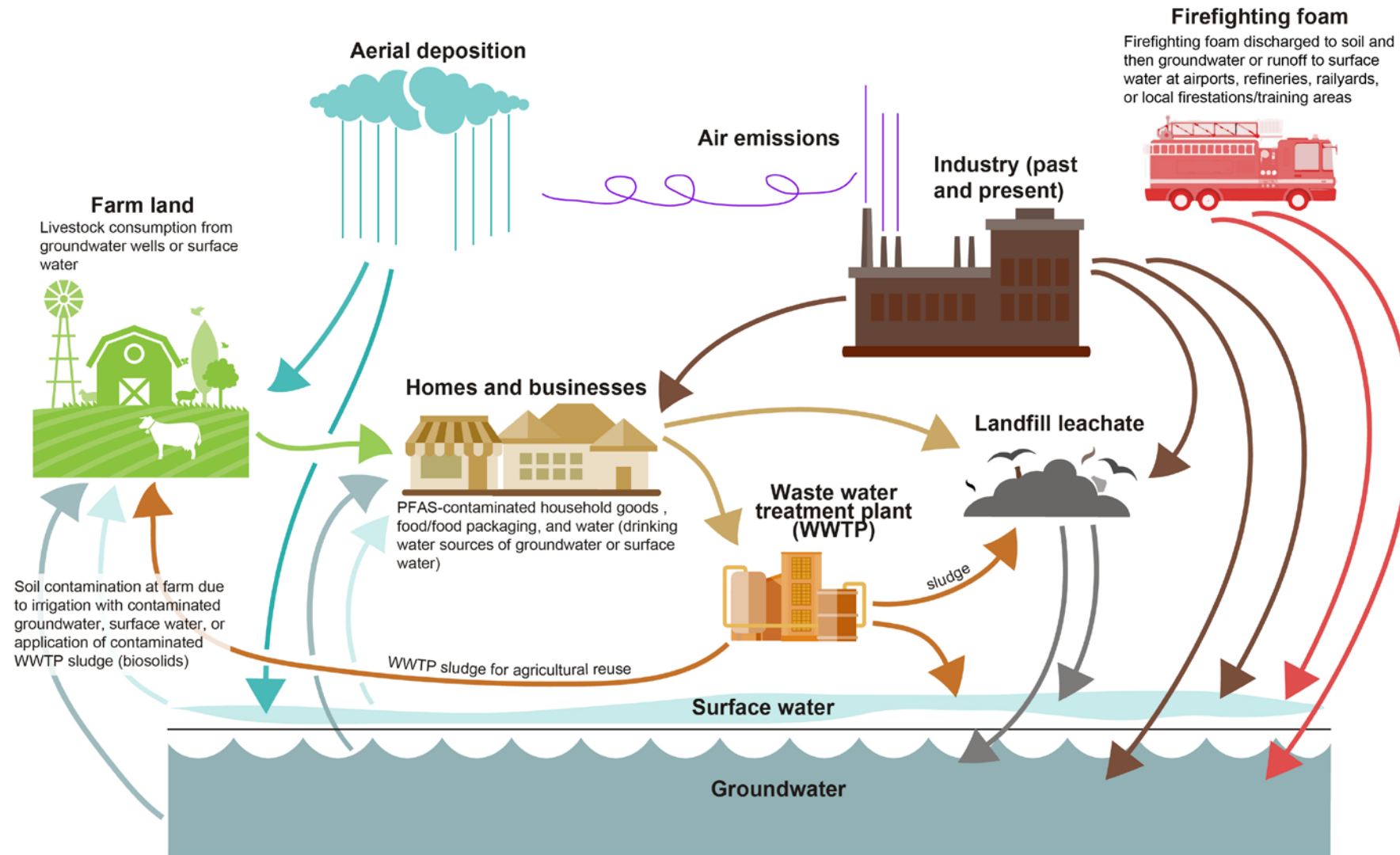
PFAS Cluster Identification: Defining the sources of PFAS by multivariate statistical methods:

A multivariate forensic analysis to detect the origin and extent of PFAS contamination in Northern Italy

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Numerous Sources and Transport Pathways



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.

