EPA United States Environmental Protection Agency

Using EPA's Stationary Source Measurement Methods for PFAS Air Emissions

Stephen R. Jackson, PhD
US EPA Office of Research and Development (ORD),
Center for Environmental Measurement and Modeling

NEWMOA PFAS Analytical Developments Webinar
September 25th, 2024

EPA United States Environmental Protection Agency

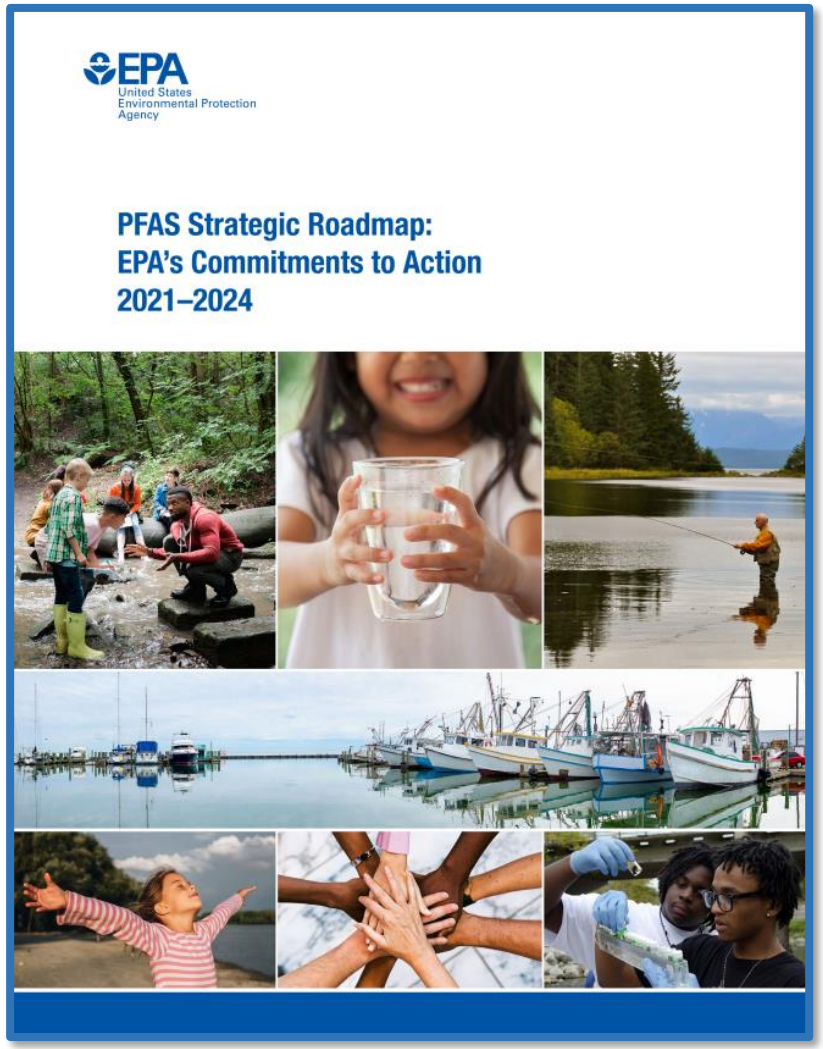
Outline

- Background
- Description of Methods
  - OTM-45, OTM-50, M0010/8270
  - **Intent and Applicability**
- Non-traditional sources
- Q&A

PFAS Air Emissions Measurements

- Robust and accurate emission measurement methods are needed to:
  - Allow for comprehensive source characterizations
  - Evaluate effectiveness of PFAS destruction technologies

- Reliable and comprehensive emissions data are needed to:
  - Support state regulatory processes
  - Inform federal decision making



"Develop and validate methods to detect and measure PFAS in the environment"

Types of Sources

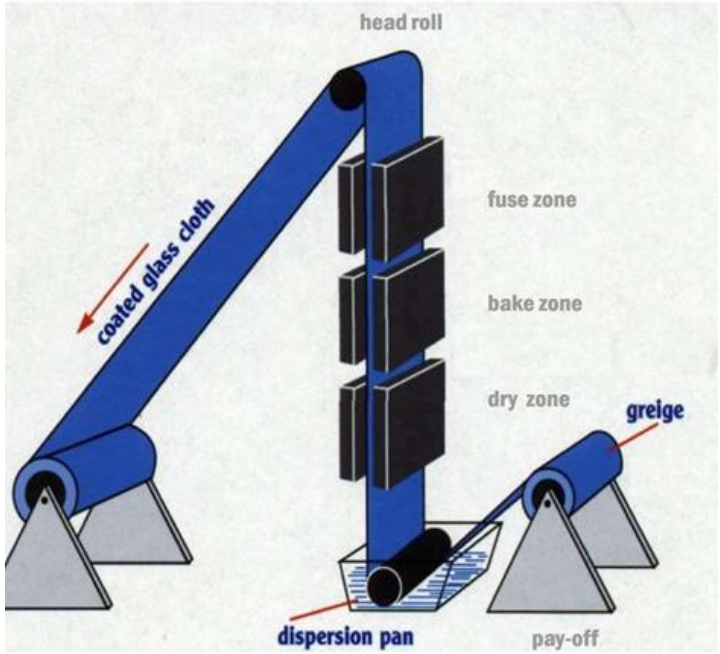
1. Industrial Sources

- Chemical production plants
- PFAS-using industries

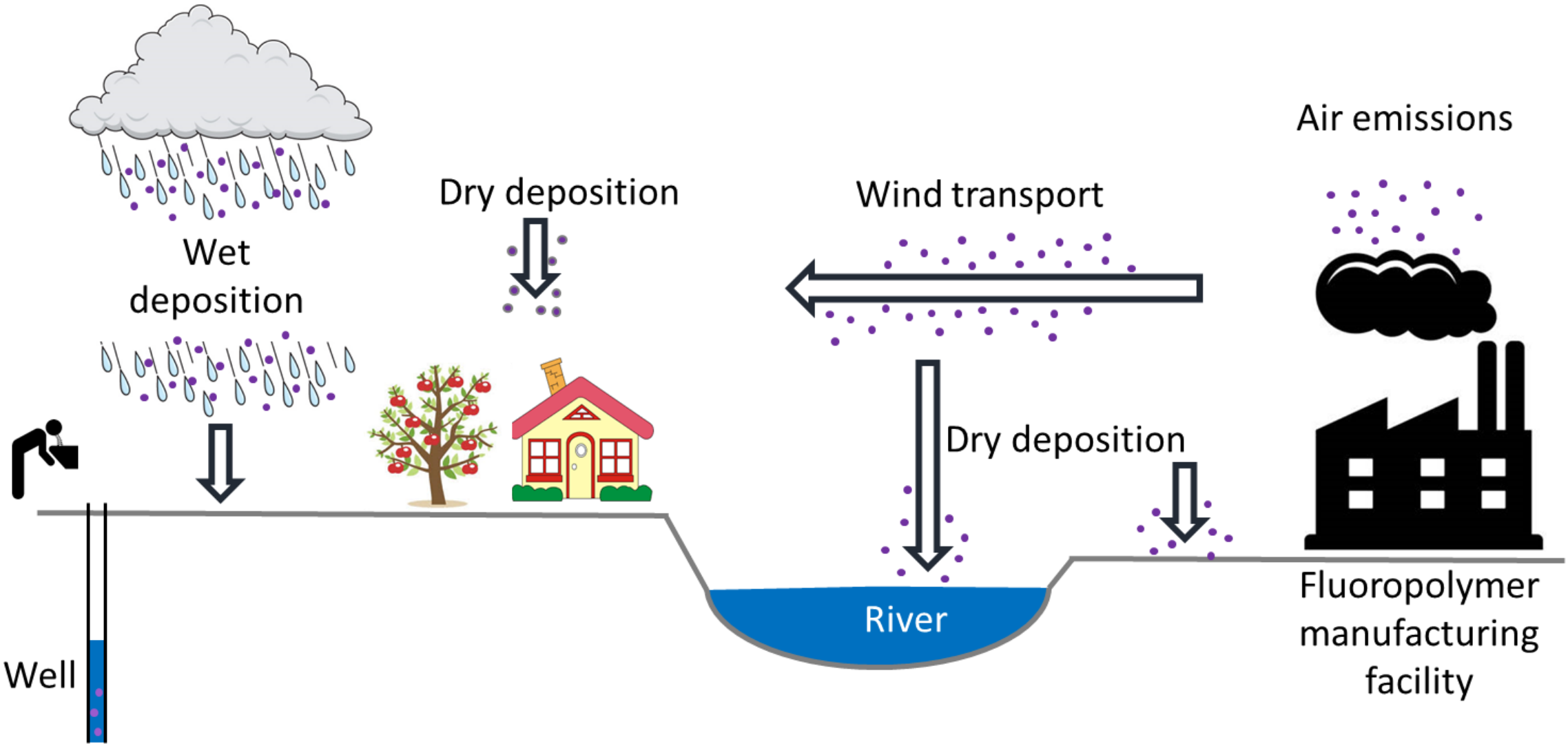
2. Destruction technologies

- Incineration
- Pyrolysis/gasification
- Emerging technologies

3. Others (landfills, wastewater treatment plants, aqueous film forming foam use)



Atmospheric Fate & Transport



Adapted from Davis et al., Chemosphere, 2007

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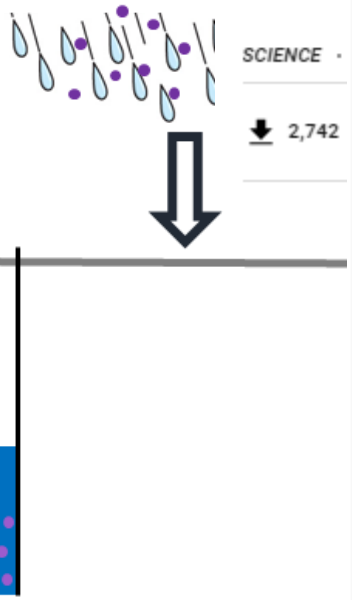

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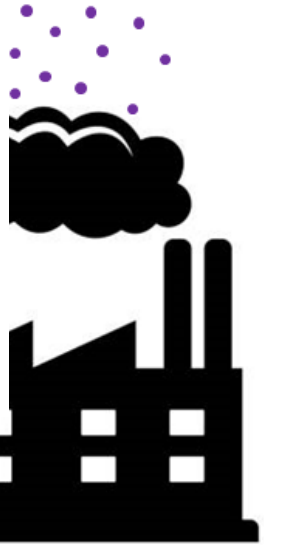

Fluoropolymer manufacturing facility

Science

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REPORT

Nontargeted mass-spectral detection of chloroperfluoropolyether carboxylates in New Jersey soils

JOHN W. WASHINGTON, CHARLITA G. ROSAL, JAMES P. MCCORD, MARK J. STRYNAR, ANDREW B. LINDSTROM, ERICA L. BERGMAN, SANDRA M. ... ns

SCIENCE

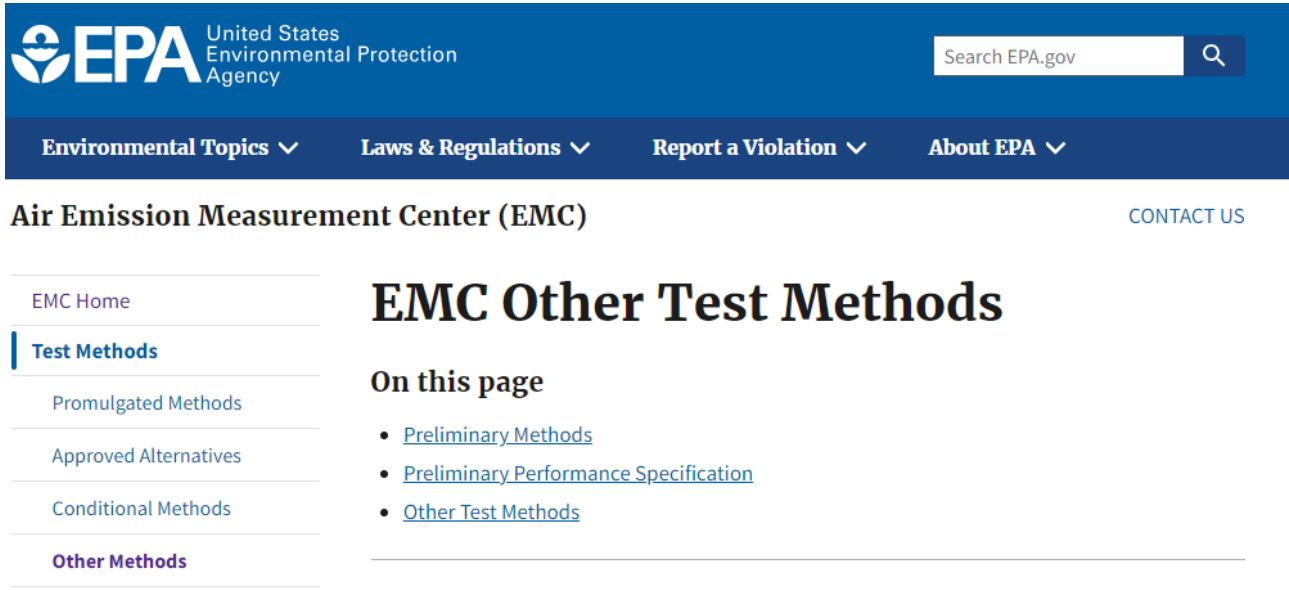
2,742

Abstract

The toxicity and environmental persistence of anthropogenic per- and poly-fluoroalkyl substances (PFAS) are of global concern. To address legacy PFAS concerns in the United States, industry developed numerous replacement PFAS that commonly are treated as confidential information. To investigate the distribution of PFAS in New Jersey, soils collected from across the state were subjected to nontargeted mass-spectral analyses. Ten chloroperfluoropolyether carboxylates were tentatively identified, with at least three congeners in all samples. Nine congeners are $\geq(CF_2)_7$. Distinct chemical formulas and structures, as well as geographic distribution, suggest airborne transport from an industrial source. Lighter congeners dispersed more widely than heavier congeners, with the most widely dispersed detected in an in-stock New Hampshire sample. Additional data were used to develop a legacy-PFAS fingerprint for historical PFAS sources in New Jersey.

