Methods and Challenges in PFAS Measurement

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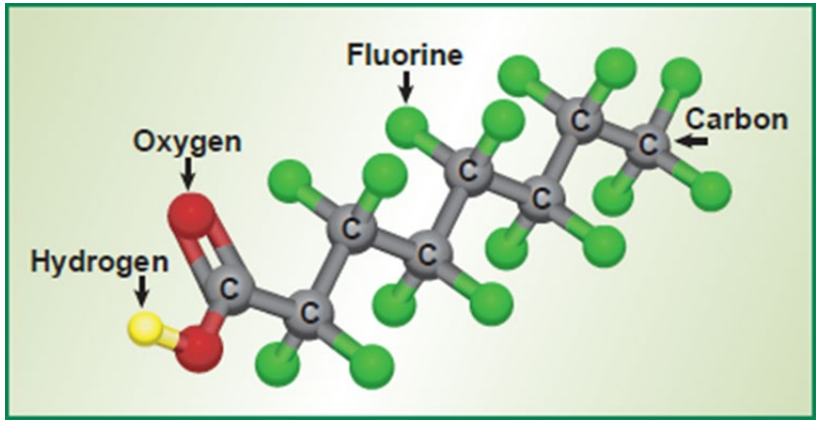
NOVEMBER 13, 2024

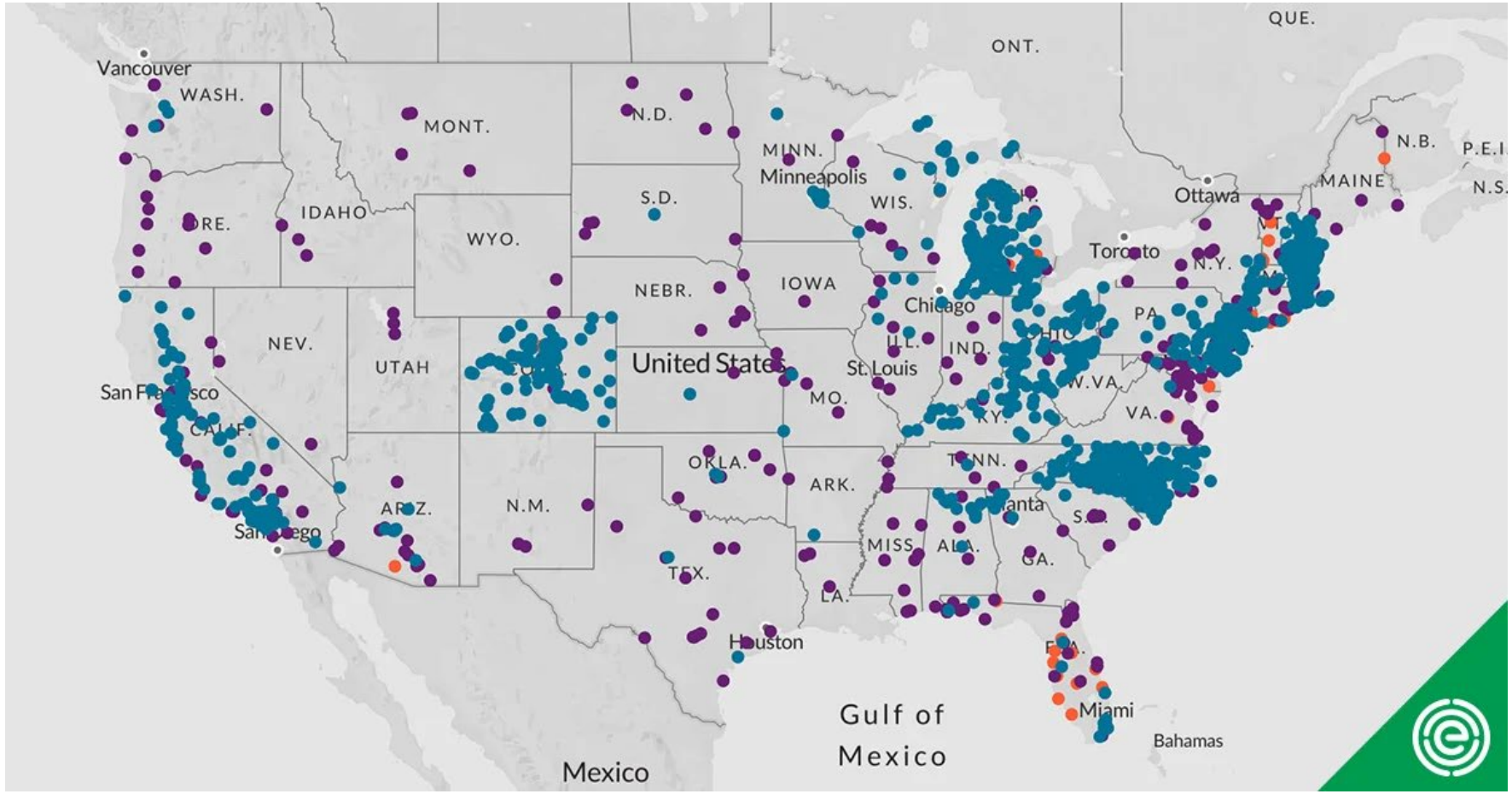
PER- AND POLYFLUOROALKYL SUBSTANCES (PFAS)
Background

