Illuminating "Dark" PFAS with Total Organic Fluorine (TOF) methods

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The **Detectable** and Undetectable "**Dark**" Types of PFAS

- PFAS are a family of **>12,000** chemicals, and growing
- Each have a unique structure, with varying numbers of **carbon – fluorine bonds**
- All PFAS contain ***fluorine*** and at least one ***carbon – fluorine bond***
  - Carbon = "organic"
  - **Organic Fluorine** ("**O-F**") also called Organofluorine compounds
- **Unmet** challenge of detecting and quantifying each type of PFAS individually (~40 currently)
- Alternative use of PFAS chemical signatures = Fluorine + Organic Fluorine (O-F) to detect **Total PFAS** in samples
  - **Total Organic Fluorine (TOF)** and **Total Fluorine (TF)** methods

Illuminating Total PFAS with Combustion + Ion Chromatography

- Carbon – Fluorine bonds = one of the **strongest** bonds in organic chemistry
- Requiring temperatures – approx. **1,000 °C**

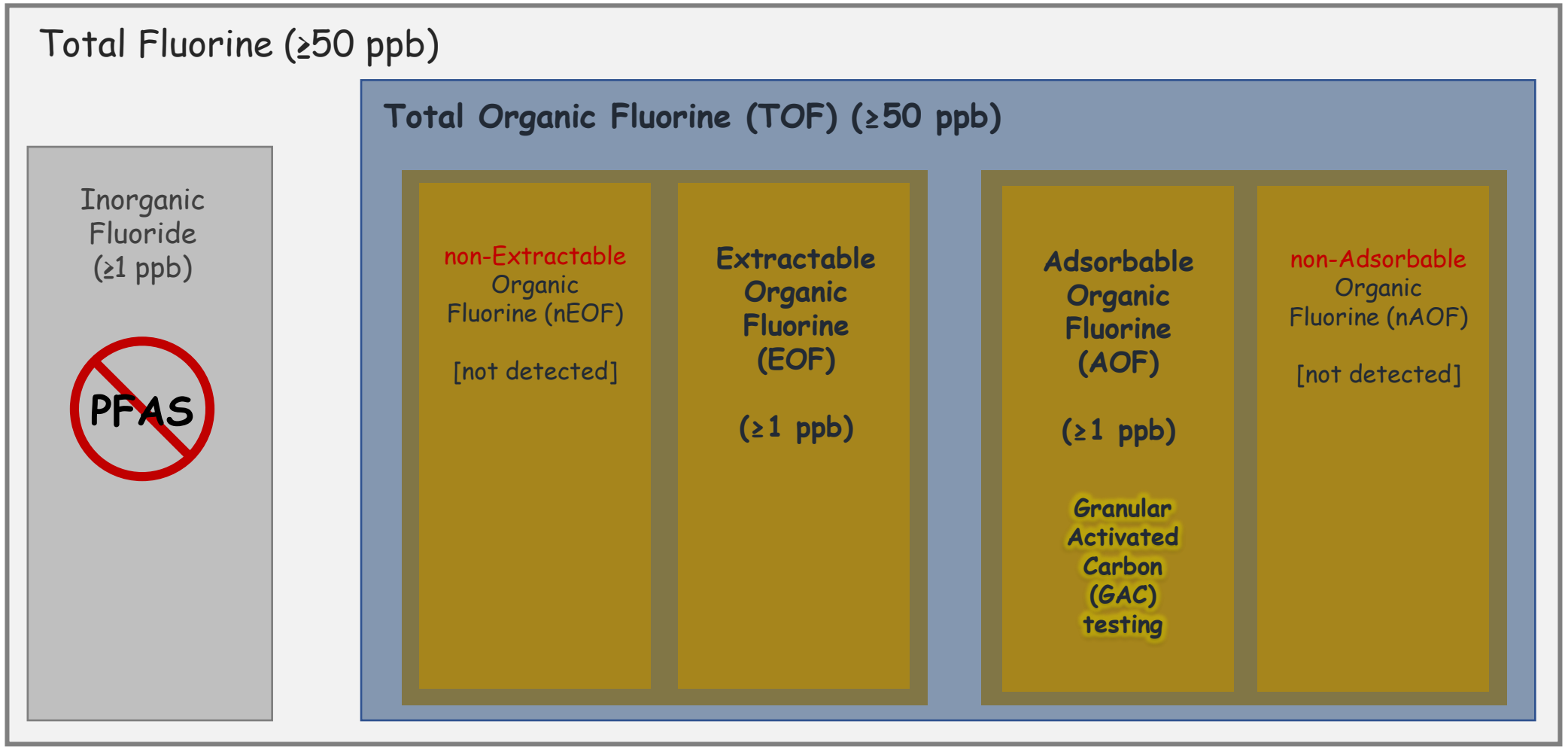
- **Total Organic Fluorine (TOF)** and **Total Fluorine (TF)** methods for Total PFAS
  - Measure the total amount of fluorine in a sample

