# PFAS Air Emissions from Solid Waste Landfills – Sources, Measurement Methods and Other Considerations

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FOLLOWING
[DOING]
LEADING

# Presentation Topics

- PFAS Primer
- Sources of PFAS in Solid Waste Placed in Landfills
- Potential PFAS Emissions Sources in Solid Waste Landfills
- Methods for Measuring PFAS Air Emissions
- PFAS in Air Emissions from Landfills and Ambient Air Near Landfills

# PFAS Primer

**PFOS Structure– all PFAS have carbon-fluorine backbone with different end groups**

*>4,700 produced/used since 1950*

**PFAS**
**Per- and polyfluoroalkyl Substances**

polymers

**PFAAs**
**Perfluoroalkyl Acids**
***(100's)***

**Polyfluorinated Compounds**
***(1,000's)***

**PFSAs**
**Perfluorosulfonic Acids**
***(10's)***

**PFCAs**
**Perfluorocarboxylic Acids**
***(10's)***

**Fluorotelomers**
**Fluorotelomer Alcohols (FTOHs)**
**Fluorotelomer Sulfonic Acids (FTSs)**

**PFOS**
**Perfluorooctane Sulfonate**
***(Individual Compound)***

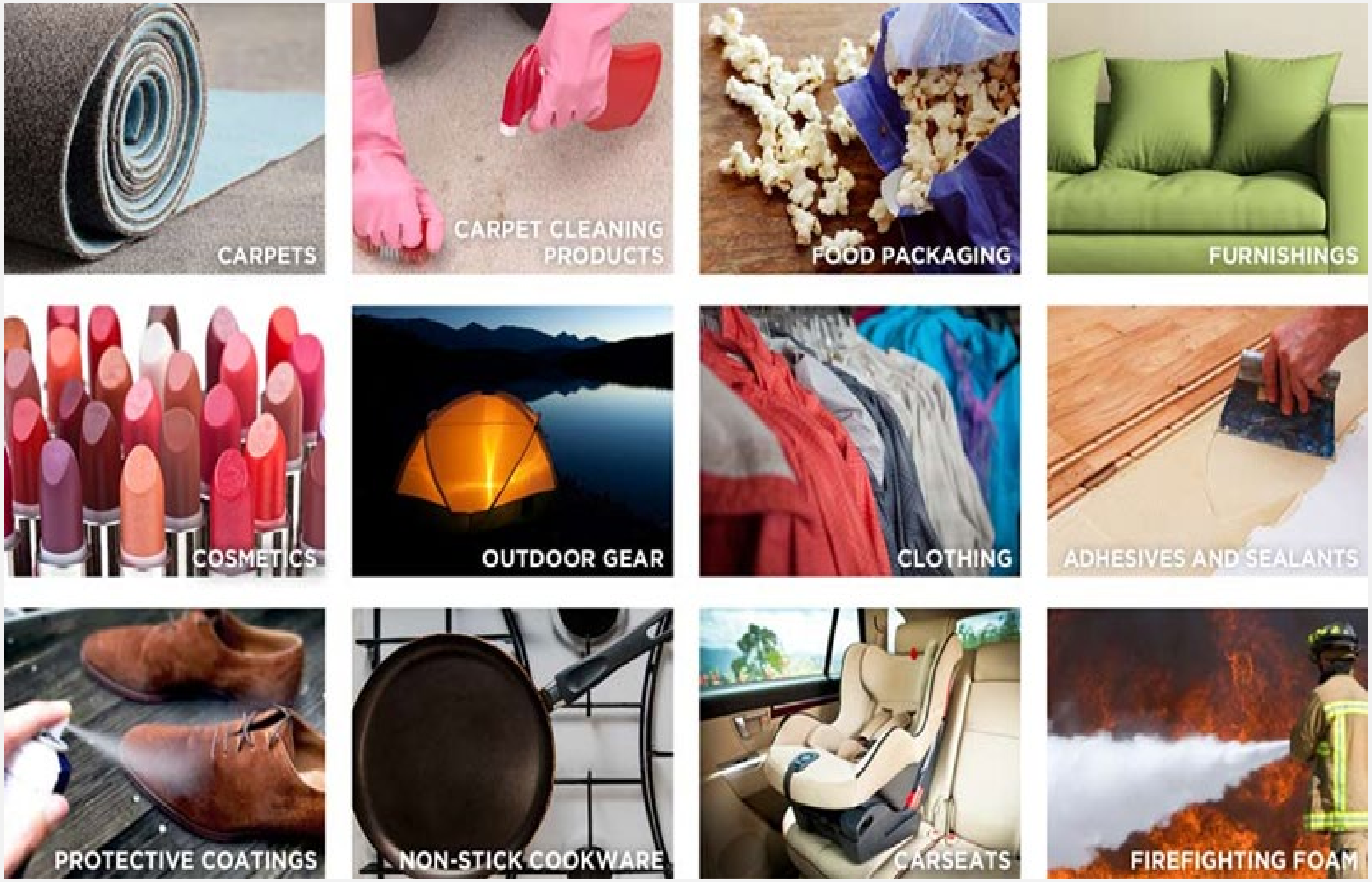
**PFOA**
**Perfluorooctanoic Acid**
***(Individual Compound)***

**Replacements**
**Ammonium 4,8-dioxa-3H-perfluoronanoate (ADONA)**
**Ammonium 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy) propanoic acid (GenX)**

# Some PFAS Sources Found in Solid Waste Landfills

**Historically consumer products contained PFAS; many still do!**

- Stain resistant clothing/carpet /furniture
- Dental floss
- Non-stick cookware
- Food packaging (pizza boxes, microwave popcorn bags)
- Some ski waxes
- Paints/polishes
- Cleaning products
- Children's and pet products



# Some Manufacturing Sources of PFAS (ITRC, 2020)

- Textiles and Leather
- Paper Products
- Metal Plating and Etching
- Wire Mfg.
- Ind. Surfactants, Resins, Molds, Plastics
- Photo-lithography and Semi-Conductors