What is an Other Test Method (OTM)?

- **Formal method posted by EPA's Office of Air Quality Planning and Standards (OAQPS) Air Emission Measurement Center**
  - Supported by field and laboratory data
  - Reviewed by OAQPS technical staff
  - Not yet subjected to federal rulemaking process
    - May be basis for promulgated method
    - Intended to solicit necessary information to inform future revisions
- **Useful and available to the measurement community**
  - Enables coordination between policy makers, facilities, & control technology development
  - Promotes consistency in measurements



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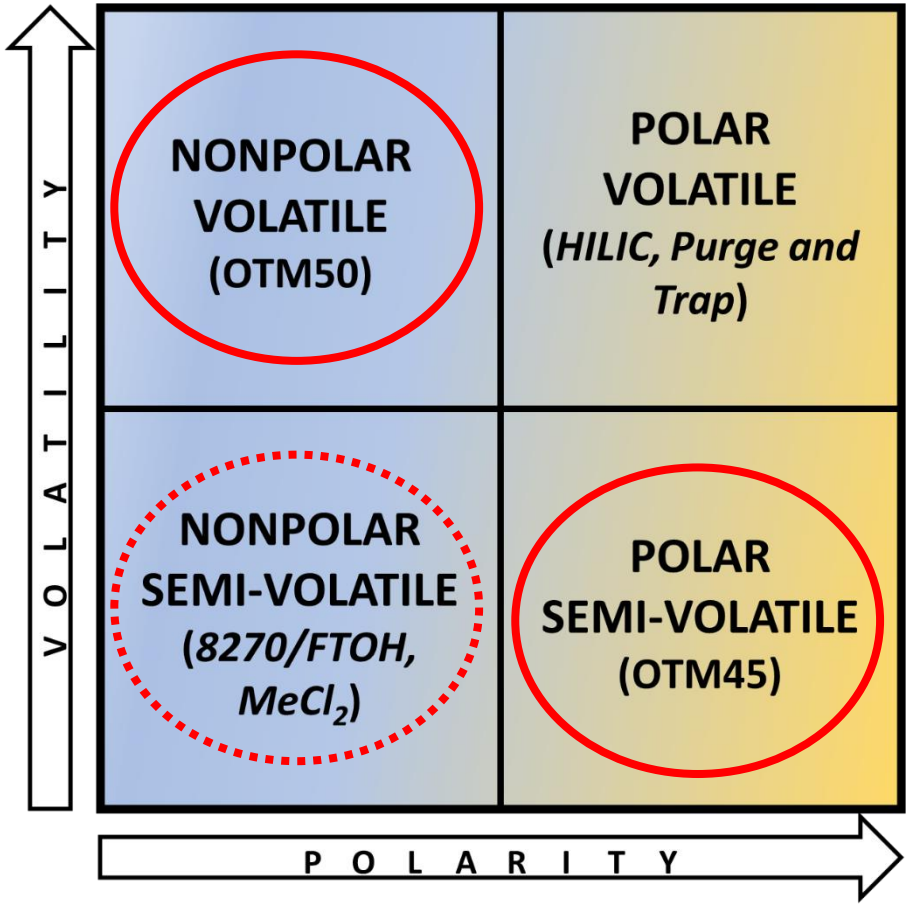

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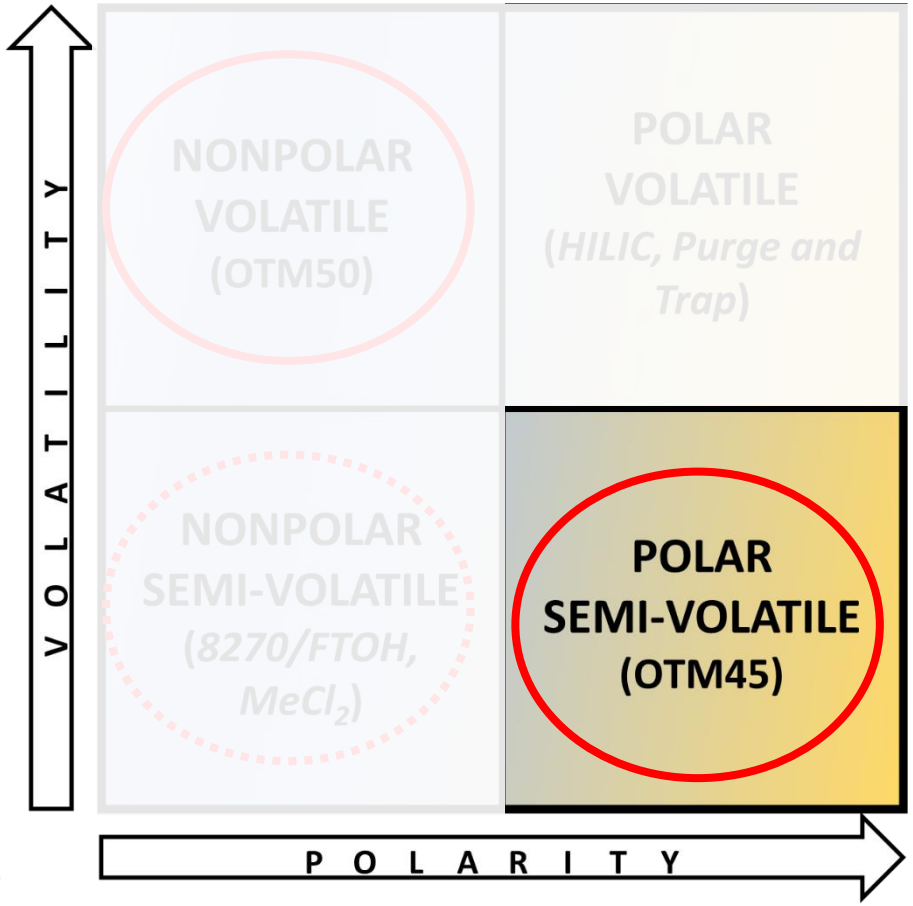

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OTM-45 for Polar Semivolatile PFAS

- Released 2021, revised 2024
  https://www.epa.gov/system/files/documents/2024-07/other-test-method-45-rev1-final-_1.pdf
- Developed through OAQPS & ORD collaboration
- Analysis significantly informed by early PFAS measurement experts
  - EPA Method 533, 537.1, 1633
  - 49 target compounds
- Sampling modeled after EPA Method 23
- Utilizes pre-sampling, pre-extraction, and pre-analysis isotopes

PFBA	PFBS	MeFOSAA	PFMBA
PFPeA	PFPeS	EtFOSAA	PFMPA
PFHxA	PFHxS	4:2 FTS	PFecHS
PFHpA	PFHpS	6:2 FTS	6:2 FTUCA
PFOA	**PFOS**	8:2 FTS	8:2 FTUCA
PFNA	PFNS	10:2 FTS	6:2 FTCA
PFDA	PFDS	ADONA	8:2 FTCA
PFUnDA	PFDoS	**HFPO-DA**	10:2 FTCA
PFDoA	FOSA	F-53Major	3:3 FTCA
PFTrDA	MeFOSA	F-53Minor	5:3 FTCA
PFTeDA	EtFOSA	NFDHA	7:3 FTCA
PFHxDA	N-MeFOSE	PFEESA	
PFODA	N-EtFOSE		

OTM-45 for Polar Semivolatile PFAS

- **Revision highlights**
  - Guidance on *minimizing* use of Teflon® in sampling
  - Improving robustness of XAD module procedure
    - Water content affected recoveries of pre-extraction surrogates
    - Solid phase extraction (SPE) shows improved precision in recoveries and removes chromatographic interferents
  - Revise list of target compounds & surrogates
    - Aligns with commercially available Method 1633 isotope groups

When to use OTM-45?