- **Combustion Ion Chromatography "CIC"**

  - **OXIDATIVE - PYROHYDROLYTIC - COMBUSTION *followed by* ION CHROMATOGRAPHY DETECTION**
  - Oxidant = oxygen
  - Pyro-hydrolytic = using heat and reactions with water to "combust" break apart the PFAS compounds into ions – with the production of heat and light

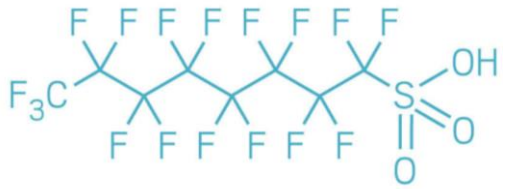
Fluorine "Signatures" for Total PFAS Analysis by CIC

Total PFAS (+12,000 chemicals) – Fluorine "Signature" Methods



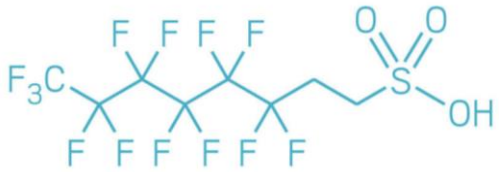
Total Organic Fluorine (TOF) Analytical Results – *What Do They Mean?*

- **Total Organic Fluorine (TOF)** and other **Fluorine "Signature"** methods = concentration of fluorine detected in a solid/liquid/gas sample



PFOS
F: 17 x 18.998 = 322.966
C: 8 x 12.011 = 96.088
S: 1 x 32.066 = 32.066
O: 3 x 15.999 = 47.997
H: 1 x 1.008 = 1.008
MW = 500.13

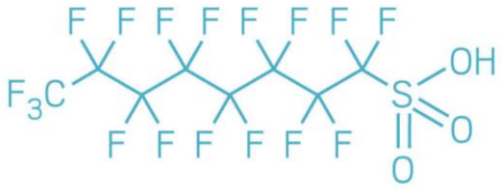
% F: 322.966/500.13 = 64.58%



6:2 FTSA
F: 13 x 18.998 = 246.974
C: 8 x 12.011 = 96.088
S: 1 x 32.066 = 32.066
O: 3 x 15.999 = 47.997
H: 5 x 1.008 = 5.04
MW = 428.17

% F: 246.974/428.17 = 57.68%

Total Organic Fluorine (TOF) – Comparison of **Knowns** and **Unknowns**



PFOS

% F: 322.966/500.13 = 64.58%

Example: (PFOS)

- (100 ug/L fluorine detected by TOF) / 0.6458 = **155 ug/L PFOS** (*calculated*)

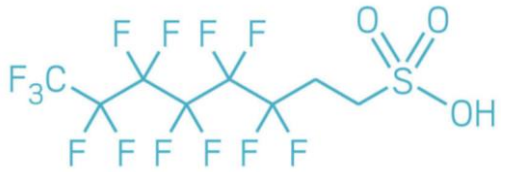
- ✓ Fluorine Percentages for individual PFAS using standards methods (*n=40*) range from **52% to 73%** fluorine contribution by mass.
- ✓ **Fluorine Concentration (TOF) > ∑PFAS (n=40)**
- ✓ **Fluorine Concentration (TOF) < Concentration of Total PFAS**

Fluorine Concentration (TOF) < Total PFAS in a sample ≤ *[CALCULATED] PFAS*

"Precursor" PFAS - *how will they impact TOF results?*

- "Precursors" are large PFAS compounds – including fluorotelomers, fluorinated polymers, and chemicals with fluorinated side chains
- Concern = the breakdown into smaller, target PFAS compounds and unknown toxicity