- In paper:
  - fast food containers/wrappers
  - microwave popcorn bags
  - pizza boxes
  - candy wrappers.

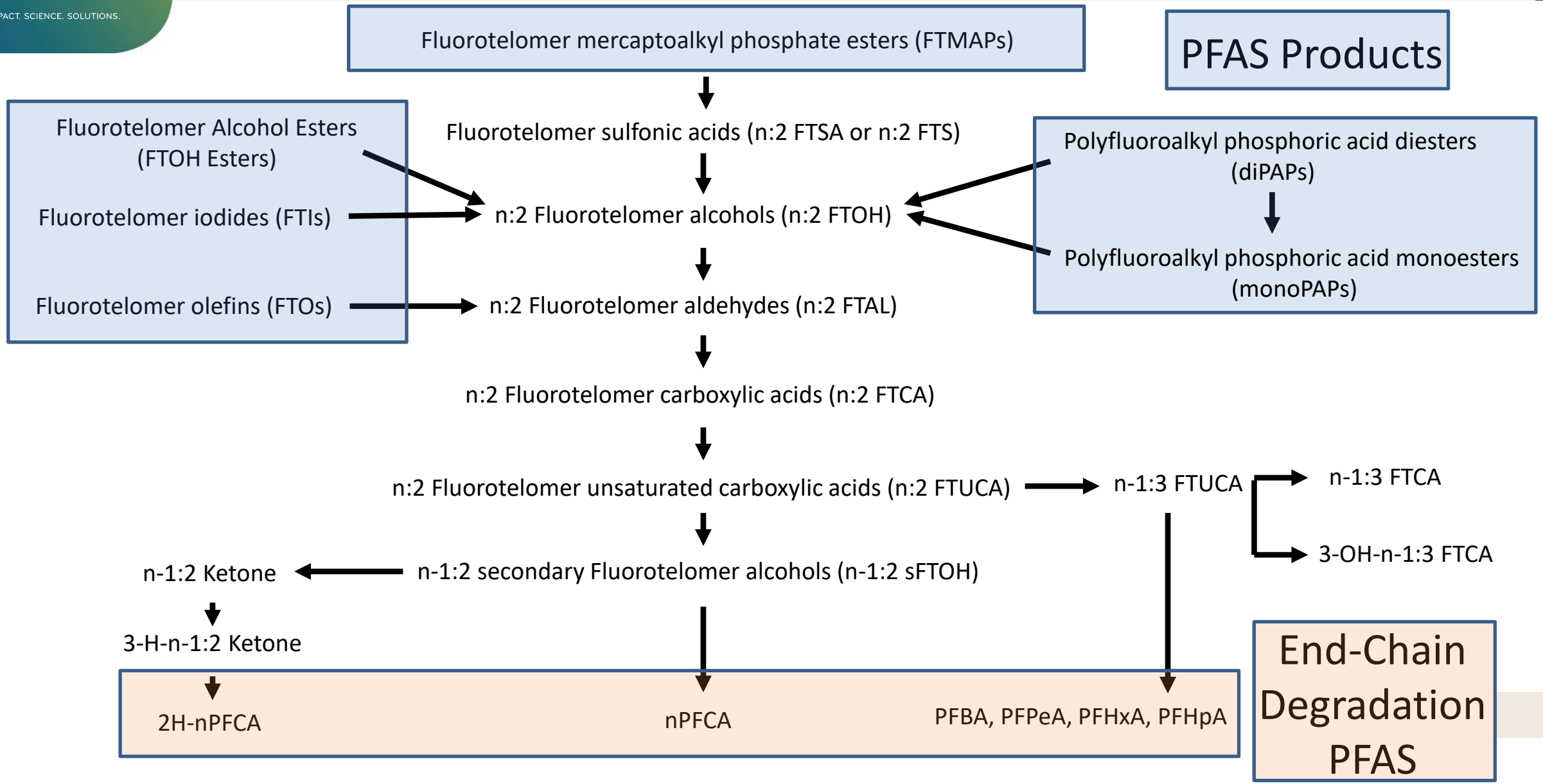
- In other products:
  - Teflon® coated pots and pans
  - Scotchguard® treated carpets and fabrics
  - Water resistant clothing such as Gore-Tex®
  - Cleaning products
  - Firefighting foams
  - Paints
  - Pesticides
  - Personal care products