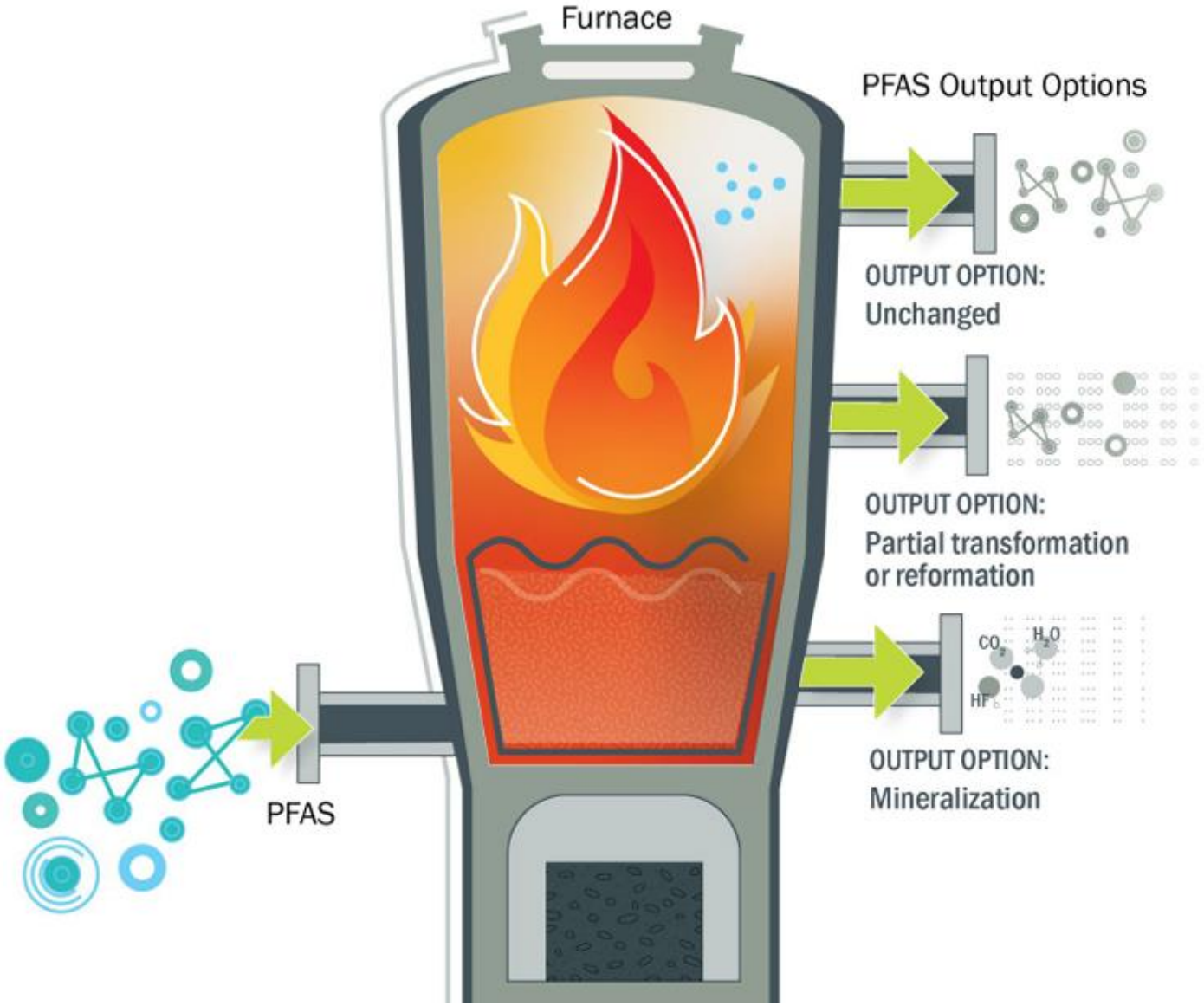

Photo Credit: Brown and Caldwell

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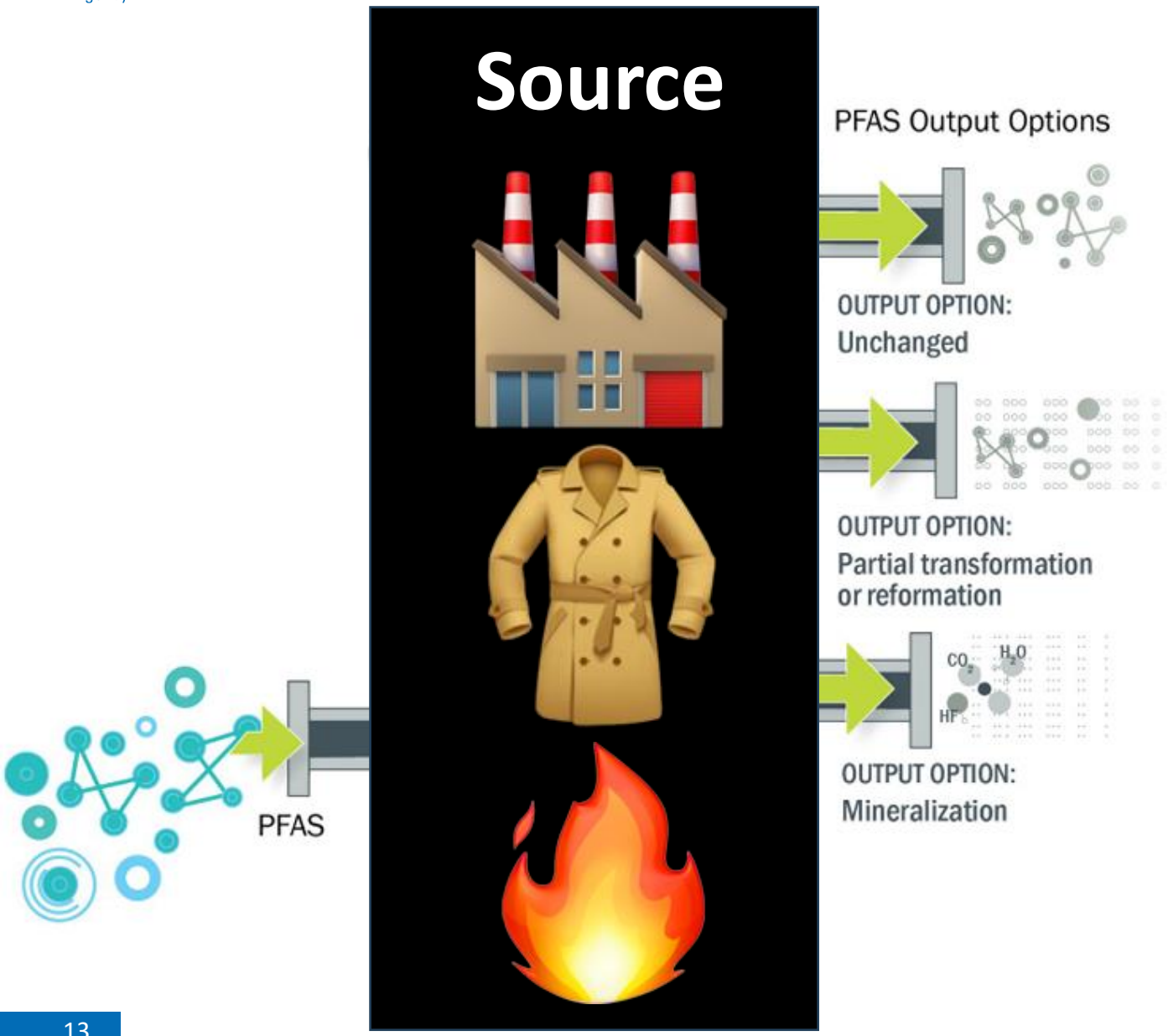

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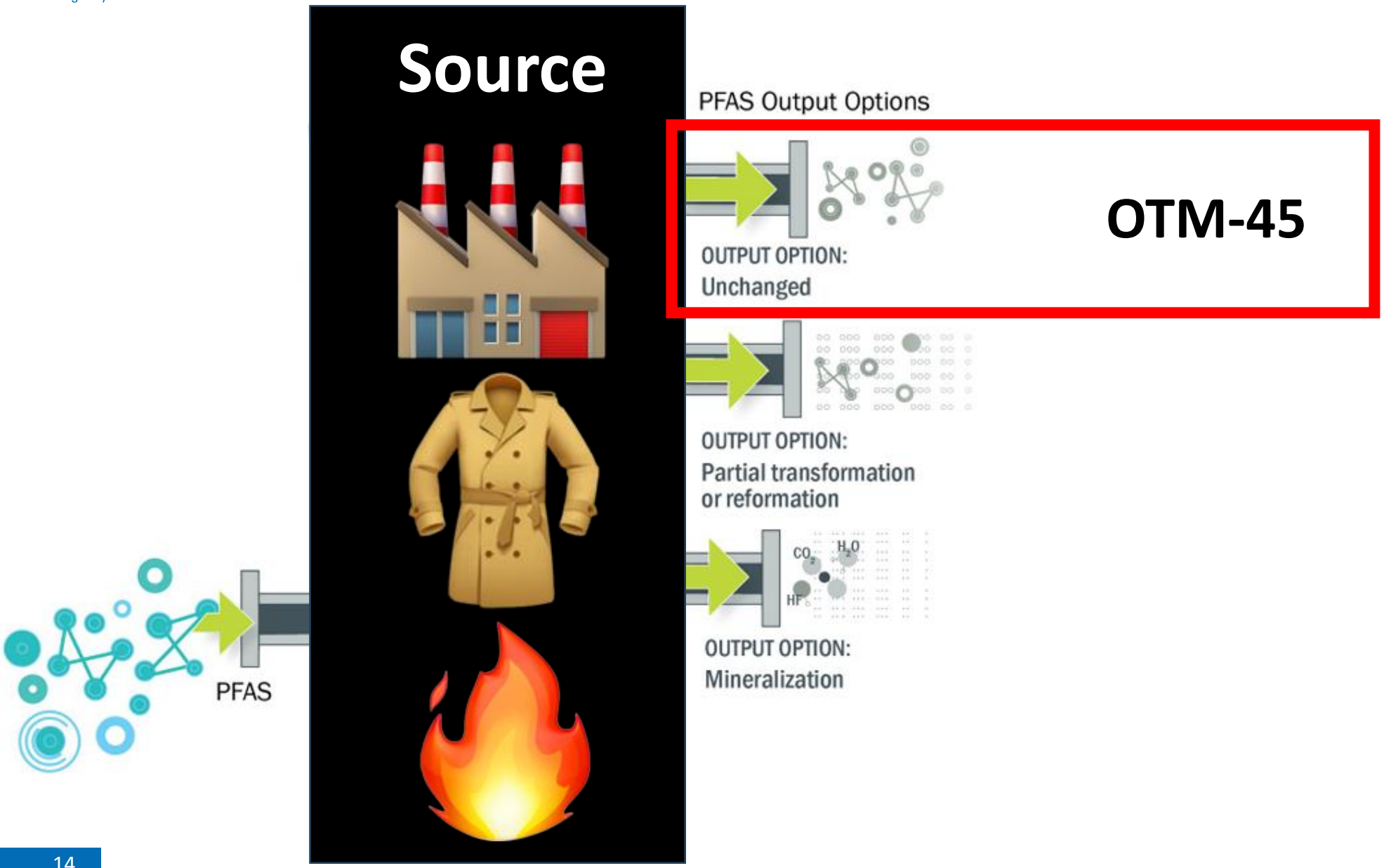

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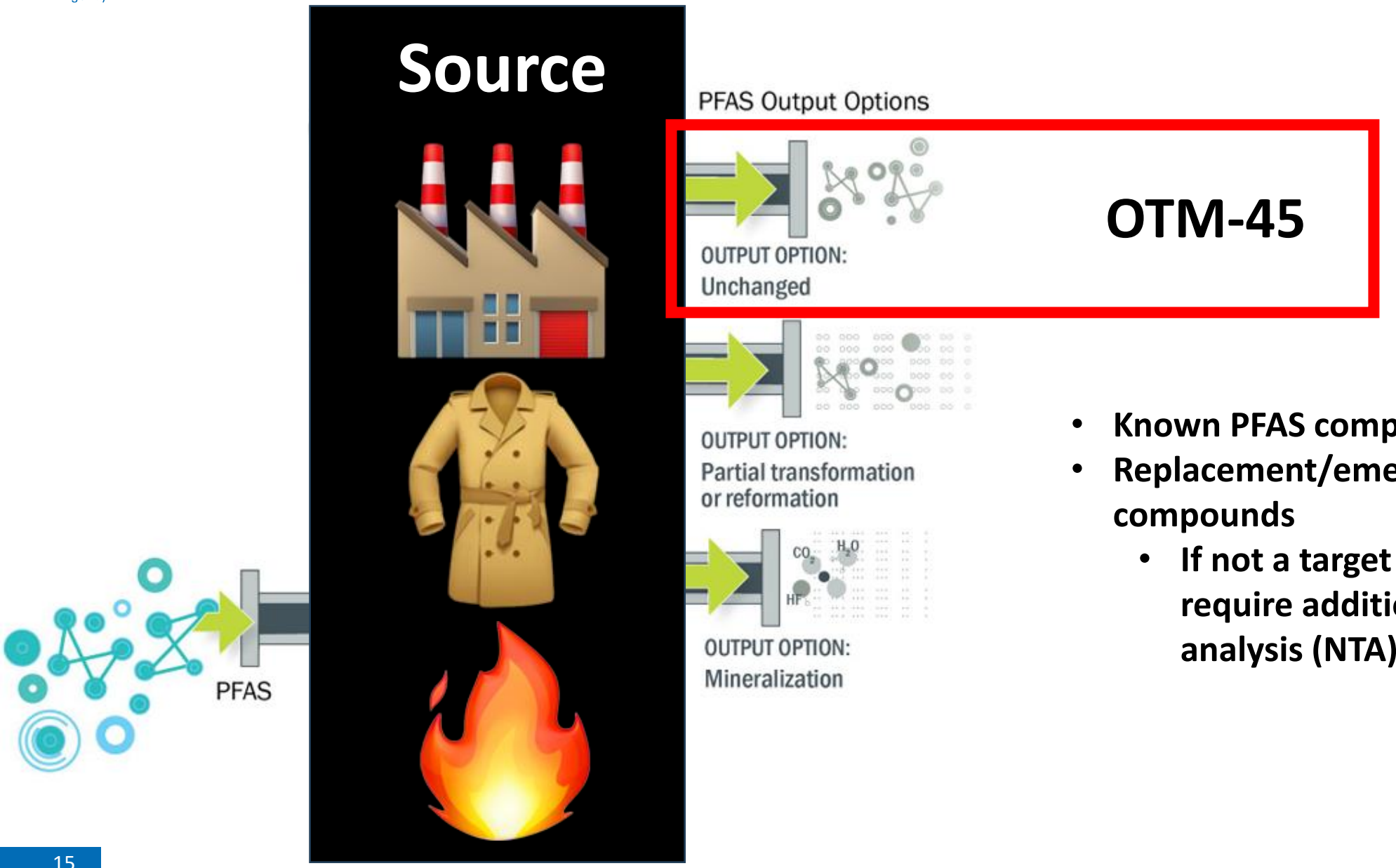

- Known PFAS compounds of concern
- Replacement/emerging industrial compounds
  - If not a target compound, will require additional non-targeted analysis (NTA)

Photo Credit: Brown and Caldwell

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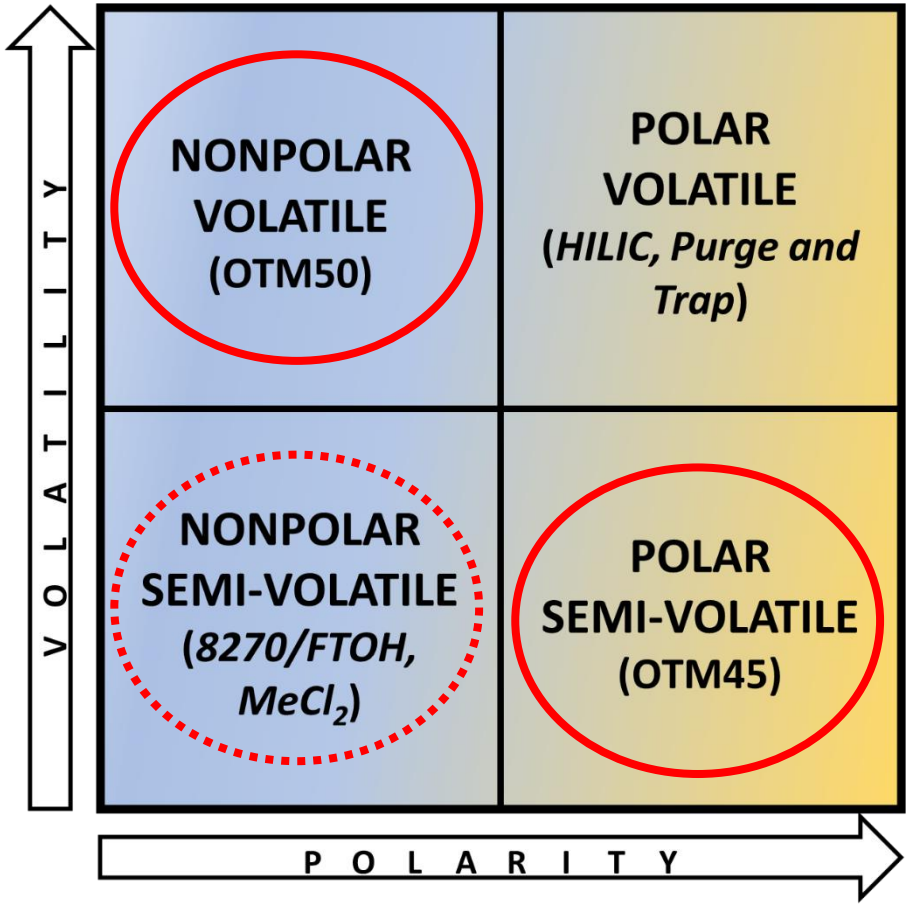