6:2 FTAB (AFFF "C6"; Capstone/Forafac)
Precursor



6:2 FTSA
Breakdown Product

- Precursors are considered one type of "Dark Matter" PFAS
  - Not detectable with individual speciation & standard methods
  - Pre-treatment of larger compound into smaller, detectable PFAS types (Total Oxidizable Precursor (TOP) Assay + standard analyses)

OR

  - Total Organic Fluorine (TOF) and Total Fluorine (TF) methods

Fluorinated Pharmaceuticals - *how will they impact TOF results?*

- Approximately 360 fluorinated pharmaceuticals (PFAS family +12,000 chemicals)
  - Over half of the 360 = contain only one fluorine
  - Only four were fully or nearly fully fluorinated aliphatic compounds

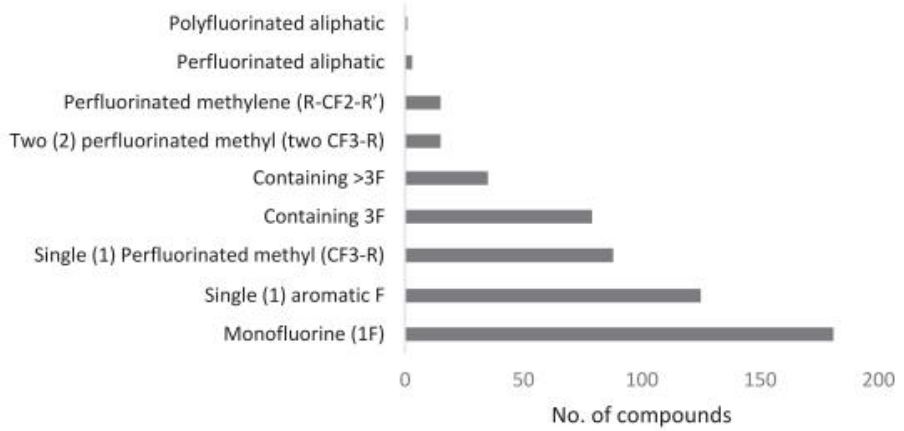
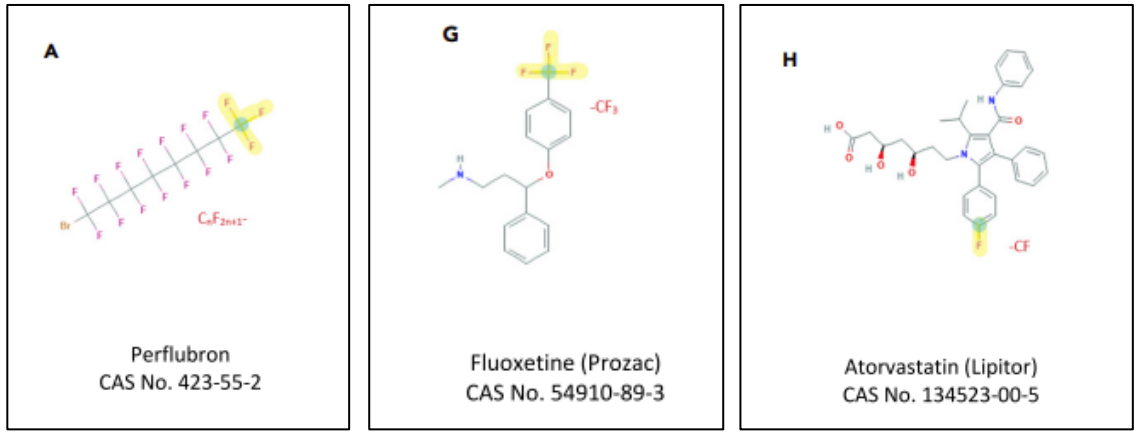
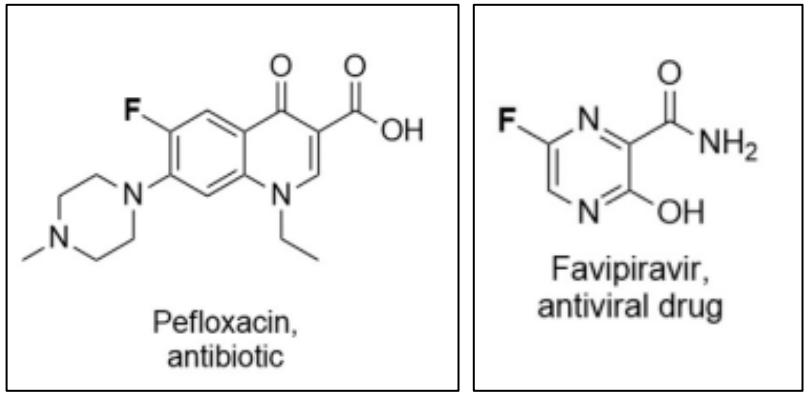