Ubiquity of PFAS in the Environment



From: Environmental Working Group, 2021


Fluorotelomer mercaptoalkyl phosphate esters (FTMAPs)
PFAS Products
Fluorotelomer Alcohol Esters (FTOH Esters)
Fluorotelomer iodides (FTIs)
Fluorotelomer olefins (FTOs)
Fluorotelomer sulfonic acids (n:2 FTSA or n:2 FTS)
n:2 Fluorotelomer alcohols (n:2 FTOH)
n:2 Fluorotelomer aldehydes (n:2 FTAL)
Polyfluoroalkyl phosphoric acid diesters (diPAPs)
Polyfluoroalkyl phosphoric acid monoesters (monoPAPs)
n:2 Fluorotelomer carboxylic acids (n:2 FTCA)
n:2 Fluorotelomer unsaturated carboxylic acids (n:2 FTUCA)
n-1:3 FTUCA
n-1:3 FTCA
3-OH-n-1:3 FTCA
n-1:2 Ketone
n-1:2 secondary Fluorotelomer alcohols (n-1:2 sFTOH)
3-H-n-1:2 Ketone
2H-nPFCA
nPFCA
PFBA, PFPeA, PFHxA, PFHpA
End-Chain Degradation PFAS

US EPA/ASTM/DoD PFAS Analytical Methods

ISO 21101 (Rev. 2014)
Unfiltered aqueous matrices
2 PFAS

ASTM D7968-17a (Rev 2017)
Soil
21 PFAS

ISO 21675 (Rev. 2019)
Water
30 PFAS

ASTM D7979-17 (Rev. 2019)
Water, Sludge, Influent, Effluent and Wastewater
21 PFAS

US EPA Method 537.1 (Rev. 2018)
Drinking water
18 PFAS

DoD QSM 5.3 (Rev. 2019)
Aqueous matrices
24 PFAS

US EPA Method 533 (Rev. 2019)
Drinking water
25 PFAS

ASTM D8427-21 (Rev. Dec-2021)
Aqueous matrices
44 PFAS

SW846 Draft Method 8327 (Rev. July 2021)
Surface Water, Groundwater, Wastewater
24 PFAS

US EPA draft method 1633 (Rev. Jun-2022)
Wastewater, solids, biosolids, tissues
40 PFAS

US EPA Draft OTM-45
Stationary Air Sources
50 PFAS

US EPA Draft method 1621 (Rev. July 2022)
Aqueous matrices
Adsorbable Organic Fluorine

Sampling for PFAS requires great care!