PFAS Source Tracing

Statistical Fingerprinting Methods

Existing Fingerprinting Methods

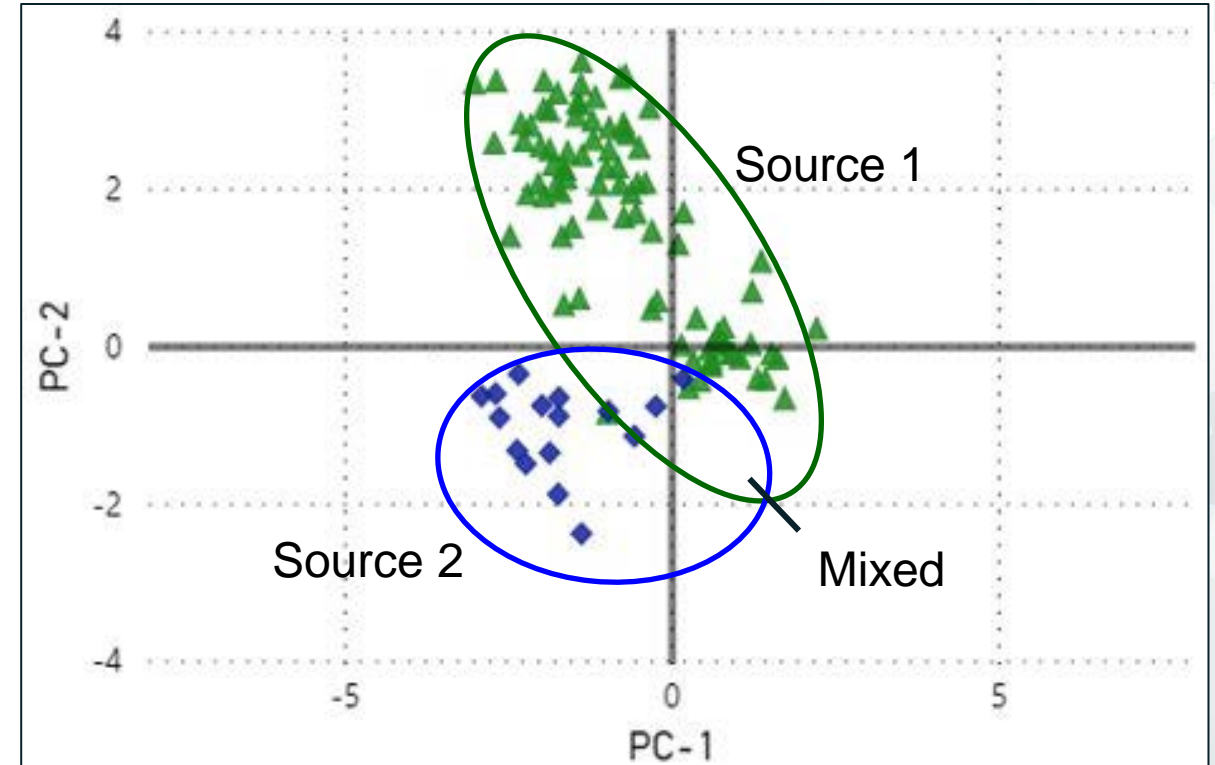
- Targeted Analysis (Typically < two dozen PFAS)
- Principal Component Analysis (PCA)
- Polytopic Vector Analysis (PVA)
- Multivariate Cluster Analysis