# Wastes as Sources of PFAS – Chemistry has Changed over Time

**Compounds manufactured have evolved through time in all industries. For example, fire fighting foam (AFFF)**

### Legacy 1st Generation PFOS AFFF 1960-2002

- PFOS based (80%)
- Telomer based (20%)
- Sold from 1960s to 2002
- Inventory remains in many locations
- **Contains or breaks down to PFOS & PFHxS and possibly PFOA**

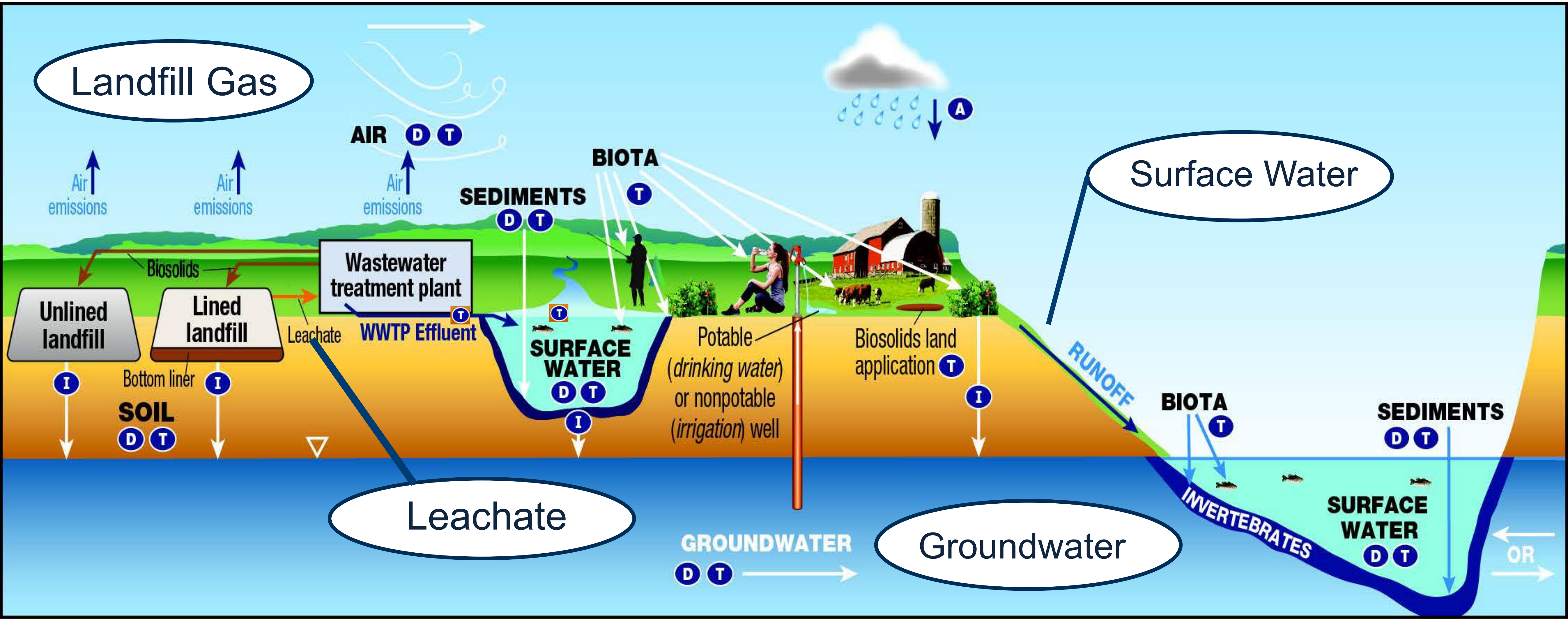
### 2nd Generation Long Chain Fluorotelomer AFFF 1970s-2016

- Telomer based
- 50%-98% short chain and 2% to 50% long chain PFAS compounds
- Sold from 1970s - 2016
- **Breaks down to PFOA**

### Modern Short Chain Fluorotelomer AFFF

- **No PFOS and no breakdown to PFOS**
- **Short-chain fluorotelomers (6:2 and 4:2 FTS)**
- **May contain trace amts of PFOA and PFOA precursors**
- Considered lower in toxicity and reduced BAP