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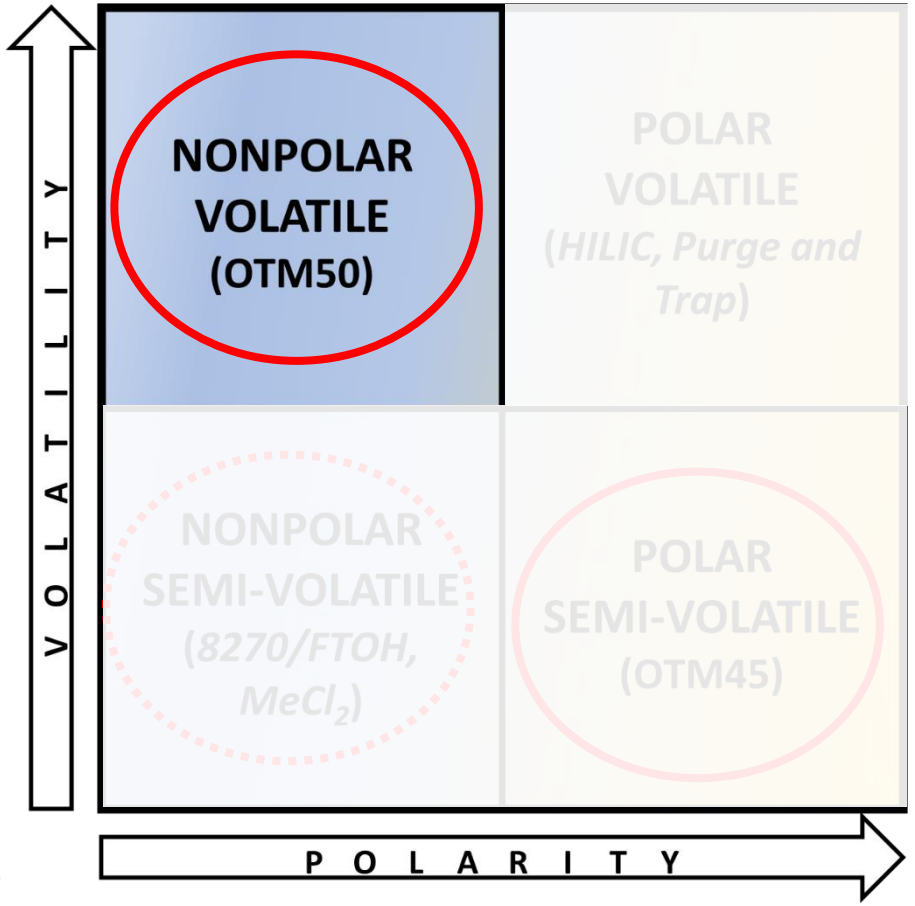

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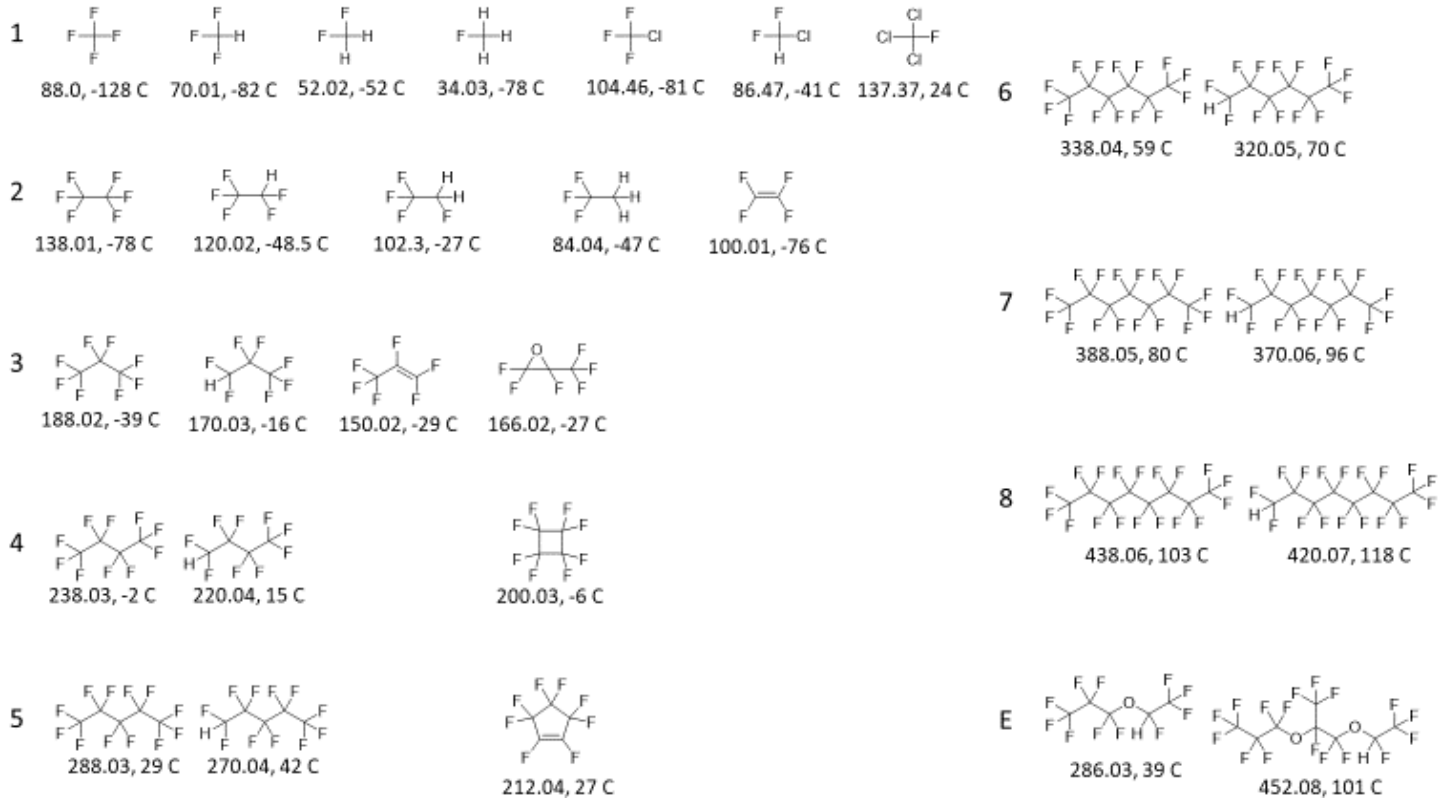
- Developed through OAQPS & ORD collaboration
- Sample collected using evacuated, passivated, stainless-steel canisters
  - Critical orifice to control flow
  - Impingers included when
    - > 3% H_2O
    - Acid gas present
- Analysis via gas chromatography-mass spectrometry (GC-MS) with preconcentrator
- Equipment required analogous to TO-15A



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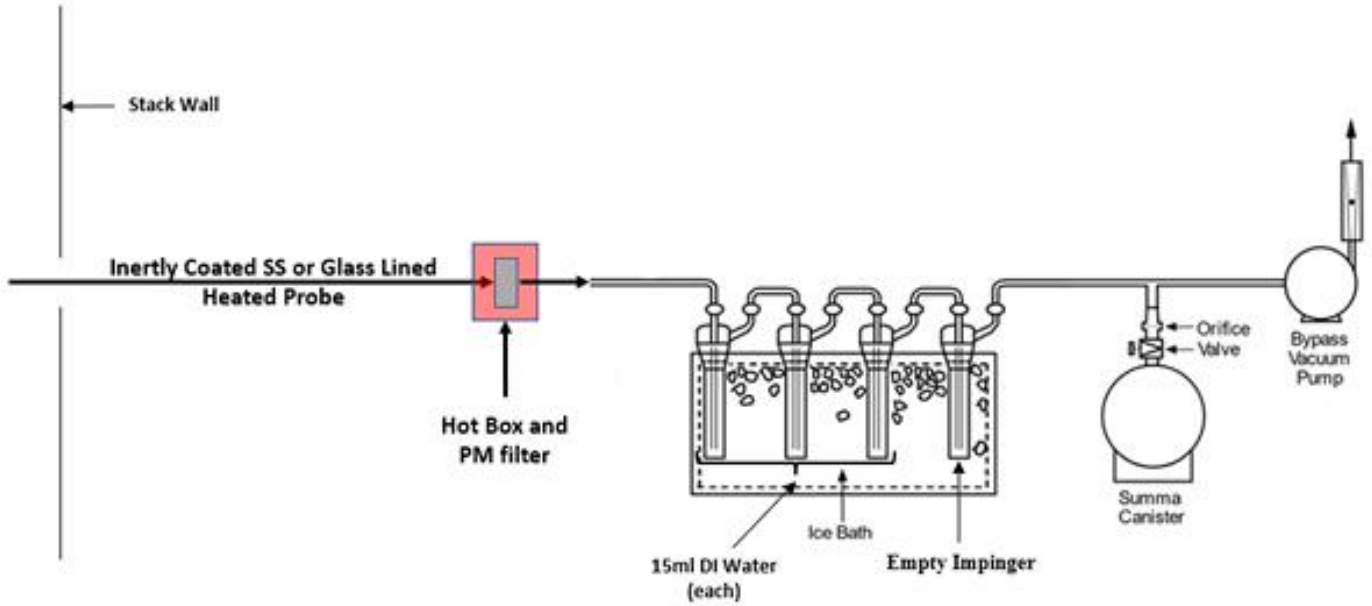
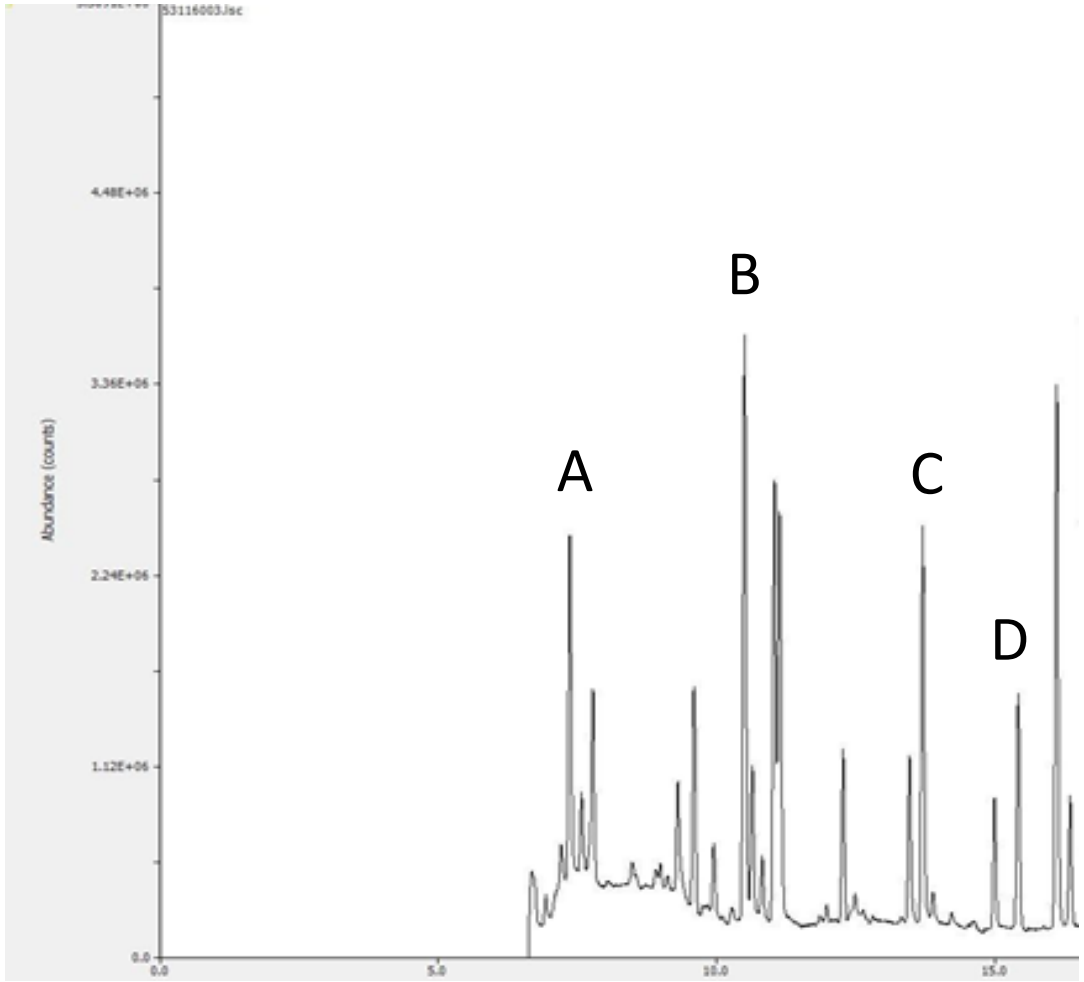