Forensic Laboratory Methods

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

Evolving Methods

- **Nontargeted Analysis** - potential to identify thousands of PFAS



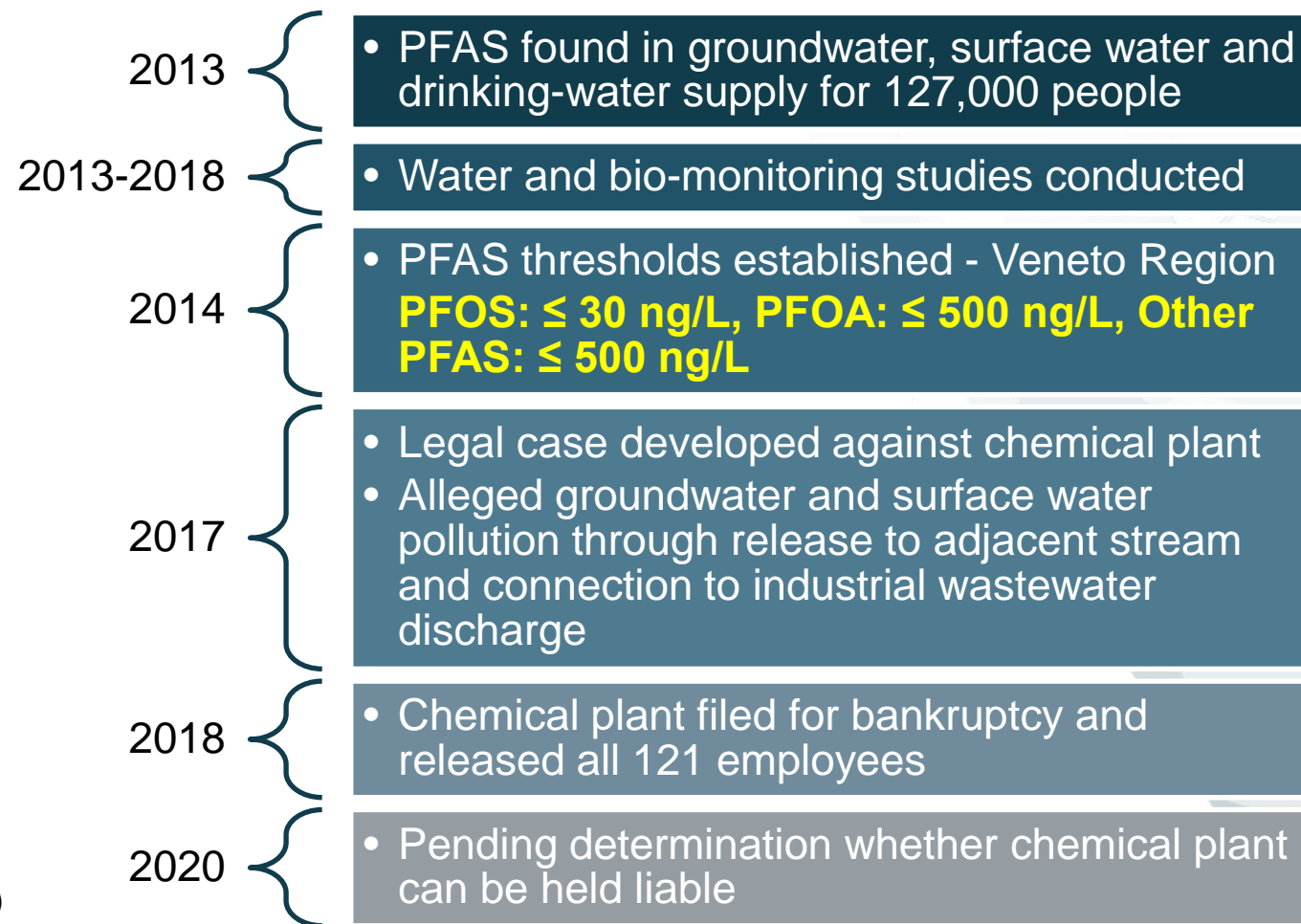
PFAS Fingerprinting Veneto Region, Italy

A PFAS manufacturer was accused of drinking water contamination with estimated damages to human health of several billion dollars



The chemical plant started in 1964, specialized in fluorochemicals used to make stain-resistant, waterproof or non-stick finishes

Monti, C., Rose, N., Negley, T., 2020. PFAS Fingerprinting: A multivariate forensic analysis to detect the origin and extent of PFAS contamination in Northern Italy. *International Network of Environmental Forensics* (submitted)



PFAS Fingerprinting Veneto Region, Italy

Public monitoring data in the region show multiple PFAS frequently exceeded Veneto performance levels

Substance	Results	Exceedances	% Exceedance	Max Detect	Detect Unit
PFBS	7384	470	22.03%	7,300.00	ng/L
PFBA	7382	453	21.24%	1,900.00	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
PFDaA	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

PFOA

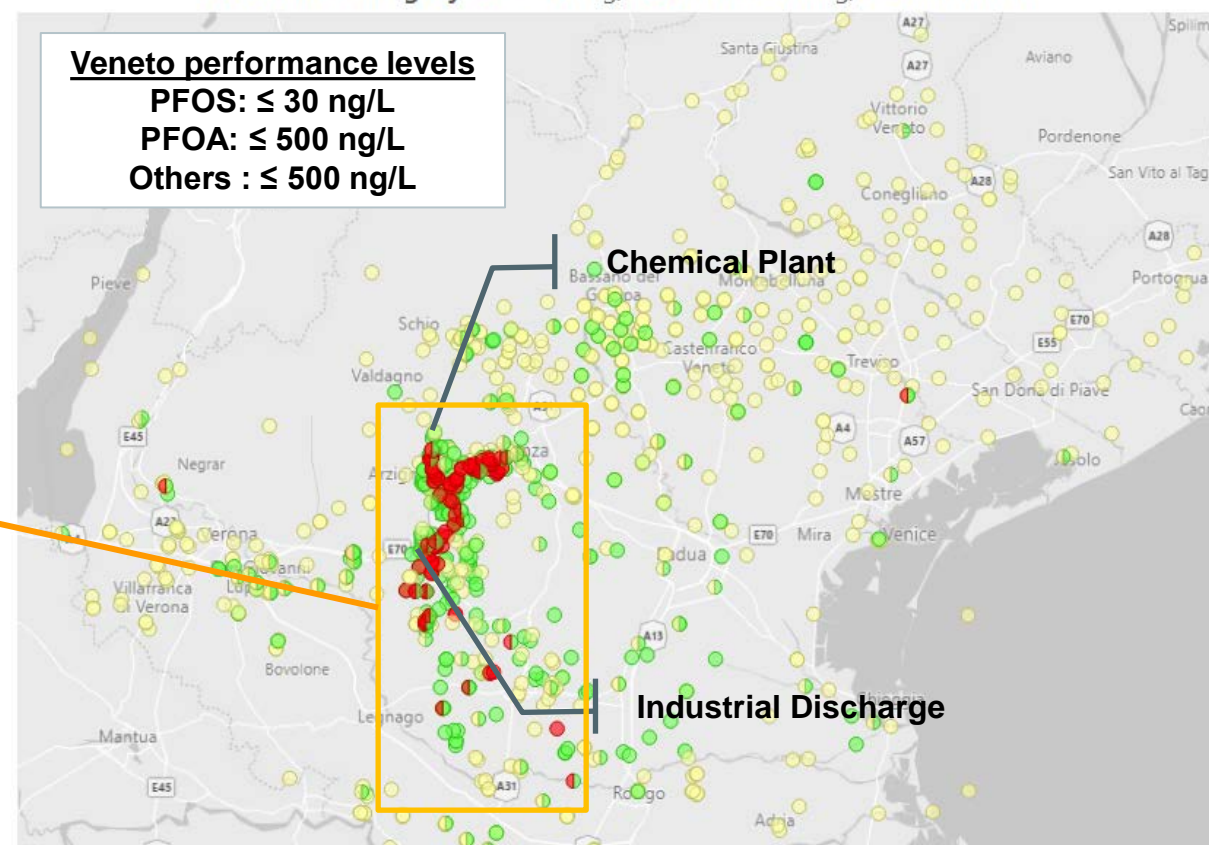
Exceedance Category ● ≤ 500 ng/L ● Exceeds 500 ng/L ● Nondetect