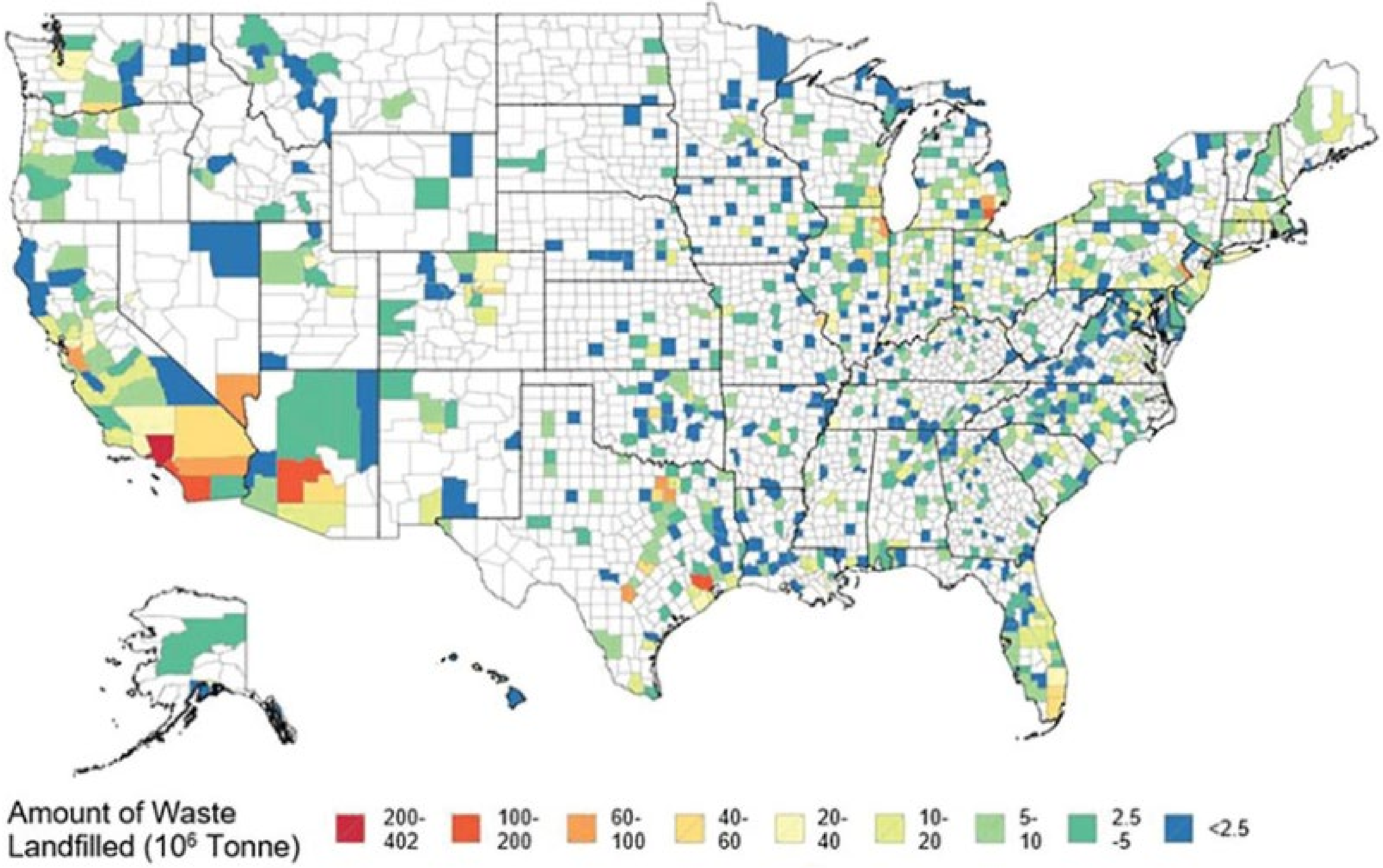
# Potential Environmental Impacts of Landfills- Leachates and Air Emissions




Adapted from Laura Trozzolo, TRC
From: ITRC, (2018b)

KEY
- A Atmospheric Deposition
- D Diffusion/Dispersion/Advection
- I Infiltration
- T Transformation of precursors (abiotic/biotic)

# Location of Landfills in the U.S. By County- They are Ubiquitous!!!




Credit:

**Waste Informatics: Establishing Characteristics of Contemporary U.S. Landfill Quantities and Practices**, September 2016, Environmental Science & Technology, by Jon Powell, José Carlos Pons, and Marian Ruth Chertow, Yale University

# Potential PFAS Air Emissions Sources in Solid Waste Management

- PFAS has been detected in ambient air downwind from landfills indicating air emissions
- PFAS in landfills is in the waste itself, dissolved in the leachate liquids, and present in landfill gases
- Because of water solubility, most PFAS will be in leachate
  – Leachate treatment can result in PFAS air emissions if  sent to  WWTP
  – Sewage sludge incineration results in PFAS air emissions
- Landfill gas has potential for air emissions
  – Escaping untreated gases (vents and fugitives)
  – Incomplete destruction in combustion can result in air emissions
    - Flares
    - Stationary Engines

# PFAS in Landfill Leachate

**US Landfill Study** (Lang et al., 2017) – 95 samples from 18 landfills

- 70 PFAS measured, 19 PFAS detected in >50% of samples
- PFOS: 3 to 200 ppt
- PFOA: 100 to 1,000 ppt
- Total PFAS: 2,000 to 29,000 ppt
- 5:3 FTCA (precursor) dominant in most leachates: 400 to 15,000 ppt

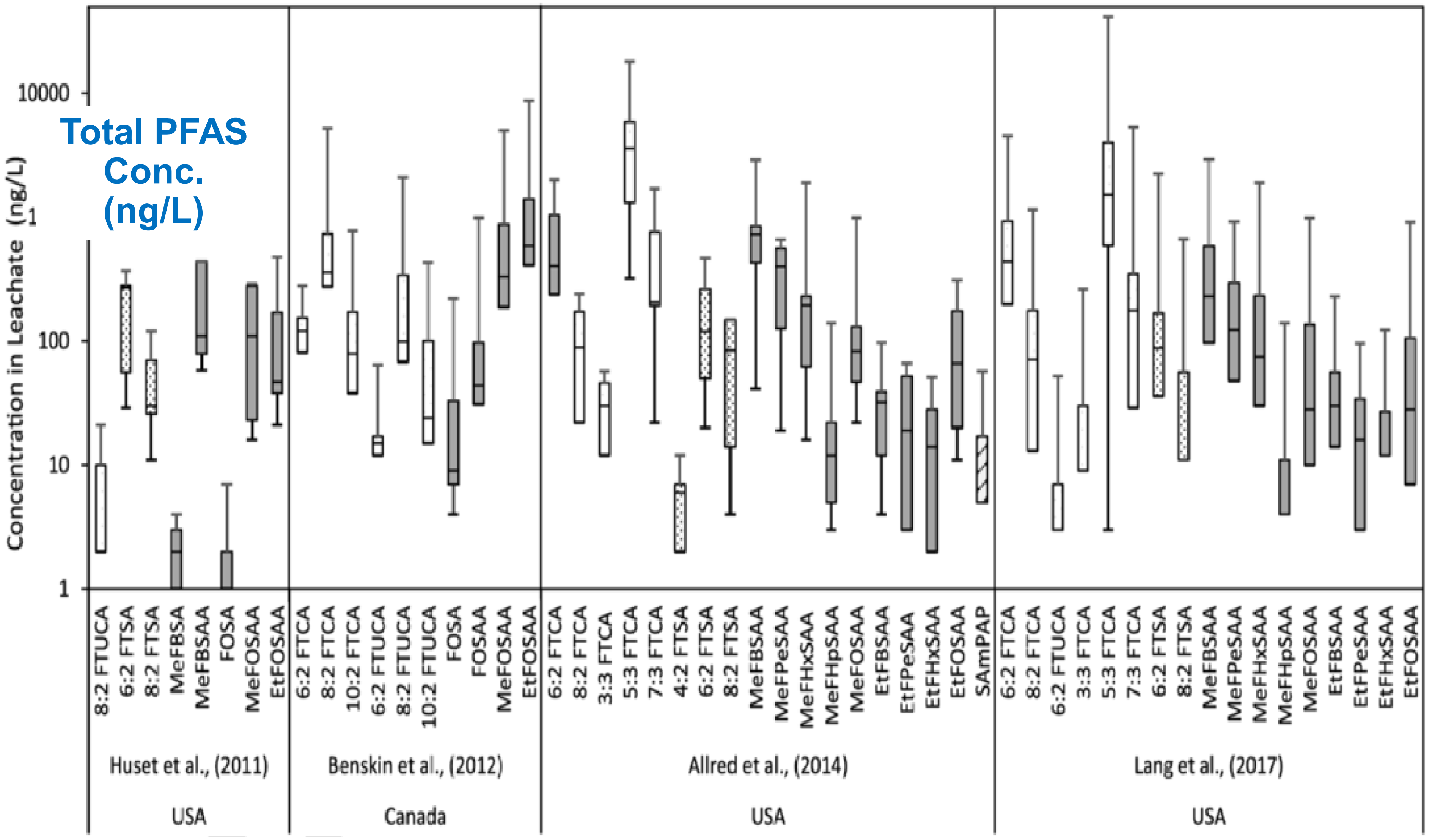
**Canadian Landfill Study** (Li, 2012)
samples for 28 landfills