OTM-50 Unknowns Analysis



- Target list not exhaustive
- NOT a “tentative identification”. Report includes:
  - Visualization of chromatographic peak
  - Retention time
  - Integrated peak area
  - Unknown spectrum
  - Top 5 spectral matches (no minimum!)
    - If >80% match, library spectrum for top hit
- Additional analysis (outside of OTM-50) may be done to identify & confirm unknowns
  - GC-HRMS
  - Possible future OTM-50 target compounds
- Allows method to respond to industry changes
- NOT specific to volatile fluorinated species
  - **May identify/track next emerging contaminant**

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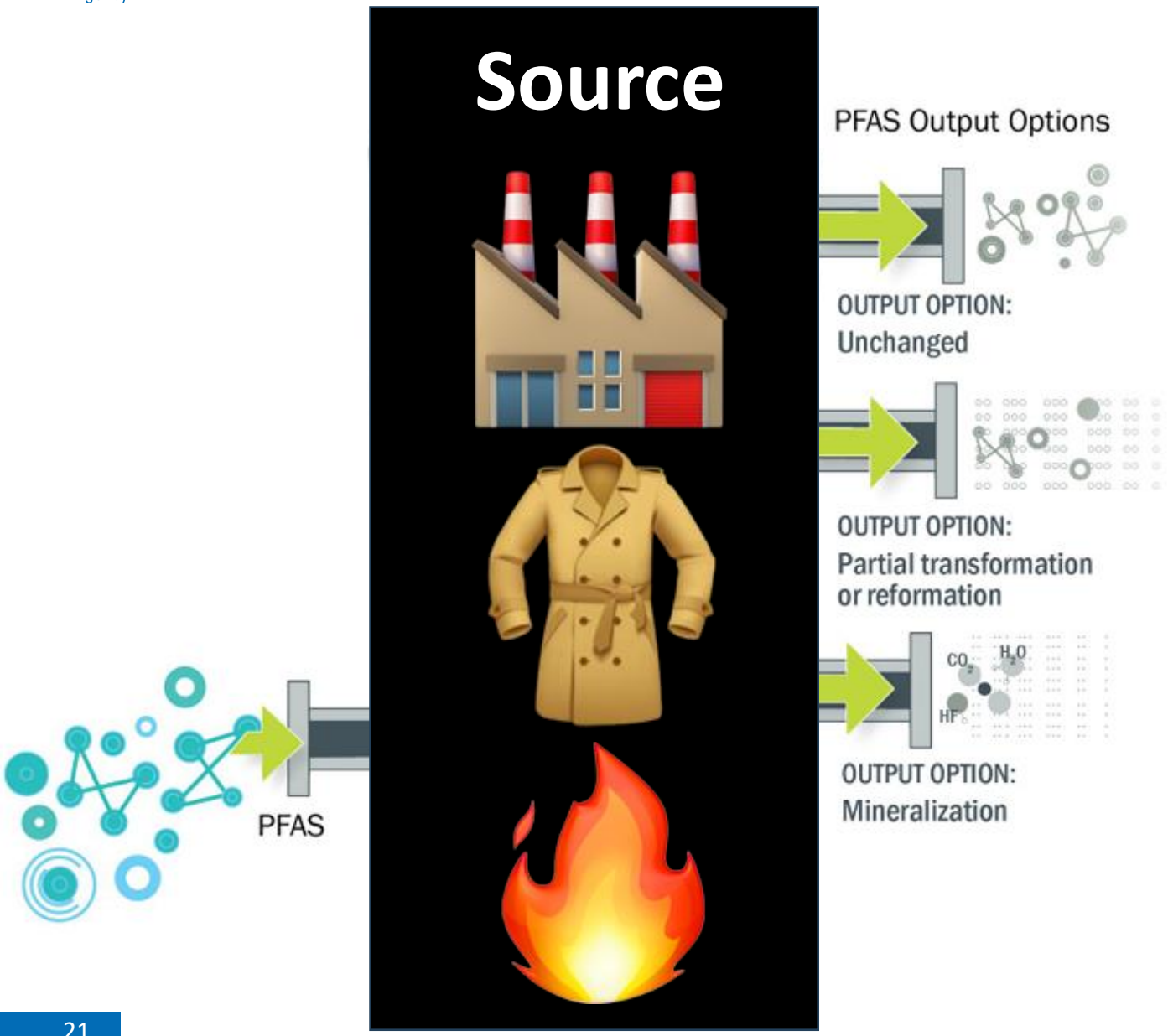

Photo Credit: Brown and Caldwell

POLL QUESTION!!!!

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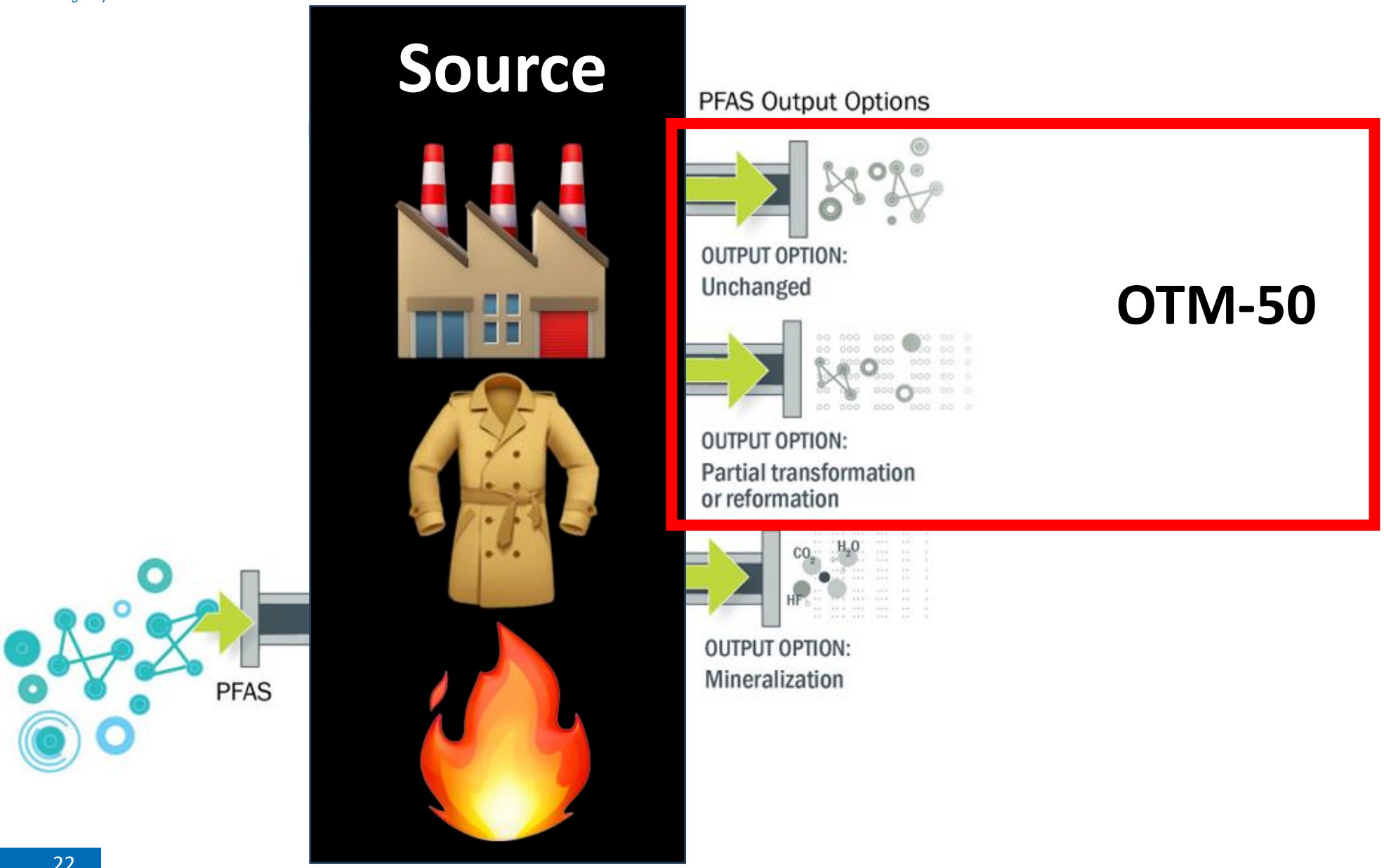

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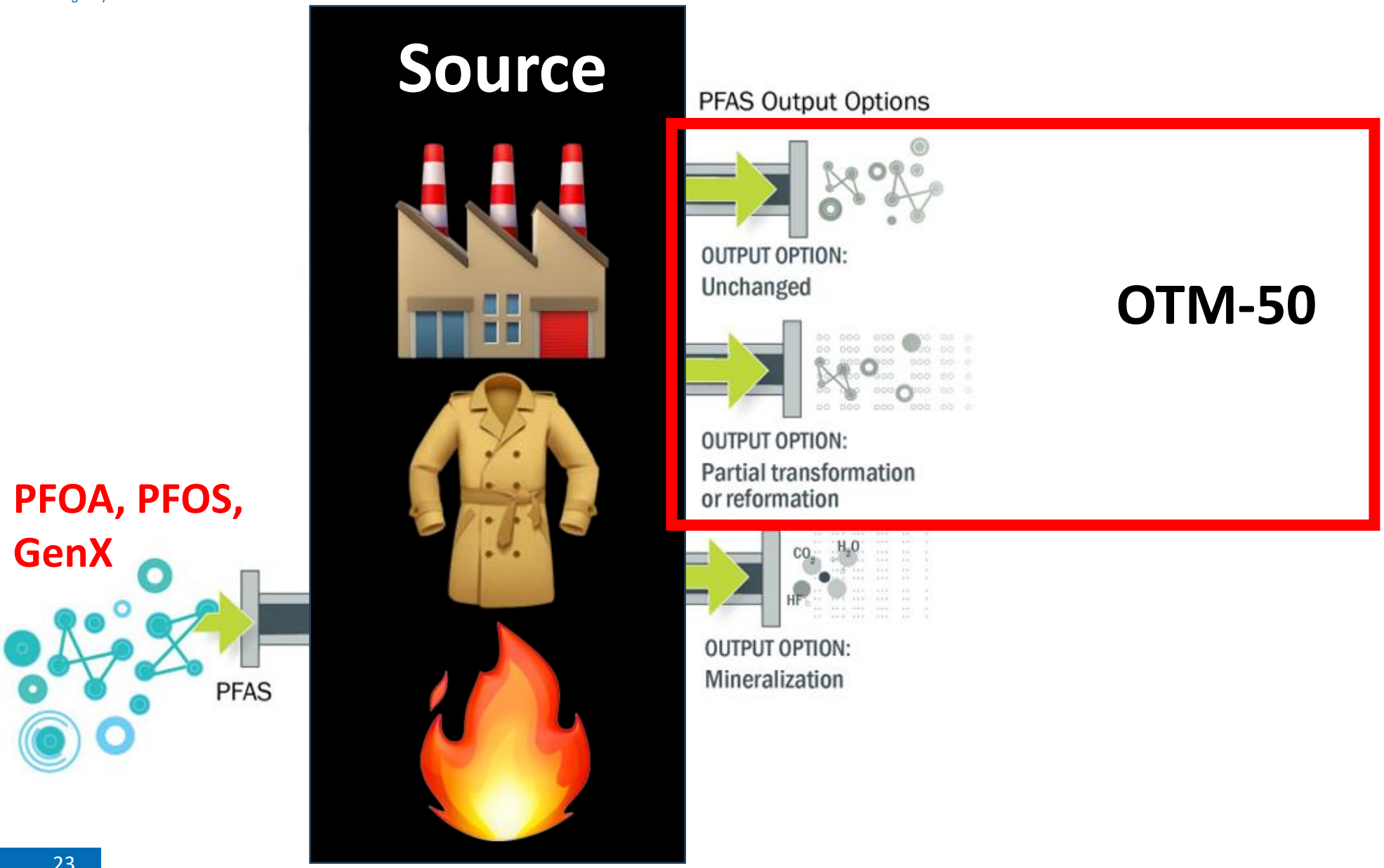