Figure 1. Substructures identified among organofluorine pharmaceuticals





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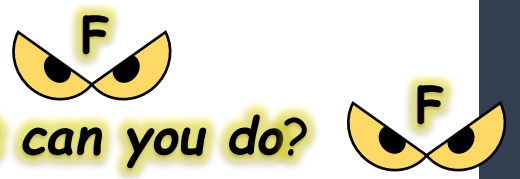
Pesticides – Fluorinated Chemicals & PFAS Leaching from Packaging

- **September 1, 2022**: EPA proposed to remove 12 PFAS from its approved list of inert ingredients for pesticides.
  - Inert PFAS - increase pesticide effectiveness and product performance, extend product shelf life or improve ease of application by preventing caking or foaming
  - 12 PFAS – "not currently used" (not listed/declared) in registered pesticide products
  - ❖ Not detectable using standard PFAS methods – ***What can you do?***
  - ❖ *What if the types of PFAS under scrutiny change tomorrow?* – ***What can you do?***



- **September 8, 2022**: EPA released results showing fluorinated coatings on high-density polyethylene (HDPE) containers leached PFAS chemicals into a mosquito control pesticide
  - "fluorous-seals" improve container stability, and make them less permeable, reactive and dissolvable = *"protective" of consumers/users*
  - Coatings leached PFAS chemicals into pesticide – sprayed directly into the environment

Consumer Packaging and "Intentionally-Added" PFAS

- **Paper or Plastic?**
  - Increased demand for "Green" and "Sustainable" packaging
  - Moving away from plastics -FOR- renewable or recyclable "natural" materials
  - PFAS is often added to meet performance criteria, increase water/grease repellence, stain-resistance in "natural" materials
  - PFAS may be added to plastics as coatings (ex. mosquito control pesticide)

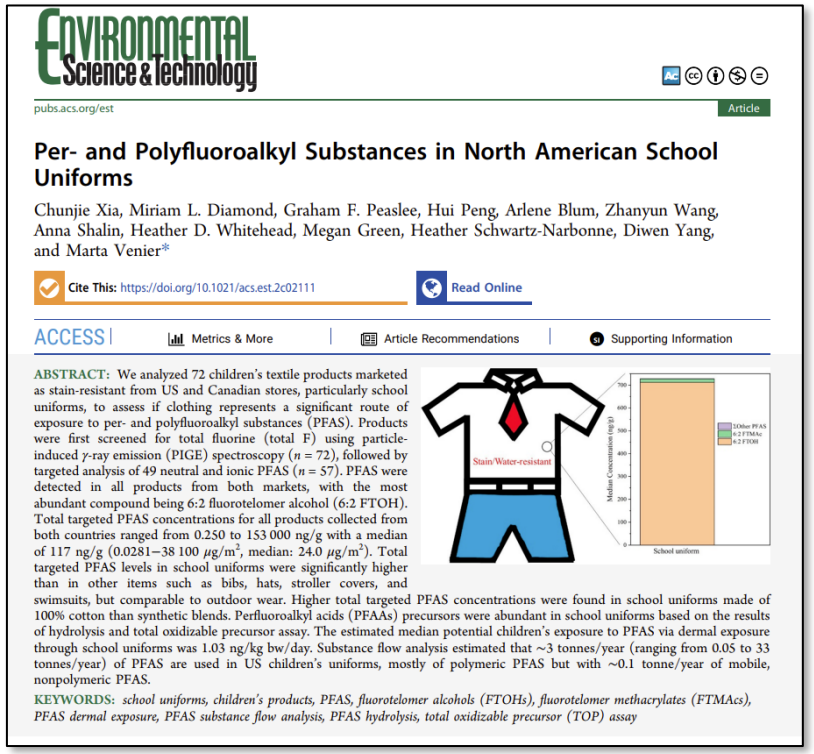
- "**Intentionally-Added**" PFAS
  - Safety Data Sheets (SDSs) may not list PFAS ingredients added in concentrations ≤ 1% (10,000 ppm), or considered "confidential", "proprietary" or a "trade secret"
  - PFAS used in packaging = non-traditional PFAS types, fluorinated side-chains, and precursors
  - Biodegradable Products Institute, Supply Chain groups, and Consumer Reports – use **Total Fluorine (TF)** or Total Organic Fluorine (TOF) testing
  - ➢ **100 ppm TF / TOF** = used to indicate "Intentionally-Added" PFAS

PFAS in Textiles and School Uniforms, September 21, 2022

PFAS in Textiles provide:

- Water-proofing/Weatherproofing
- Stain-resistance
- Wrinkle-resistance
- Durability
- Mostly "**outdoor wear**", right?