- PFAS detections in all 28 samples
- PFOA detected in all samples, mean concentration of 439 ppt

**German Landfill Study** (Busch, 2009) – 22 German landfills

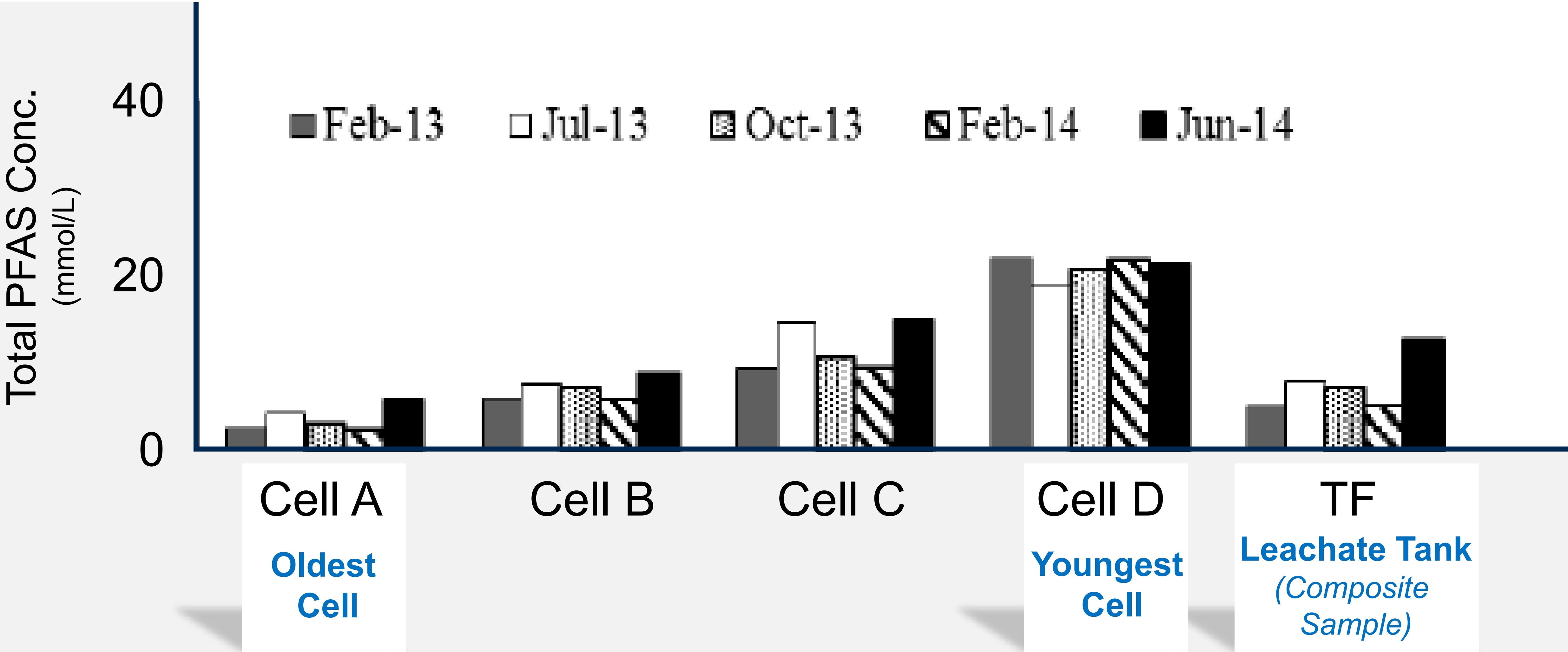
- 38 PFAS detected
- Total PFAS: 30.5 ppt to 13,000 ppt

# PFAS in Landfill Leachates




Ref: Hamid, H., et al., (2018)