Veneto performance levels

PFOS: ≤ 30 ng/L

PFOA: ≤ 500 ng/L

Others : ≤ 500 ng/L

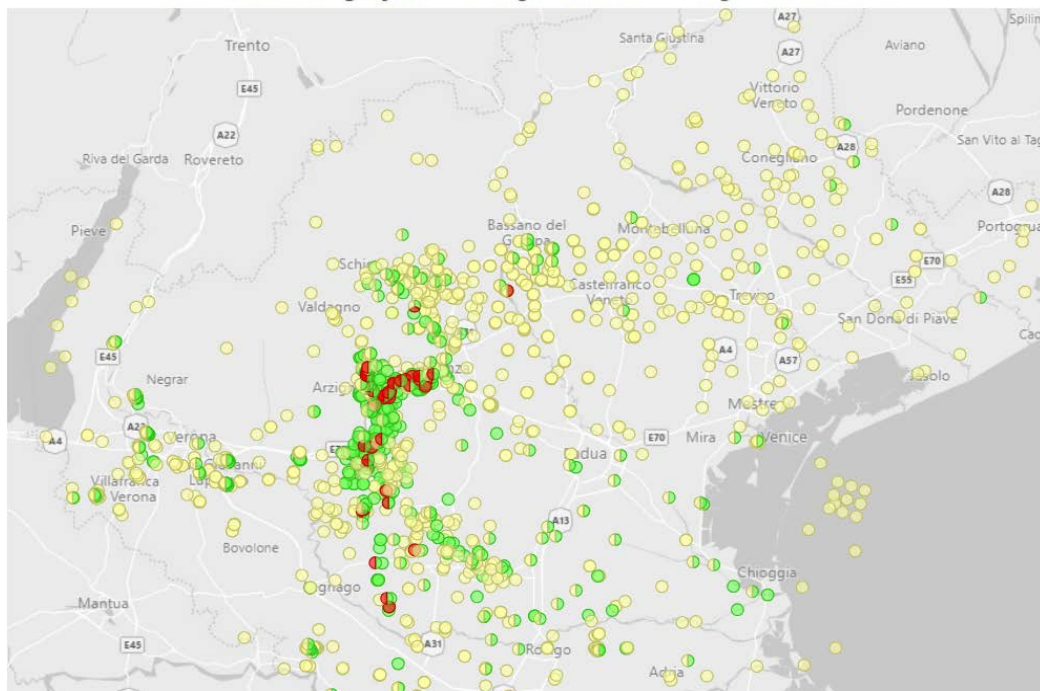


PFAS Fingerprinting Veneto Region, Italy

The two PFAS that exceeded performance levels most frequently were PFBS and PFBA

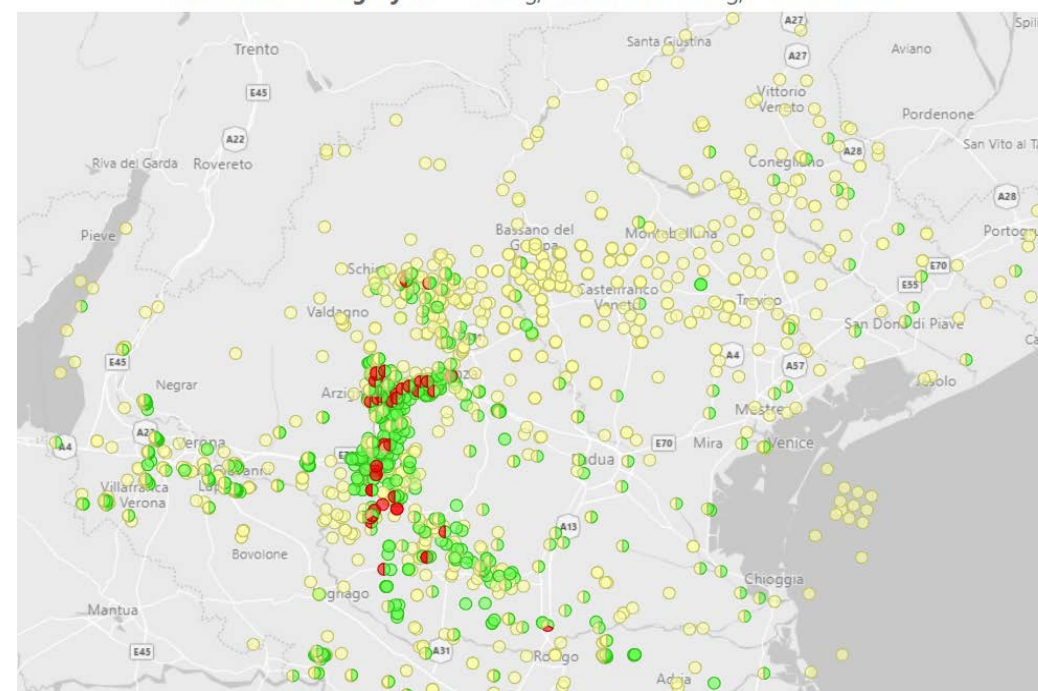
PFBS

Exceedance Category ● ≤ 500 ng/L ● Exceeds 500 ng/L ● Nondetect



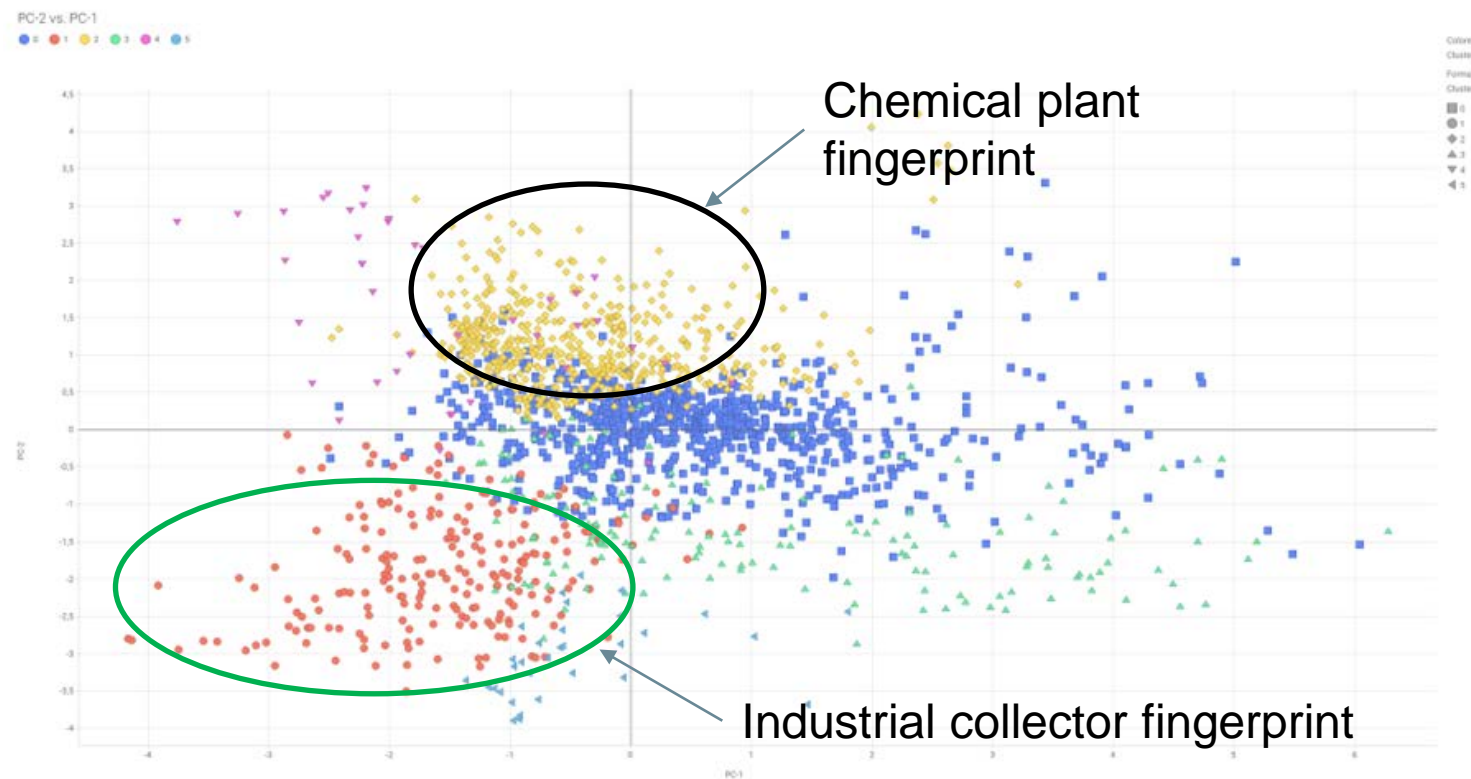
PFBA

Exceedance Category ● ≤ 500 ng/L ● Exceeds 500 ng/L ● Nondetect



PFAS Fingerprinting Veneto Region, Italy