September 21, 2022



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Article

Per- and Polyfluoroalkyl Substances in North American School Uniforms

Chunjie Xia, Miriam L. Diamond, Graham F. Peaslee, Hui Peng, Arlene Blum, Zhanyun Wang, Anna Shalin, Heather D. Whitehead, Megan Green, Heather Schwartz-Narbonne, Diwen Yang, and Marta Venier*

Cite This: https://doi.org/10.1021/acs.est.2c02111 Read Online

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ABSTRACT: We analyzed 72 children's textile products marketed as stain-resistant from US and Canadian stores, particularly school uniforms, to assess if clothing represents a significant route of exposure to per- and polyfluoroalkyl substances (PFAS). Products were first screened for total fluorine (total F) using particle-induced γ-ray emission (PIGE) spectroscopy (n = 72), followed by targeted analysis of 49 neutral and ionic PFAS (n = 57). PFAS were detected in all products from both markets, with the most abundant compound being 6:2 fluorotelomer alcohol (6:2 FTOH). Total targeted PFAS concentrations for all products collected from both countries ranged from 0.250 to 153 000 ng/g with a median of 117 ng/g (0.0281−38 100 μg/m^2, median: 24.0 μg/m^2). Total targeted PFAS levels in school uniforms were significantly higher than in other items such as bibs, hats, stroller covers, and swimsuits, but comparable to outdoor wear. Higher total targeted PFAS concentrations were found in school uniforms made of 100% cotton than synthetic blends. Perfluoroalkyl acids (PFAAs) precursors were abundant in school uniforms based on the results of hydrolysis and total oxidizable precursor assay. The estimated median potential children's exposure to PFAS via dermal exposure through school uniforms was 1.03 ng/kg bw/day. Substance flow analysis estimated that ~3 tonnes/year (ranging from 0.05 to 33 tonnes/year) of PFAS are used in US children's uniforms, mostly of polymeric PFAS but with ~0.1 tonne/year of mobile, nonpolymeric PFAS.

KEYWORDS: *school uniforms, children's products, PFAS, fluorotelomer alcohols (FTOHs), fluorotelomer methacrylates (FTMAcs), PFAS dermal exposure, PFAS substance flow analysis, PFAS hydrolysis, total oxidizable precursor (TOP) assay*

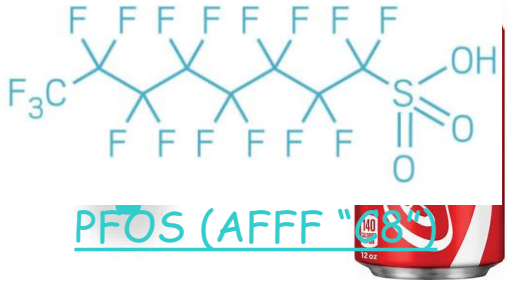
- High PFAS levels found in children's **school uniforms**
- Direct contact with **skin**
- Levels similar to **outdoor wear**
- Large amounts of unknown "**Dark Matter**" PFAS

Identify Total PFAS Risk with TOF / TF testing!

Chemical Substitutions and Aqueous Film Forming Foams (AFFFs)

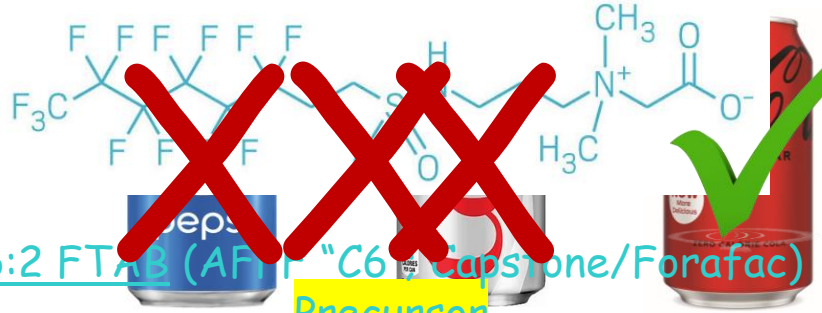
With so many undetectable "**Dark**" types of PFAS:

Choose a chemical/product replacement ? ≠ Regrettable Substitution



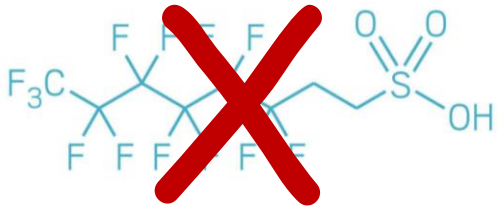
PFOS (AFFF "C8")

≠≠



6:2 FTAB (AFFF "C6 Capstone/Forafac")

Precursor



6:2 FTSA

Breakdown Product

Fluorine-Free Foams

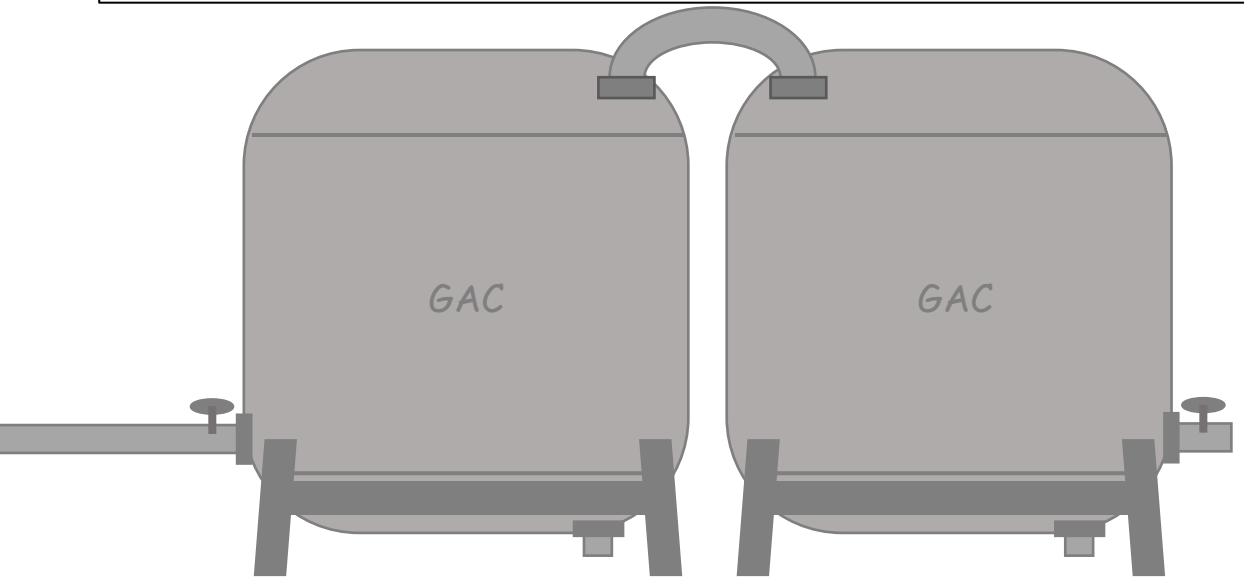
≤ 1ppb Total PFAS

Detect all "**Dark**" types of PFAS with

Total Organic Fluorine methods

TOF Testing – Industrial Processes, Treatment Systems and Disposal

- **Mobile Laboratory** – Fluorine Testing Methods
  - Total Organic Fluorine (TOF), Total Fluorine (TF), Extractable Organic Fluorine (EOF), Adsorbable Organic Fluorine (AOF), Inorganic Fluoride
- Rapid analysis = ~20 min run time
- Liquids and Solid Matrices (air/gas option)
- Influents, effluents, GAC, resin, wastes…and more!
- **PFAS Field Sampling**
- **Subsurface Investigations and Drilling Services**



- ✓ *Do my chemicals, products or packaging….*
- ✓ *Does my influent….*
- ✓ *Does my effluent…..*
- ✓ *Does my waste….*
- ✓ *Does the soil/water/air of a site or property…..*

CONTAIN ANY PFAS?

QUESTIONS?

BROWN Environmental, LLC

Providing Answers To Your Total PFAS Questions!

Audra Liggenstoffer, Ph.D.

President & Owner

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