# PFAS in Leachates and Cell Age



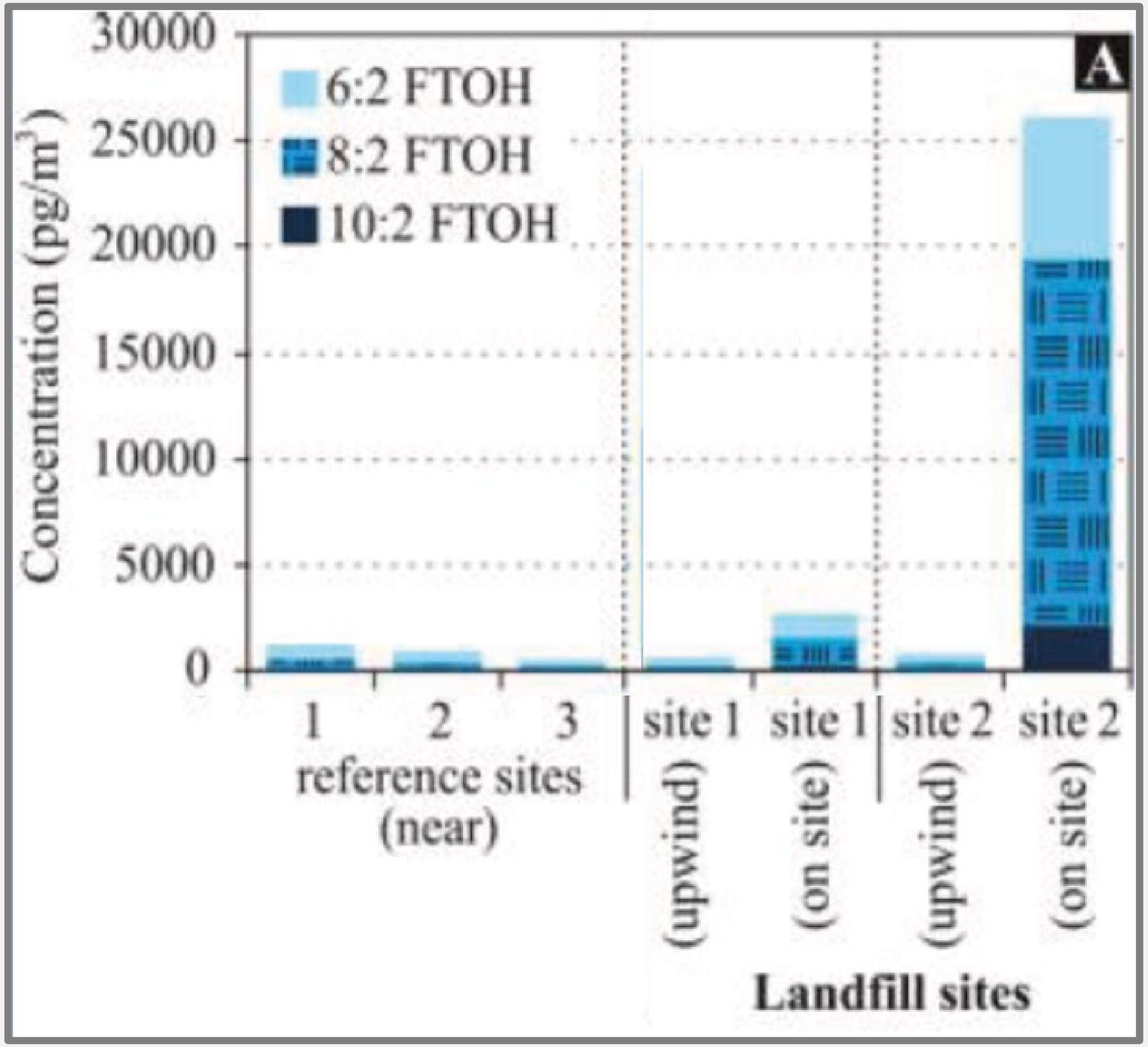

**Ref: Lang, J., et al., (2017)**

# Landfill Gases and Impacts on Ambient Air On Site

Research study by Ahrens, L., et al., (2011)

- Semi-volatile precursors are predominant
- 8:2 FTOH dominant compound
- PFAS in air 5 to 30 times higher at landfills vs. upwind background

Ref: Ahrens, L., et al., (2011)



# PFAS in Ambient Air - Landfills (pg/m3)

| PFASs (Other Sum) | FTOHs ** | FOSAs/ FOSEs | Comment | Reference |
|---|---|---|---|---|
| 130-320 | 2500-26000 | 60-120 | Active Landfill | Ahrens 2011 |
| 5-10 | 70-100 | 6-20 | Closed Landfill | Weinberg 2011 |

** FTOHs or Fluorotelomer alcohols like 8:2 FTOH have moderate volatility. These compounds can break down to form regulated PFAS such as PFOA and PFNA.. Significant PFAS (mostly FTOHs) emissions (> 1000 grams/year) have been estimated from landfills (Ahrens et al, 2011)

# Landfill Gas Sources

**Flare**
(~1,200º F or 650º C)

Note: PFAS Destruction Needs > 1,100º C for long periods of time. Much greater than typical flare temperatures

**Landfill Gas to Energy**
(Combustion Engine)

**Direct Discharge**
(Old Landfills)

**Vents**

**Fugitives**

# Types of Air Sampling Methods for PFAS

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### Dynamic Pumping / Active Sample Collection

- EPA OTM-45 Sampling Train
- Low/High Volume Samplers Fitted with Sorbent Traps (e.g. XAD-2)