- Refrain from using:
  - Plastic clipboards, binders, spiral notebooks, waterproof field books
  - Decon 90™ (surface active cleaning agent/radioactive decontaminant)
  - Blue ice or artificial ice products
  - Teflon® lined tubing or containers
  - Aluminum foil
  - PFAS containing bottle cap liners.
  - Glass containers (due to potential loss of analyte through adsorption)
  - Sticky notes
  - Fluoropolymer bailers or pump bladders
  - Fluoropolymer tubing, valves and other parts in pumps
  - Personnel hygiene items (cosmetics, lotions, moisturizers)
  - Sunscreens, insect repellants
  - New or unwashed clothing
  - Clothing washed in fabric softeners
  - Treated clothing (waterproof, water resistant, stain-resistant)
  - Treated boots (waterproof, water resistant, stain-resistant)
  - Coated Tyvek® suits

Overview of PFAS Method 1633

- The USEPA published the Method 1633 in January 2024 and was "**finalized**" for analysis of 40 Per- and Polyfluorinated Substances (**PFAS**) (but not promulgated).
    - Aqueous (including wastewater, groundwater, and surface water)
    - Solid
    - Tissue matrices

- Method 'need to know' issues:
    - Implementation of method varies across labs, which impacts results (NCASI has the data!).
    - Most historical data is based on 537M - - 1633 results will be different!
    - Cost: $400 - $550 per sample.
    - Same contamination issues exist, sampling must use care (and field blanks).

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Testing in Products

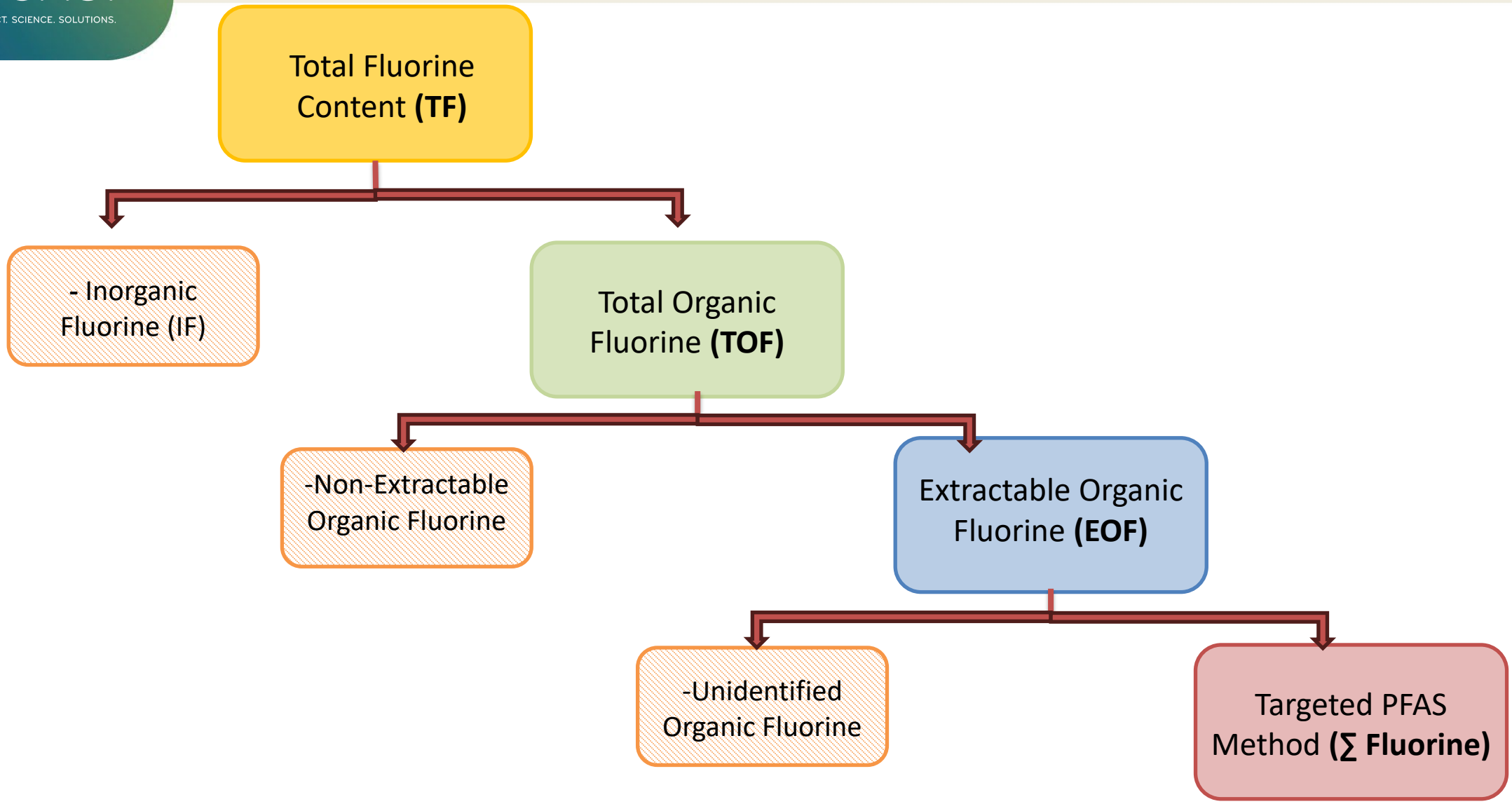
Total Fluorine Testing (TF)