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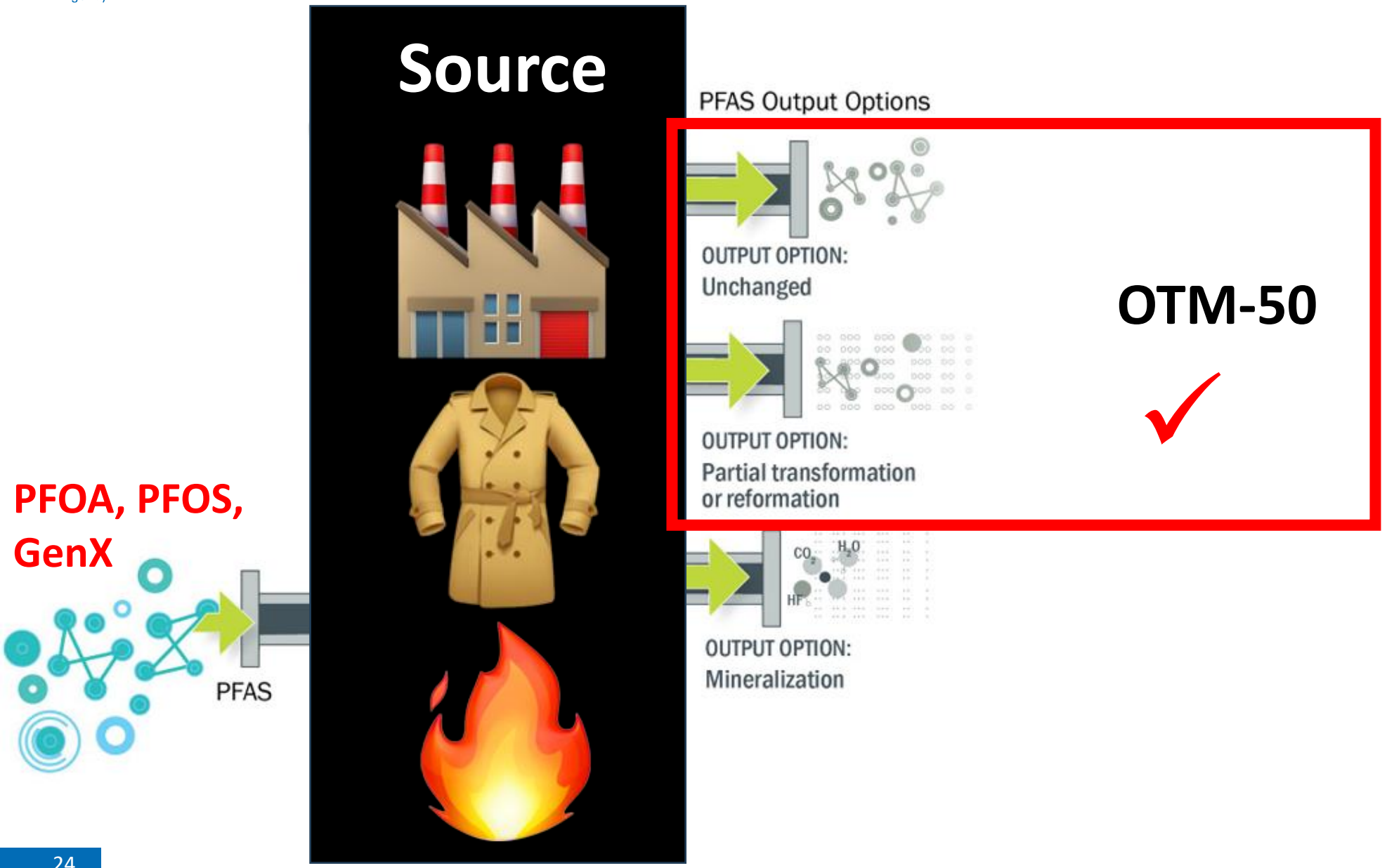

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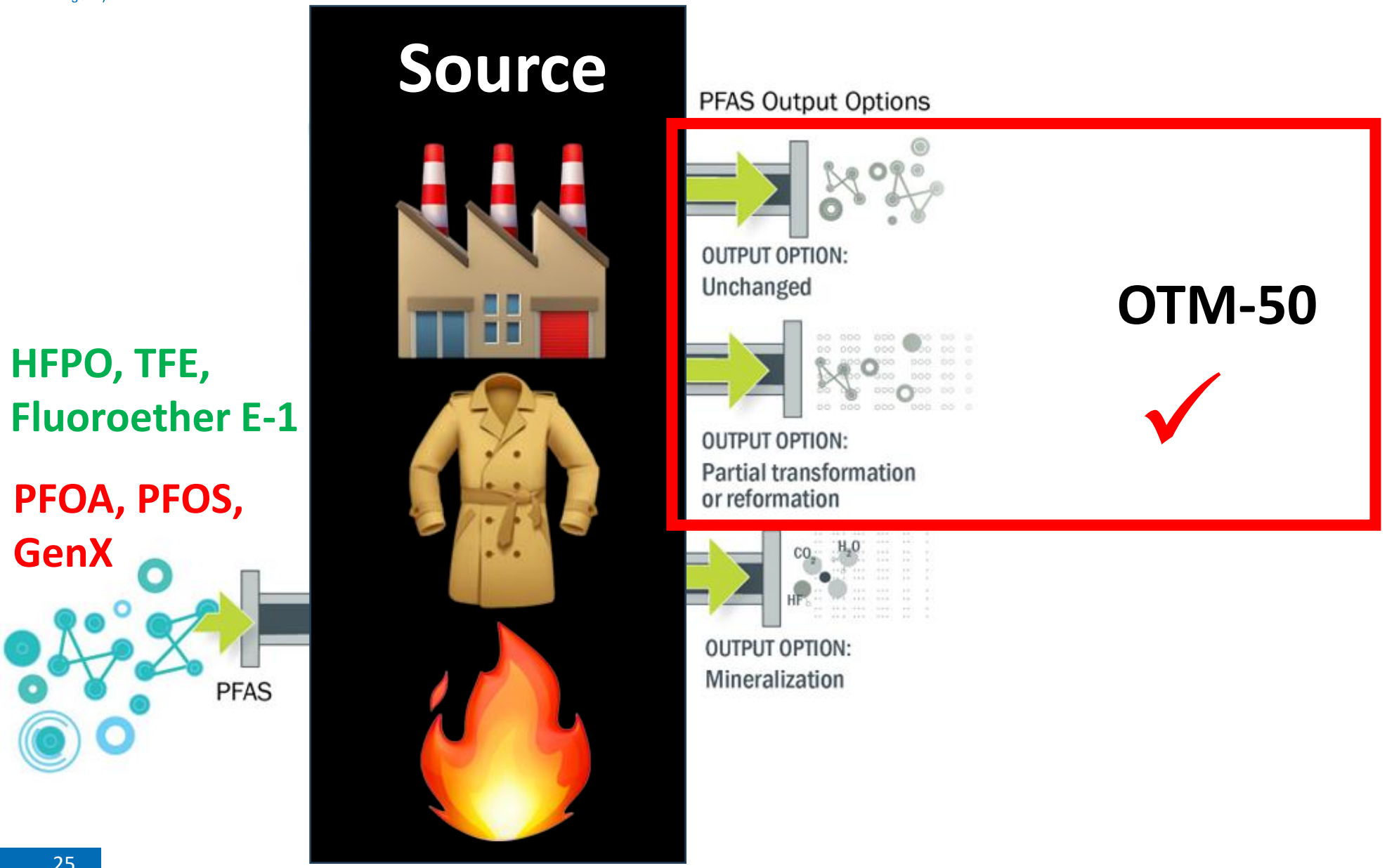

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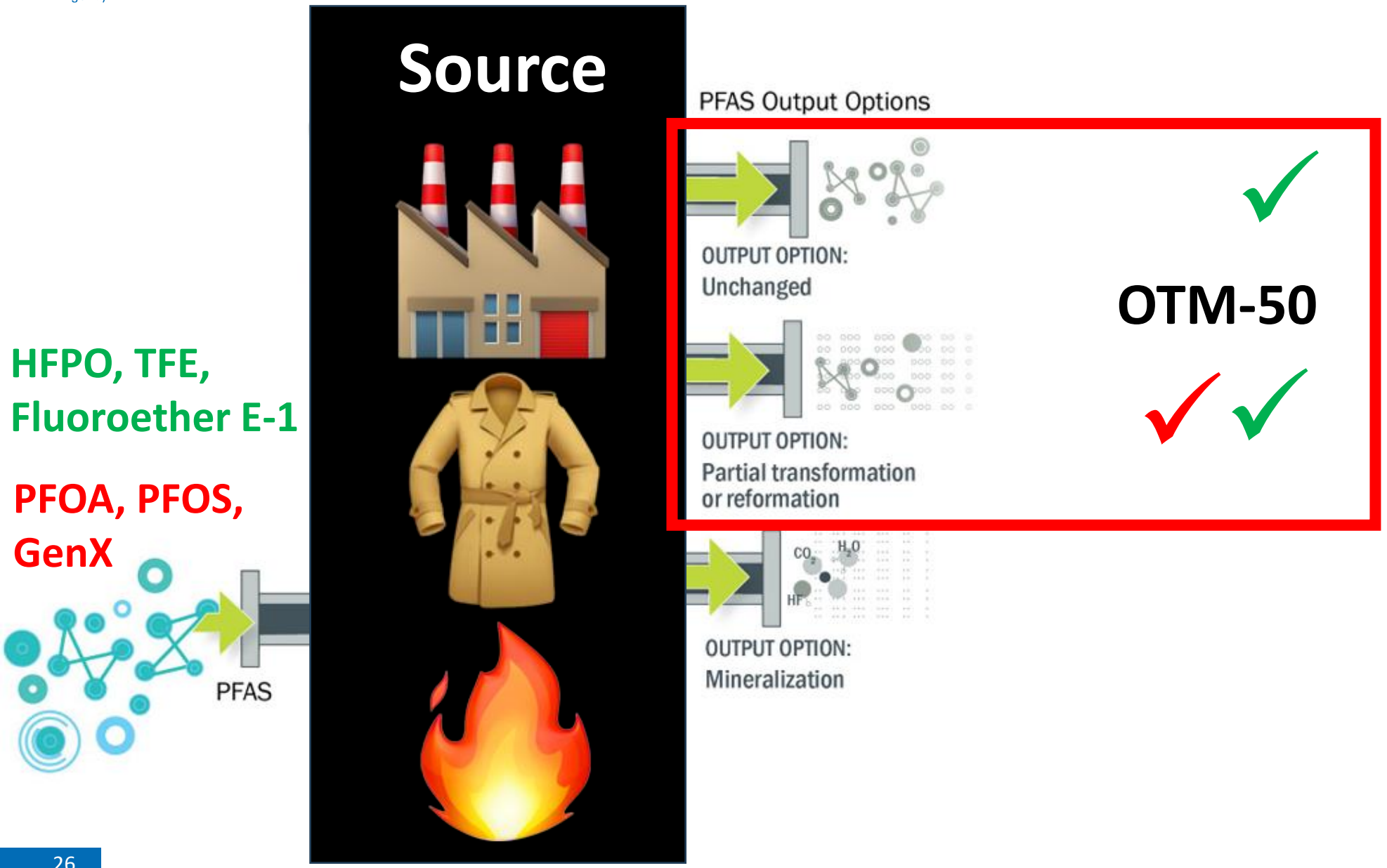