### Whole Air Sampling

- Canister Sampling- EPA Method TO-15

### Passive Sorbent Samplers

- Polyurethane Foam (PUF) Disks
- Sorbent (XAD-4) Impregnated PUF Disks

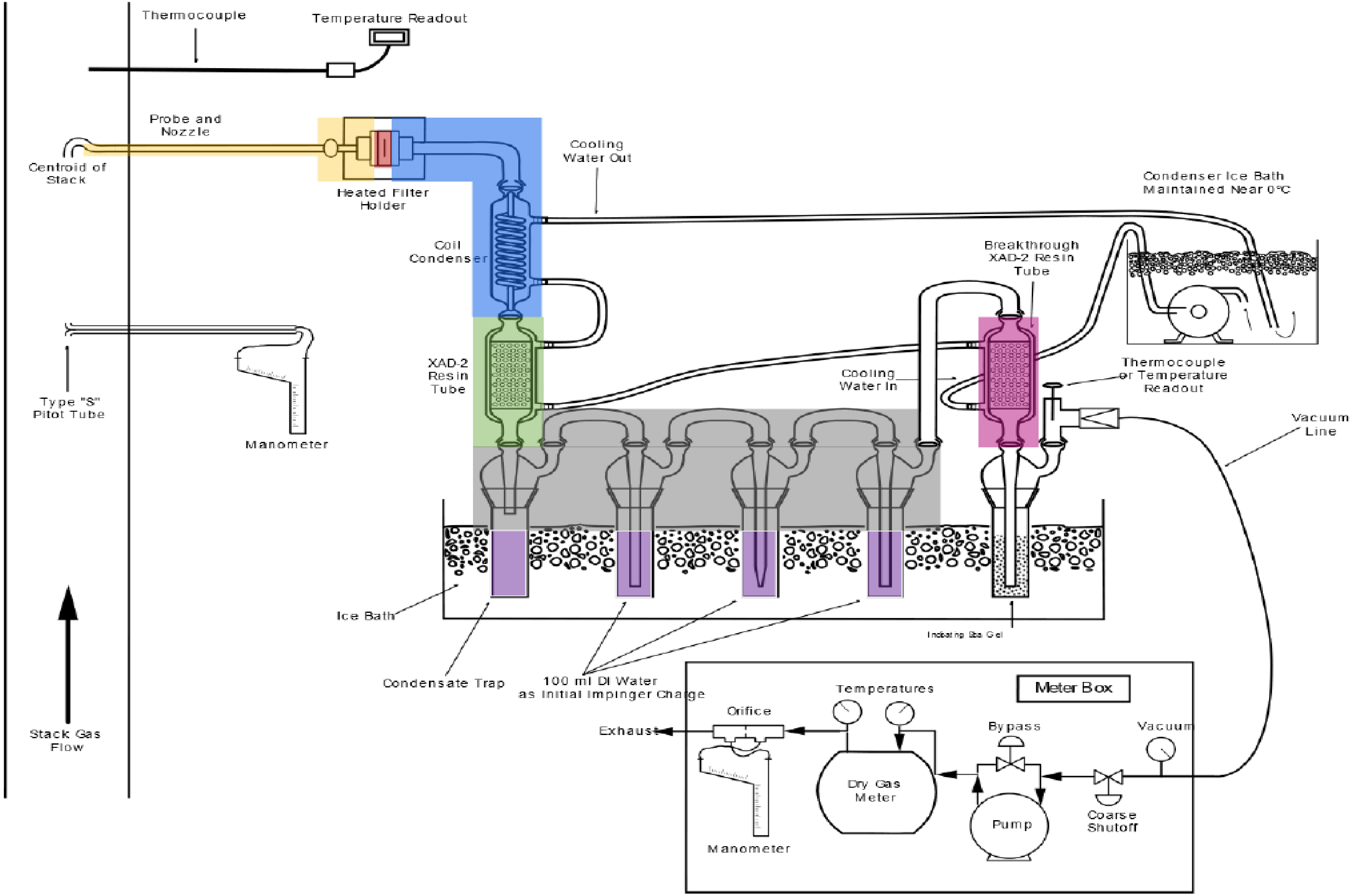
# Other Test Method OTM-45 - Measurement of Selected PFAS Substances from Stationary Sources- USEPA

- Method meets EPA commitment identified within the 2020 National Defense Authorization Act guidance for PFAS disposal and destruction
- First EPA air emissions PFAS test method –very important to standardize the approach to sample collection
- EPA issued OTM-45 in January 2021
- Can be used for compliance and diagnostics testing
- Applicable to stationary sources such as landfill gas engines

# OTM-45 Sample Train

- PFAS captured on a filter, XAD-2 sorbent, impingers, and 5% ammonium hydroxide in methanol rinses of sample train surfaces
- Second XAD-2 sorbent module after impingers for breakthrough determination
- Detailed glassware cleaning and sample recovery procedures to avoid PFAS contamination
- Clean room for recovery of samples is imperative
- No PFAS containing tools used for setup/sampling/recovery