Total Fluorine (TF) test methods are analytical techniques used to quantify the TF content in various matrices, including environmental, biological, and industrial samples.

These methods typically involve converting all fluorine-containing compounds into a detectable form, such as hydrogen fluoride (HF), through processes like high-temperature combustion or neutron irradiation[1,2].

- **Combustion Ion Chromatography (CIC)** is widely recognized for its high sensitivity and accuracy, involving the combustion of samples to convert fluorine to HF, which is then analyzed via ion chromatography.
- **Particle-Induced Gamma-ray Emission (PIGE) Spectroscopy** offers a non-destructive approach by using a proton beam to induce gamma-ray emission from fluorine atoms, allowing for rapid analysis.
- **Instrumental Neutron Activation Analysis (INAA)** provides high precision by irradiating samples with neutrons, causing fluorine atoms to emit gamma rays that are subsequently measured.
- **Other approaches:** ICP-MS, Molecular Absorption Spectroscopy, Fluorine NMR, and X-Ray Photoelectron Spectroscopy

Relationship Between CIC Techniques



TF/TOF Sampling Guidance

Sampling Equipment:

- Composed of HDPE, polypropylene, silicone, nylon, stainless steel, PVC, acetate, and cotton
- Decontaminate any sampling equipment by washing with PFAS-free DI water and cleaners like Liquinox® then triple rinse with PFAS-free water.

    - Decontaminate sampling collection agent between samples and change gloves between sample types
    - Products are placed in HDPE bags that are lot certified to be PFAS free

      Additional quality control (QC) samples are recommended like:

        - Equipment blanks
        - Field blanks
        - Duplicates
        - Matrix spikes
        - Method blank

General PFAS Sampling Guidance. https://www.michigan.gov/-/media/Project/Websites/PFAS-Response/Sampling-Guidance/General.pdf?rev=6217442052bf4fedb89bbf786560d645.

TF/TOF Sampling Guidance

Samples for Testing:

- **Complete foodservice packaging** must be ground to **<20 mesh** for homogenization (lab assistance available).
- Requires typically 4-5 grams of sample (dependent on the lab).
- Place all samples into PFAS-free zip top bags and seal properly and ship to appropriate lab.

Additional Samples (If Necessary):