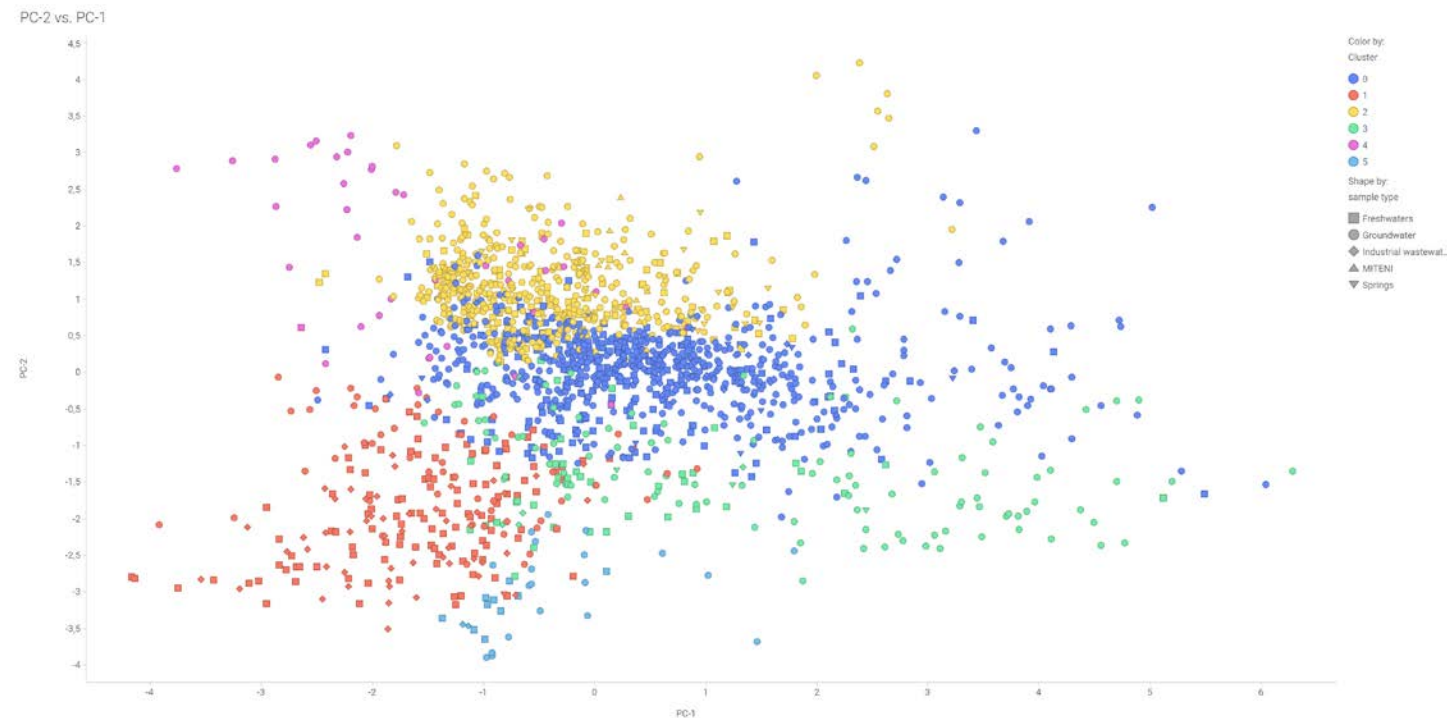
- Of 8000+ samples, about 1,400 samples for eight (of 18) PFAS were deemed useable for fingerprinting
 - Methodology: PCA, cluster analysis, and TIG's proprietary PVA algorithm
-
- Chemical plant was dissimilar to industrial waste water
 - Chemical plant was dissimilar to many groundwater and freshwater samples
 - Further evaluation of source contributions evaluated with PVA



PFAS Fingerprinting

Veneto Region, Italy – Principal component analysis

- A clustering analysis has been done on the data set. The results of the clustering have been used to analyze the PCA results;
- Manufacture's samples belong to the Cluster 2 (in yellow) and are indicated as triangle.
- The industrial discharge samples are included in cluster 1 and are indicated as diamond in the figure;
- Manufacturer and Industrial discharge samples are included in two distinct clusters meaning that other sources are loading PFAS to the industrial discharge.