# OTM 45 Visua Container Guide

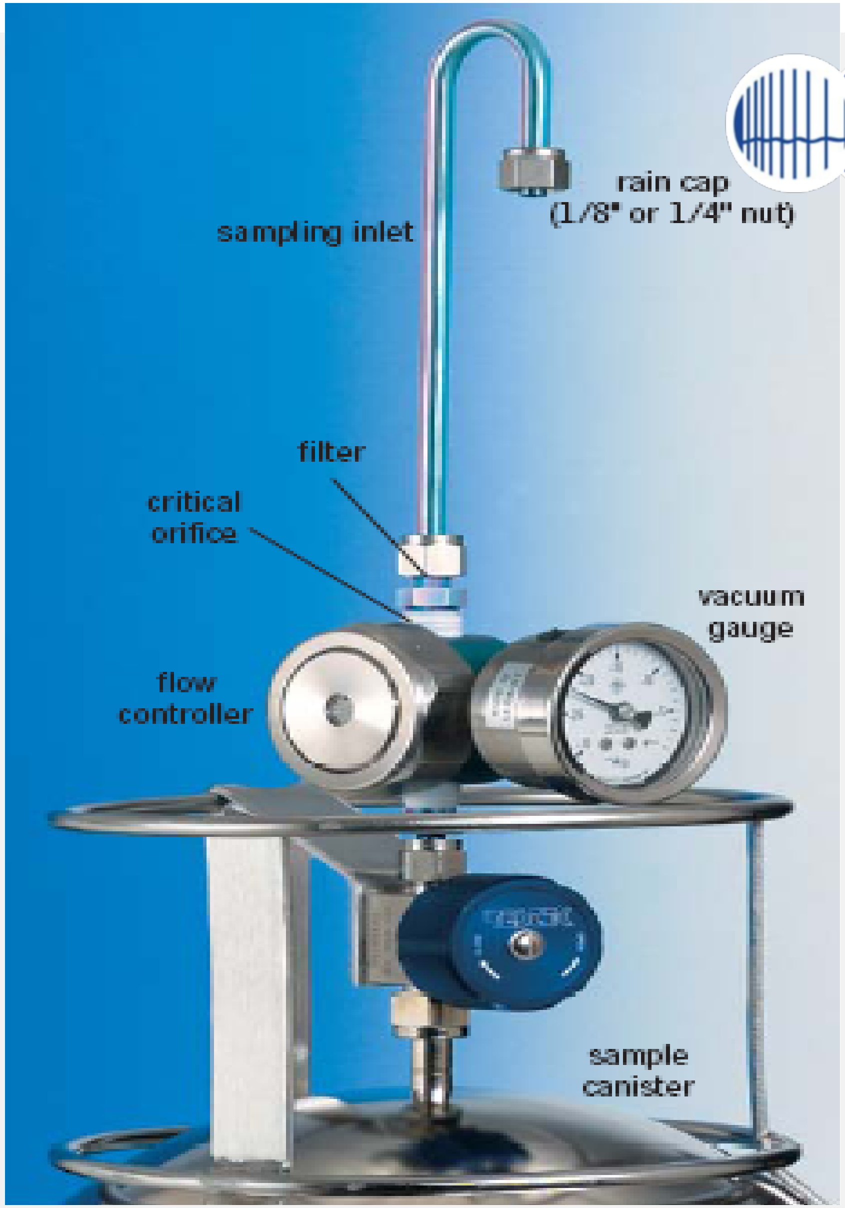



- #1 Filter
- #2 Front Half Rinse
- #3 XAD-2
- #4 Back half Rinse
- #5 Condensate and Impinger Water
- #6 Impinger Rinse
- #7 Breakthrough XAD-2

# What Does the OTM-45 Method Measure?

- OTM-45 measures a specified set of ionic PFAS compounds (***50*** listed in method)
- QRLs are < 2 $ng/m^3$ for 26 compounds (3 $m^3$ gas sampled, lower DL if more volume sampled)
- OTM-45 does not measure:
  - Non-ionic PFAS (EPA looking at alternate rinse solvents)
  - Volatile PFAS (EPA evaluating Summa canister sampling)
  - PFAS not on the target analyte list (Non-target analysis methods in development)
  - Total Organic Fluoride (Sum of all PFAS via ion chromatography – not possible if HF present)

# Canister Sampling Train




EPA Method TO-15

# Canister Sampling for Volatile PFAS

## The Principle of Operation

Use of differential pressure (Δ P) to induce flow of air at atmospheric pressure outside into an evacuated (under vacuum) canister. This flow is monitored using a controller in combination with a critical orifice.

## Applicability

Ambient and source samples especially suitable for volatile PFAS such as FTOHs.

**Photos courtesy of Alpha Labs**

# Features of Canister Air Sampling Method

EPA Method
TO-15

- A whole air sample
- The sample and its chemical composition should represent a time weighted average (TWA) for each sampling interval.
- Interior surface (wall) of canister is inert (SUMMA  coated).
- Vacuum gauge to monitor interior pressure of canister.
- Controller and critical orifice to regulate flow of air into canister.
- No power needed of course

# EPA ORD Emissions Methods Development Research

## Volatiles:

- Modified TO-15 for targeted and non-targeted compounds
- Using SUMMA canisters
- Limiting sample volume to avoid moisture condensation
- GC/MS analysis for targeted and non-targeted compounds
- On-Line Mass Spec for polar compounds

**Source: USEPA Office of Research and Development, North Carolina 2019**

# Critical Orifice Diameter vs Flow Rate
(Courtesy of Alpha Labs)

| Orifice Diameter (in) | Flow Rate Range (mL/min.) | Canister Volume / Sampling Time 1L | 3L | 6L | 15L |
|---|---|---|---|---|---|
| 0.0008 | 0.5–2 | 24 hr. | 48 hr. | 125 hr. | — |
| 0.0012 | 2.4 | 4 hr. | 12 hr. | 24 hr. | 60 hr. |
| 0.0016 | 4–8 | 2 hr. | 6 hr. | 12 hr. | 30 hr. |
| 0.0020 | 8–15 | 1 hr. | 4 hr. | 8 hr. | 20 hr. |
| 0.0030 | 15–30 | — | 2 hr. | 3 hr. | 8 hr. |
| 0.0060 | 30–80 | — | — | 1.5 hr. | 4 hr. |
| 0.0090 | 80–340 | — | — | 0.5 hr. | 1 hr. |