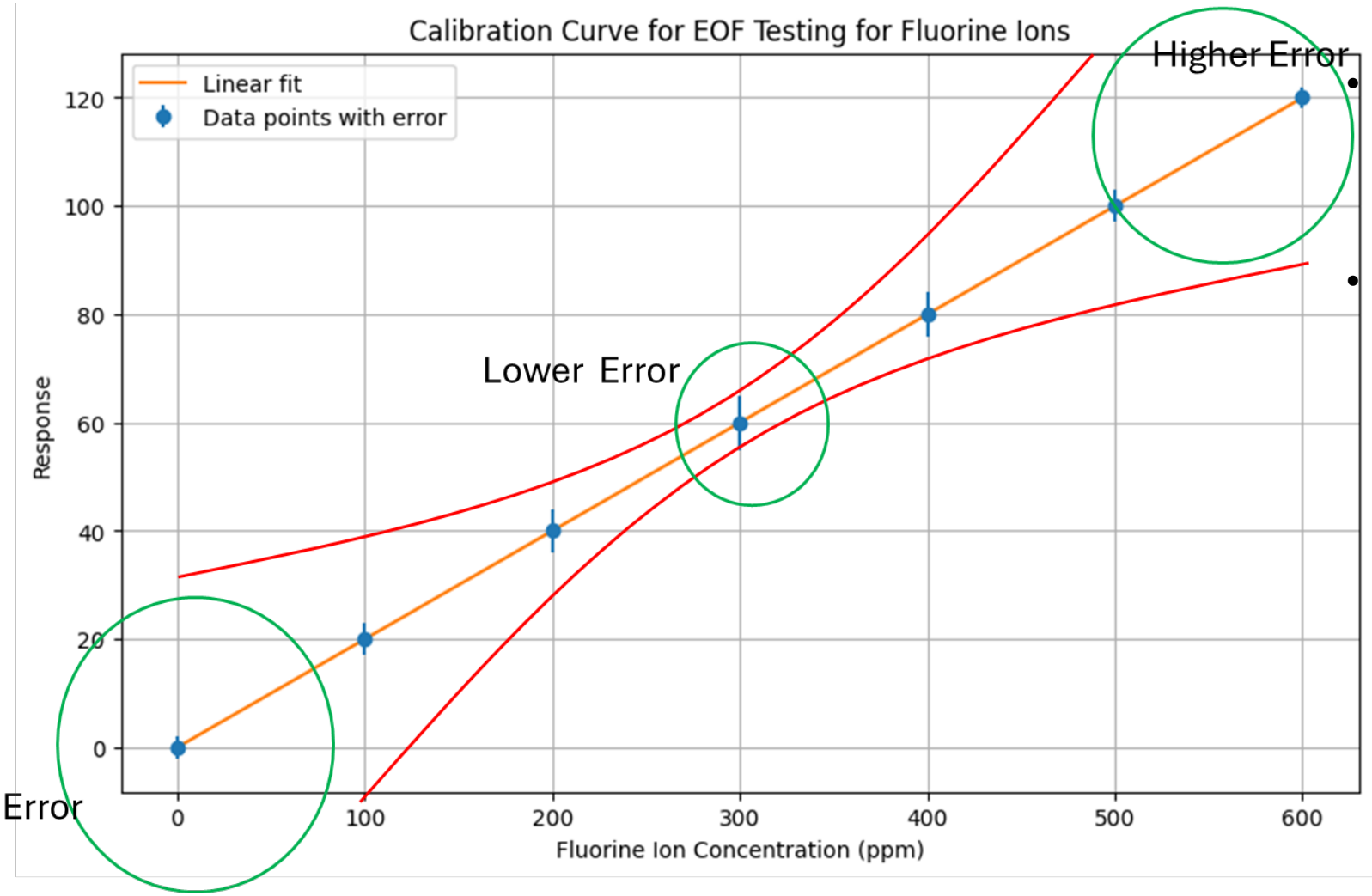
1. **Fluorine-containing dry end sizing/release agents:**
    1. Submit an extra sample with the agents **wiped off** or without these agents during production.
    2. Specify if the sample was prepared by **wiping** or by **omitting** agents in production.
    3. Provide details: source and grade.
2. **Packaging with mineral additives:**
    1. Submit each mineral from the same batch/lot, ground to **<20 mesh**.
    2. Provide details: source, grade, and **mining/production location**.
    3. Include **percent mineral loading** in the formulation.

TOTAL FLUORINE ANALYSIS. https://compostmanufacturingalliance.com/wp-content/uploads/2022/03/Total-F-Analysis-Protocol-100820-Rev1-Final.pdf.