PFAS Fingerprinting Veneto Region, Italy

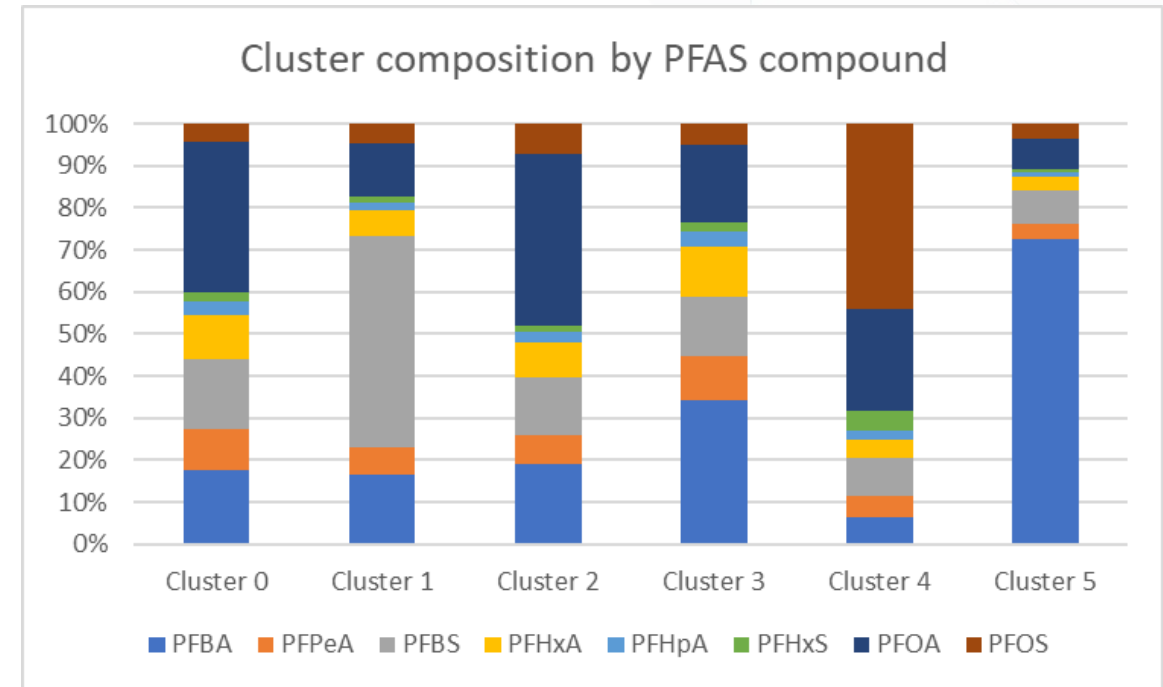
- PVA Results:** TIG's proprietary PVA algorithm suggested more than one source, each source dominated by specific PFAS, all of which exceeded the Veneto performance levels
 - PFBS (Source 1)
 - PFBA (Source 5)
 - PFOS (Source 4)
 - PFOA (Source 2)
 - Mixture (Source 3)
- The methodology demonstrated one source dominated, but other less dominant sources also appear to contribute.