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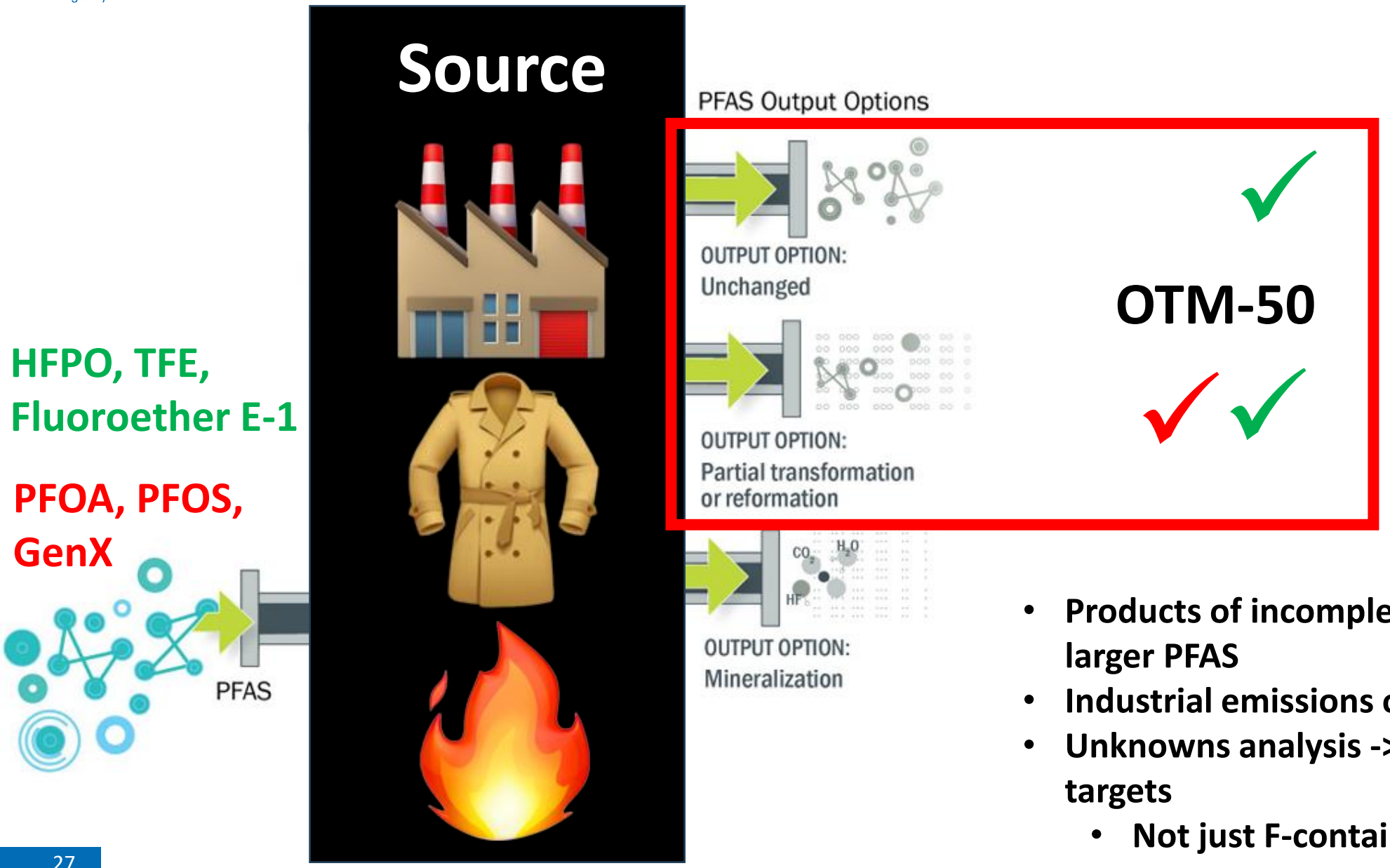

HFPO, TFE, Fluoroether E-1

PFOA, PFOS, GenX

- **Products of incomplete destruction of larger PFAS**
- **Industrial emissions of nonpolar VOCs**
- **Unknowns analysis -> not limited to 30 targets**
  - **Not just F-containing compounds**

Photo Credit: Brown and Caldwell

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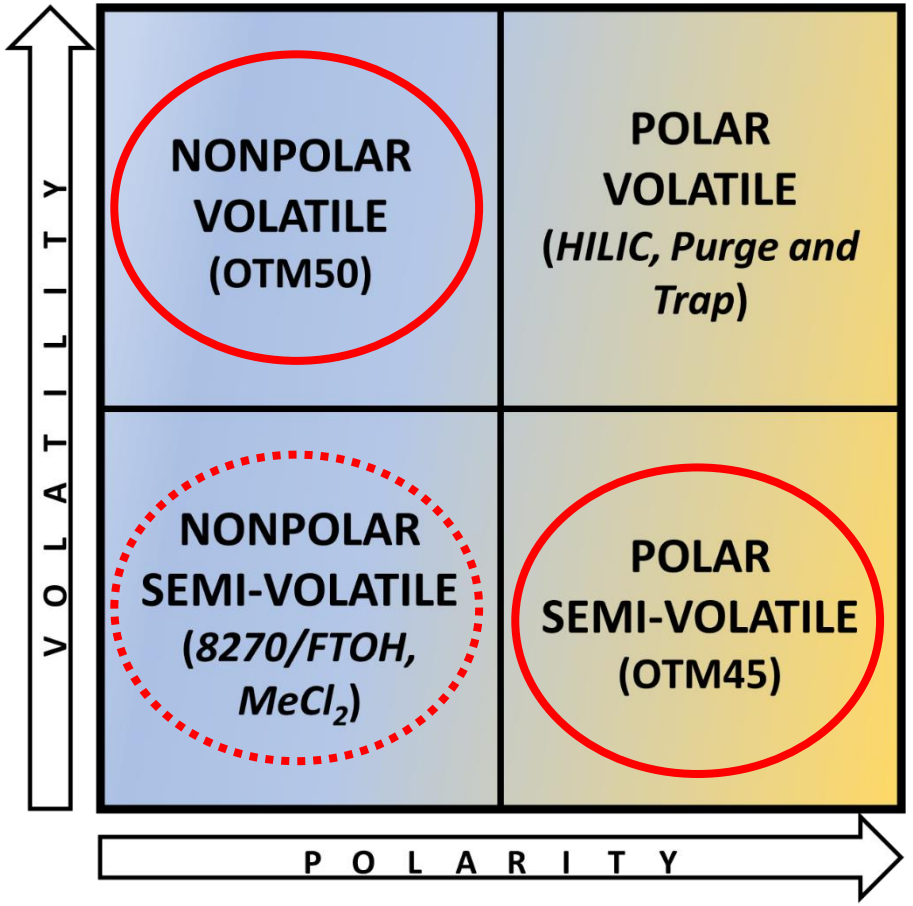

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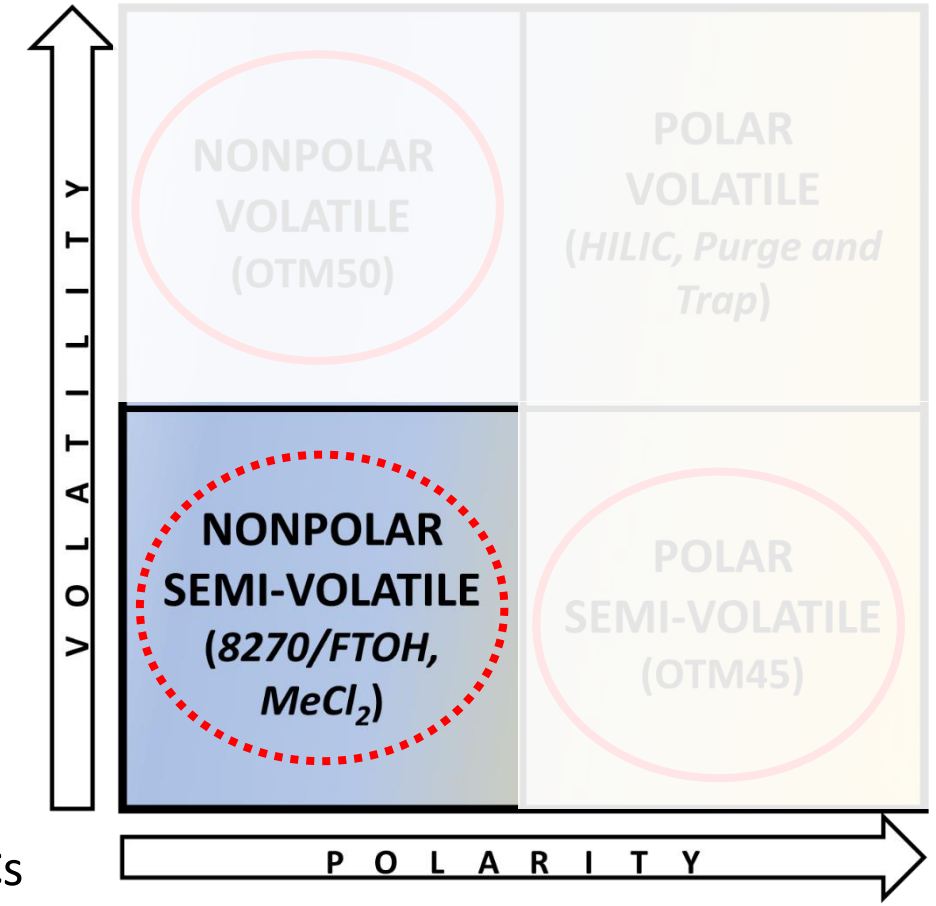

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Nonpolar Semivolatile Fluorocarbons

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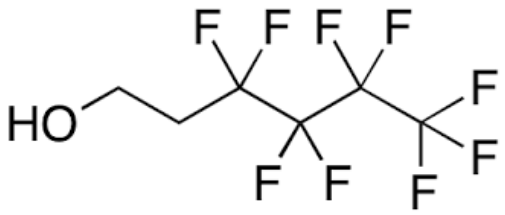

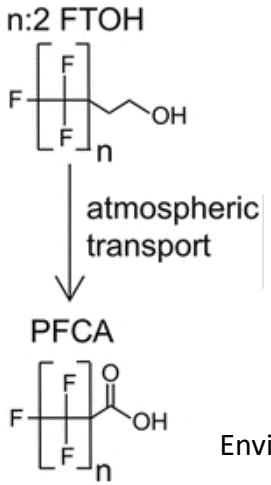

Environ. Sci. Technol. Lett. 2024, 11, 7, 730–737

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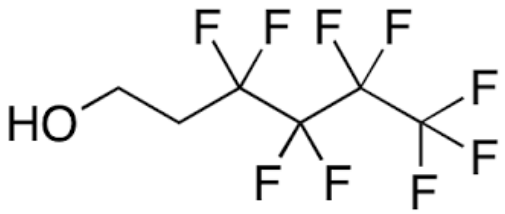

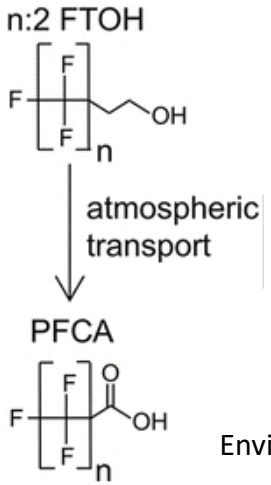

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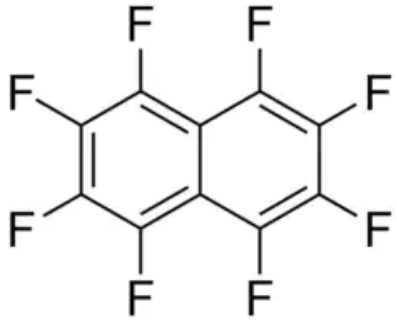

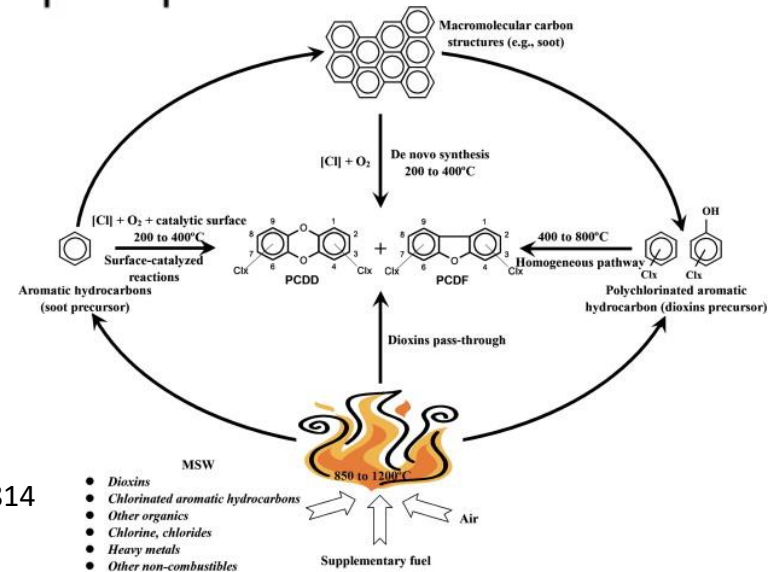

Environmental Pollution 2010, 158, 9, 2809-2814

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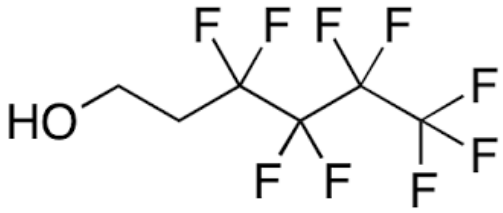