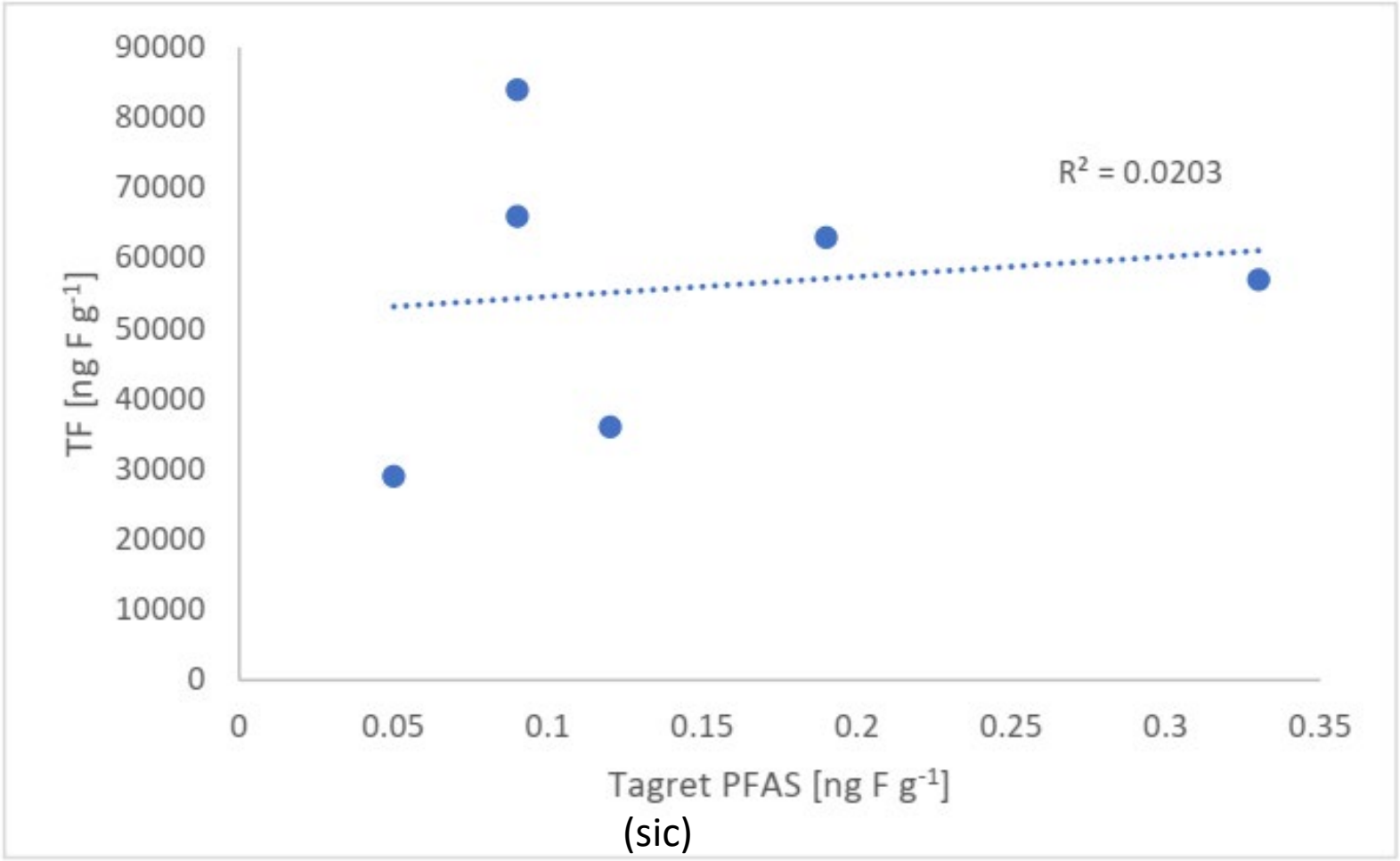
Interferences, Biases, and Challenges

Aspect	Total Fluorine (TF) Methods	Total/Extractable Organic Fluorine (TOF/EOF) Methods
Interferences	Other halogens (chlorine, bromine), matrix effects	Presence of inorganic fluorine, incomplete removal during sample preparation
Biases/ Residual Inorganic Fluorine	Overestimation of organic fluorine due to inclusion of inorganic fluorine. High reporting limits in available application methods leading to non-detect results.	Even small amounts of inorganic fluorine can cause significant positive bias (e.g., 8 mg/L of inorganic fluorine causing a positive bias of ~2 µg/L in TOF measurements) High reporting limits in available application methods leading to non-detect results.
Challenges In Separating Organic and Inorganic Fluorine	Adsorption and elution issues in sample preparation. Ensuring inorganic fluorine is not included in Combustion Ion Chromatography (CIC)	Sensitivity and specificity of analytical techniques. Matrix effects interfering with separation and detection

RELIABILITY AT DIFFERENT CONCENTRATION THRESHOLDS



- Above 50 PPM, most combustion methods perform well providing appropriate standard calibration.
- For concentrations at 20 PPM, ion chromatography may perform better than a selective ion probe or electrode.



(sic)

- Total Fluorine was not correlated to detections in targeted analysis.
- From Jovanović et al. 2024

Questions or Information Requests

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