Substance	Results	Exceedances	% Exceedance	Max Detect	Detect Unit
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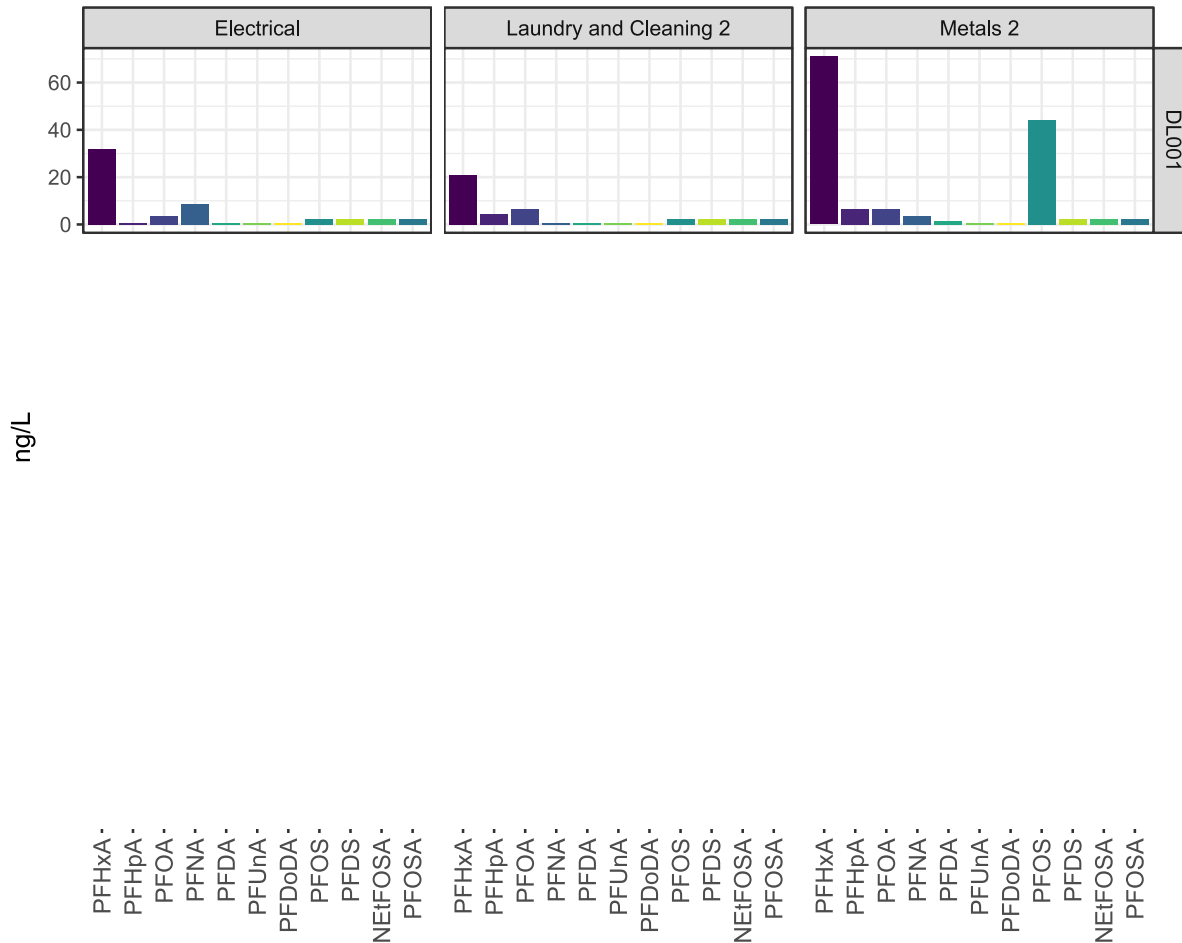
PFAS Fingerprinting

Veneto Region, Italy - Clusters fingerprint and sample composition

- 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.



Confounding Factors: Detection Limit Issues Can Obscure Profiles

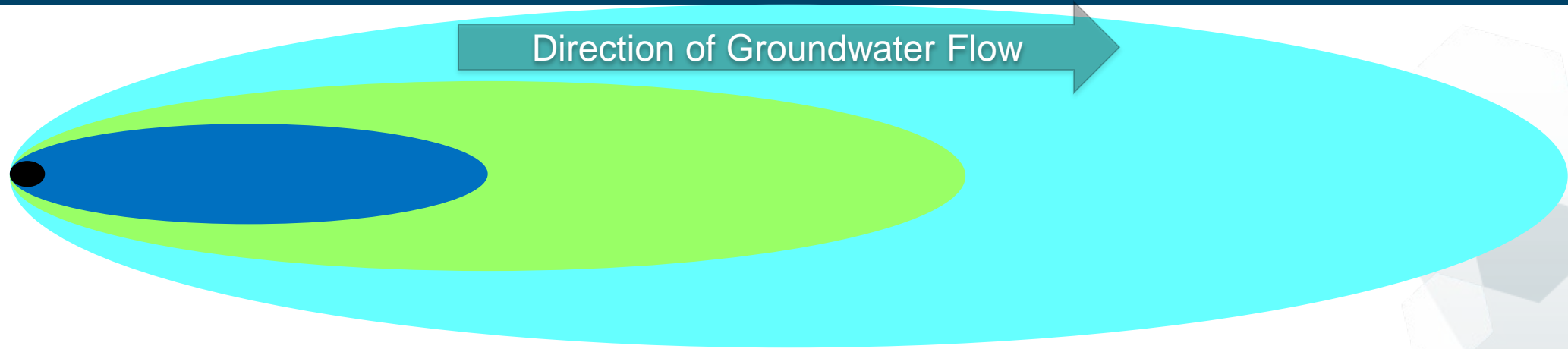


As the PFAS concentrations fall, the number of PFAS compounds detectable by the laboratory also falls

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




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

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