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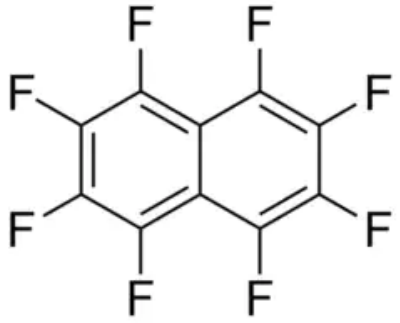
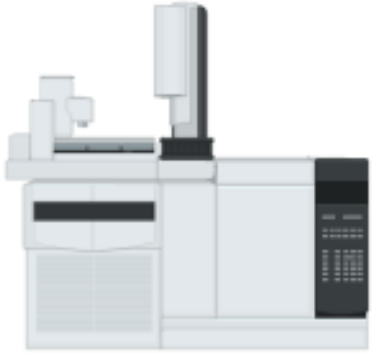


Approach based on SW-846 Methods 0010/3542/8270 – PAHs and other semivolatile organic compounds



2024 Destruction & Disposal Guidance

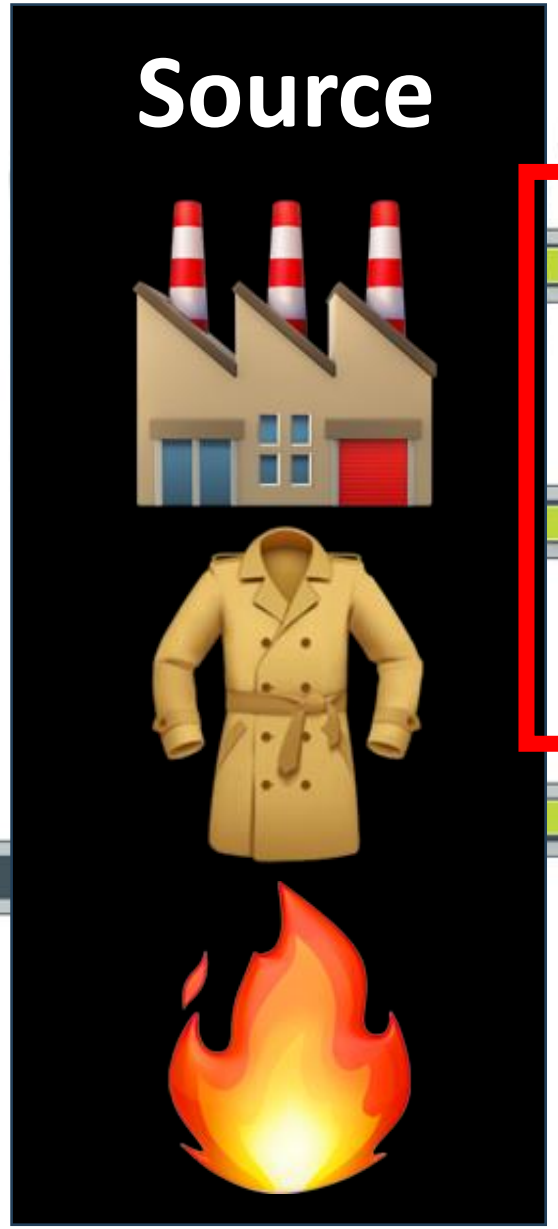
Appendix A: EPA Guidance to Conduct PFAS Emissions Field Testing at Commercial Thermal Destruction Sources

EPA's Other Test Method (OTM) 45 would be used to collect polar semivolatile PFAS compounds for targeted analyses. The method's 50+ target analytes include many PFAS commonly found in AFFF. This would enable DE, DRE, and emission rate determination as appropriate for a known list of PFAS compounds.

The OTM-50 canister sampling method would be used to collect nonpolar volatile PFAS compounds for targeted compound analyses. The current target list includes CF_4 and C_2F_6 as well as a procedure to identify unknown volatile fluorocarbons.

- Samples would be collected for other semivolatile target compounds using methods SW-846 Methods 0010/3542/8270 with the inclusion of the Method 8270 procedure. Carbon hexafluoride (C_2F_6) and carbon tetrafluoride (CF_4) could be injected during one day of testing, ideally at multiple injection locations, as a surrogate measure of destruction efficiency if appropriate and permitted.

When to use 0010/3542/8270?



PFAS Output Options

OUTPUT OPTION:
Unchanged

OUTPUT OPTION:
Partial transformation or reformation

OUTPUT OPTION:
Mineralization

FTOHs, other semivolatile PFAS

PFOA, PFOS, GenX

PFAS

0010/3542/8270

- **Potential PICs/PIDs**
- **Semivolatile nonpolar/neutral PFAS**
- **Unknowns analysis**

Photo Credit: Brown and Caldwell

OTM-55?

What we know:

- 0010*/3542/8270
- Unknowns analysis
- Pre-sampling, pre-extraction, and pre-analysis surrogates

What we still don't know:

- Target compounds
- Quantitation approach(es)
- Sequential extraction viability

Data from early experiments will largely inform what is needed for OTM-55

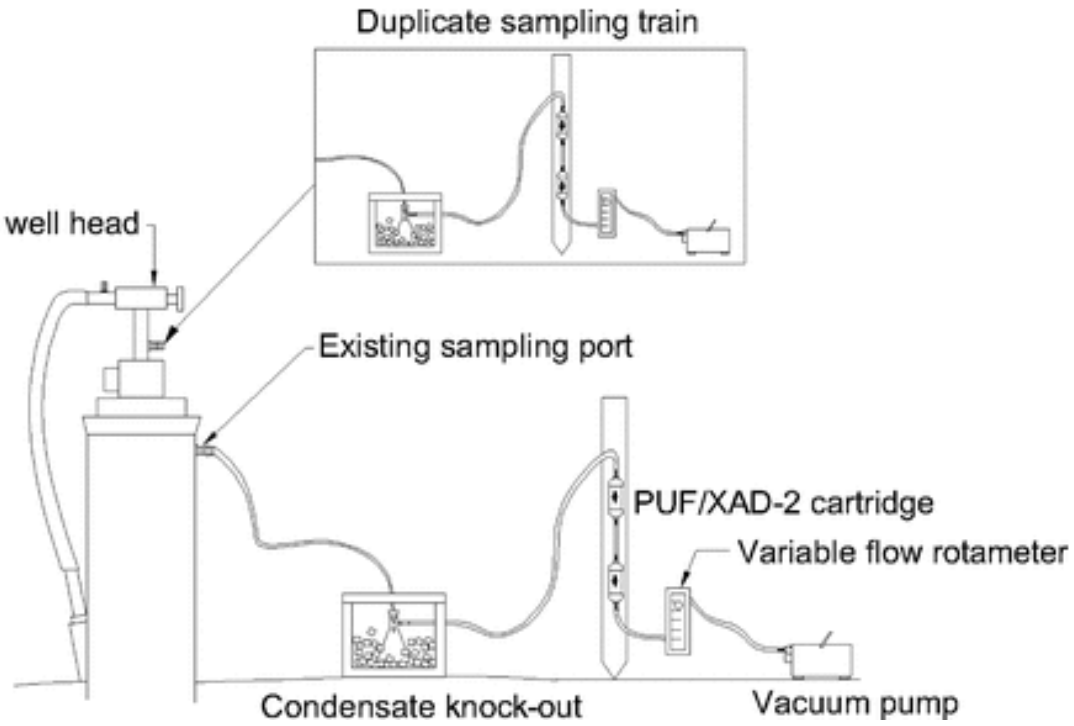
*Modified

Other (non-traditional) sources

Landfills?
Low-flow, pilot-scale systems?

OTMs may not apply directly, but principles of sound measurement & analysis do!

- Appropriate sample/analysis strategy for compounds of interest
- Pre-sampling, pre-extraction, pre-analysis surrogates
- Performance-based methods: QA/QC guidelines are the backbone and designed to evaluate success of measurement



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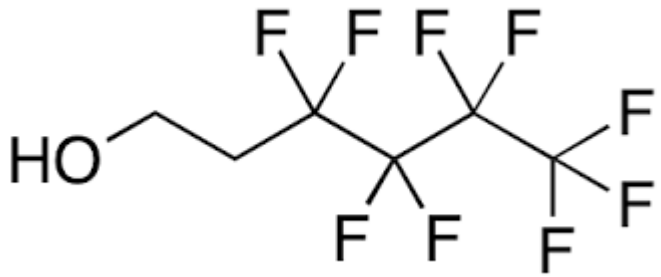
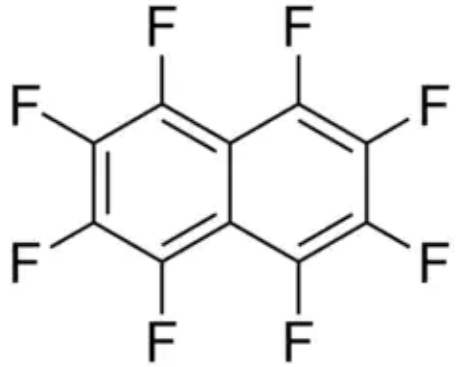
Concluding Key Points

- ***Accepted*** PFAS and PFAS-related emissions measurement methods are needed for multiple purposes & sources
- OTMs are recognized as what's needed for accepted use
  - OTM-45 is currently available for polar semi-volatile PFAS
  - OTM-50 is currently available for nonpolar VFCs
  - Developing a method for nonpolar semi-volatile fluorocarbons (OTM-55)
- **Access to actual sources to evaluate methods and conduct comprehensive source characterization is critical**
- Collaboration and partnership, both internal and external, is integral
- We continue to make significant progress!





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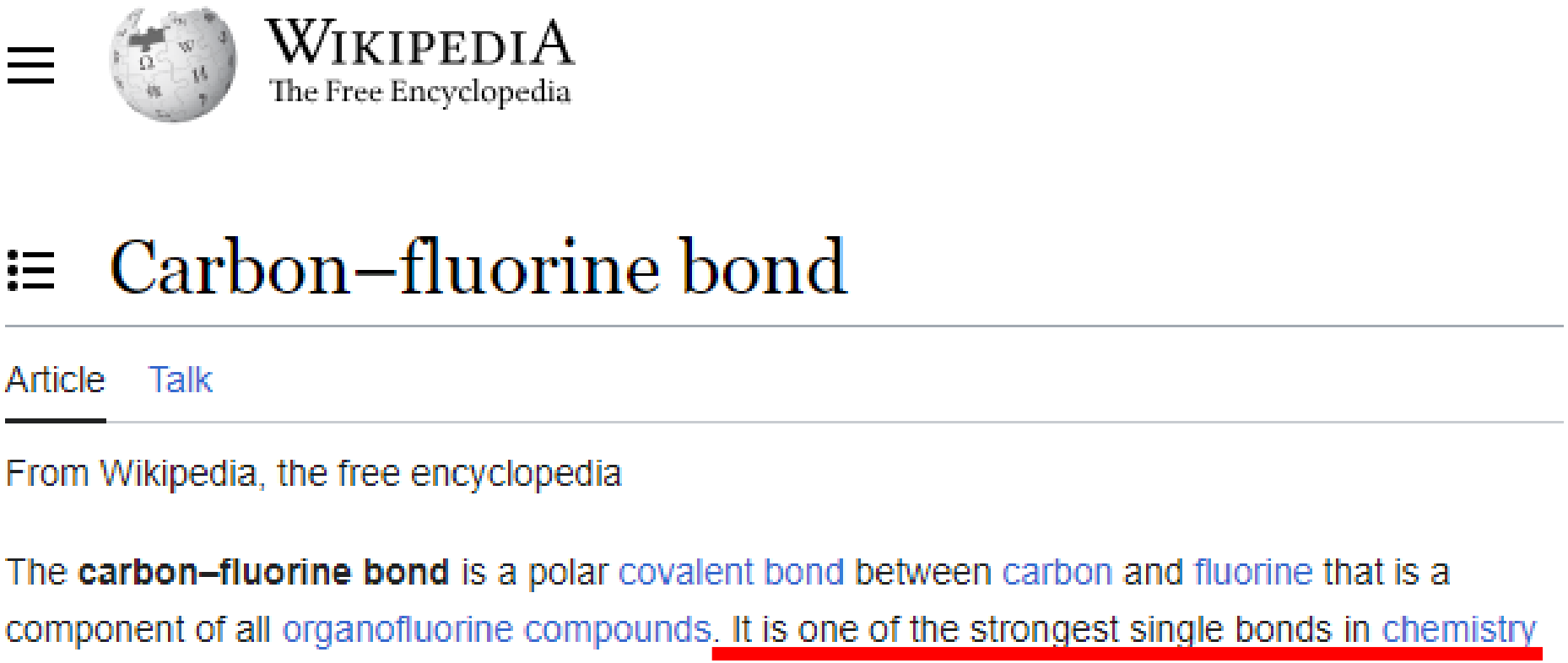
PFAS are Difficult to Destroy

- “Forever” chemicals



WIKIPEDIA
The Free Encyclopedia

Carbon–fluorine bond

Article Talk

From Wikipedia, the free encyclopedia

The **carbon–fluorine bond** is a polar covalent bond between carbon and fluorine that is a component of all organofluorine compounds. It is one of the strongest single bonds in chemistry

EPA United States Environmental Protection Agency

- “Forever” chemica

Article Talk

From Wikipedia,

The **carbon–fluo** uorine that is a component of all e bonds in chemistry