# Passive Sampling – Indoor Location

# States Taking Lead in Setting PFAS Air Limits

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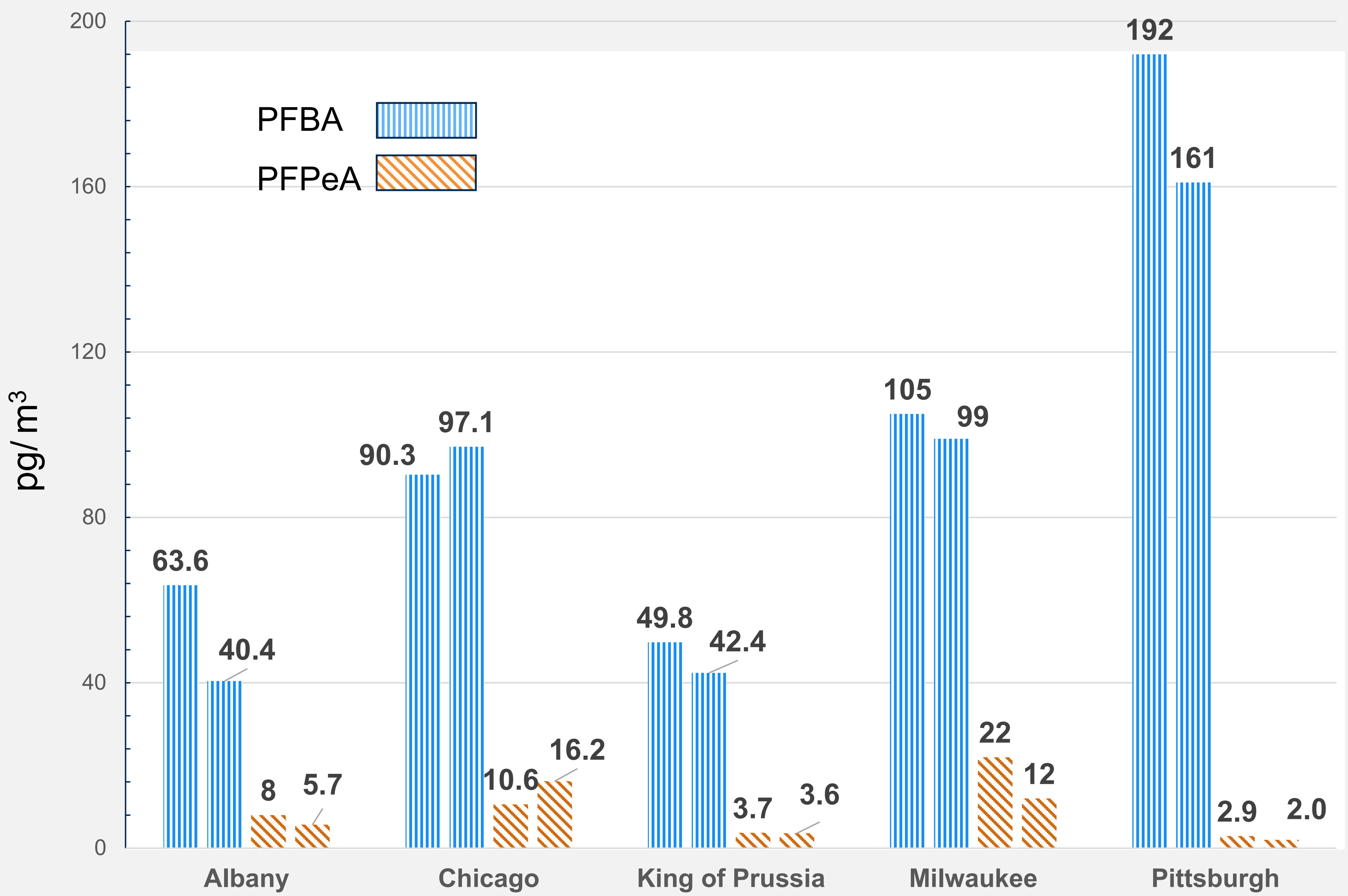
**Federal action on PFAS limits in air have been slow to develop. Some states have acted to set ambient air exposure limits:**

- **Michigan (initial threshold screening level)**
  - PFOA Advisory level: 0.07 µg/m3
  - PFOS Advisory level: 0.07 µg/m3
- **New Hampshire (ambient air; APFO is a specific PFAS compound)**
  - APFO Regulatory level (24-hour): 0.05 µg/m3
  - APFO Regulatory level (annual): 0.02 µg/m3
- **Texas (occupational health)**
  - PFOA Advisory level (based on annual average): 0.005 µg/m3
  - PFOS Advisory level (based on annual average): 0.01 µg/m3
- **New York (2021 annual guideline concentration)**
  - PFOA Advisory level (based on annual average): 0.0053 µg/m3
  - NYSDEC classifying PFOA as a high-toxicity air pollutant, will set an annual source emission limit above which air dispersion modeling will be required to show compliance




# PFAS Ambient Air Data – 2020 Sampling Events ($pg/m^3$)

# PFAS Air Emissions from Solid Waste Under Study

## PFAS Behavior in Solid Waste Combustion Treatment at Landfills

**Investigators:** University of Vermont; Sanborn Head & Associates; Weston Solutions; North Carolina State University,

**Start Date:** September 2021

- Measure PFAS emissions from combustion sources at landfill facilities and assess PFAS behavior in combustion systems
- Examine intra-and inter-facility emissions variability and characteristics
- Evaluate PFAS destruction efficiencies in LFG combustion sources
- Evaluate PFAS impacts to ambient air and exposure due to combustion emissions

Source: https://erefdn.org/pfas-behavior-in-solid-waste-combustion-treatment-at-landfills/

# PFAS In Landfill Gas is Under Study

## 2020 Progress Report: Characterization and Quantification of per- and polyfluoroalkyl substances in landfill gas and estimate of emissions from U.S. Landfills

Research objective: Estimate mass of PFAS that are present in landfill gas (LFG) and the mass of PFAS emitted as fugitive emissions. Funded by EPA, project continues in 2022.

- Develop methods to sample and analyze LFG for targeted and non-targeted PFAS
- Measure PFAS concentrations at cross section of U.S. landfills in different climatic regions
- Develop a model to estimate PFAS production and emissions at the U.S. national scale
- Evaluate the potential impact of soil attenuation on PFAS emissions
- Measure gas-phase PFAS release from mixed waste and food packaging materials

Source: https://cfpub.epa.gov/ncer_abstracts/index.cfm/fuseaction/display.highlight/abstract_id/10990/report/2020

# Summary

- PFAS are likely present in most landfills as evidenced by leachate data
- All MSW landfills will likely contain PFAS waste
- PFAS amounts and chemistry may vary by age and sources of cells
- Emissions tests have been performed on a very limited number of facilities
- PFAS air test method development is a focus at EPA
- The solid waste management industry has potential PFAS air emissions from flares, stationary engines, vents and fugitive emissions from landfill gases
- Rapidly developing technology, regulations, and policy

# Some References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# Thank You

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