Challenging today.
Reinventing tomorrow.

Performance Testing of a PFAS Methods for Soil Gas, Sewer Gas, and Indoor Air

Chris Lutes, Elsy Escobar and Taylor Salsburg; Jacobs

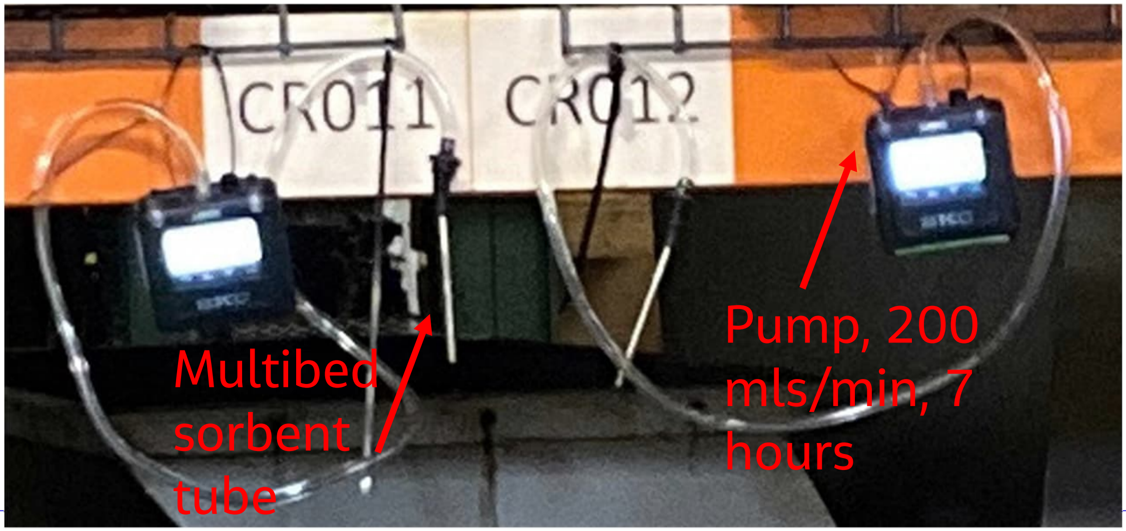
Heidi Hayes, Eurofins Environment Testing

Kate Bronstein, RTI International, Research Triangle Park, NC

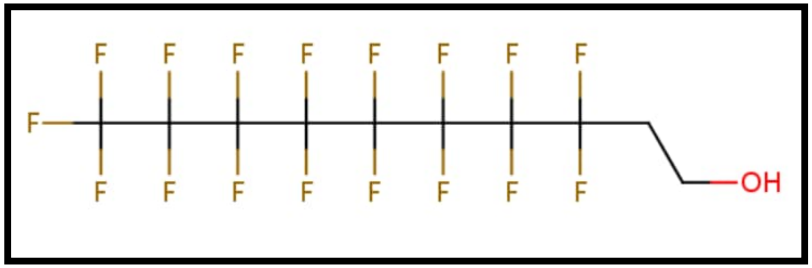
Brian Schumacher, John Zimmerman and Alan Williams, U.S. Environmental Protection Agency

Agenda

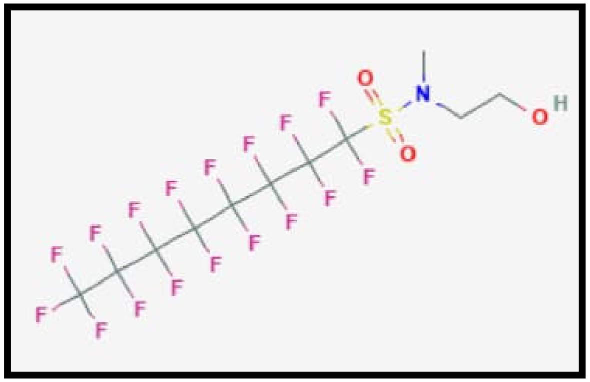
- Need, context, target compounds
- Overview of method – sorbent tube, thermal desorption, tandem Mass spectrometry
- Work previously reported/published
- Method validation studies
- Performance evaluations with indoor air, simulated soil gas and simulated sewer gas
- Field applications
- Path forward



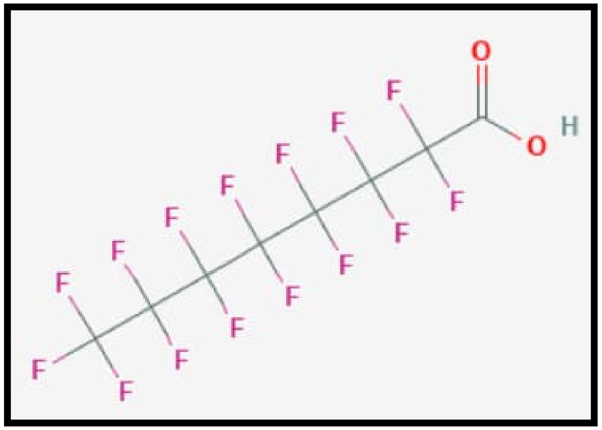
Technical Background – Volatile PFAS classes



Fluorotelomer alcohols (FTOH)



Perfluoro-1-octansulfonamide (FOSA) – n-Ethyl and n-Methyl



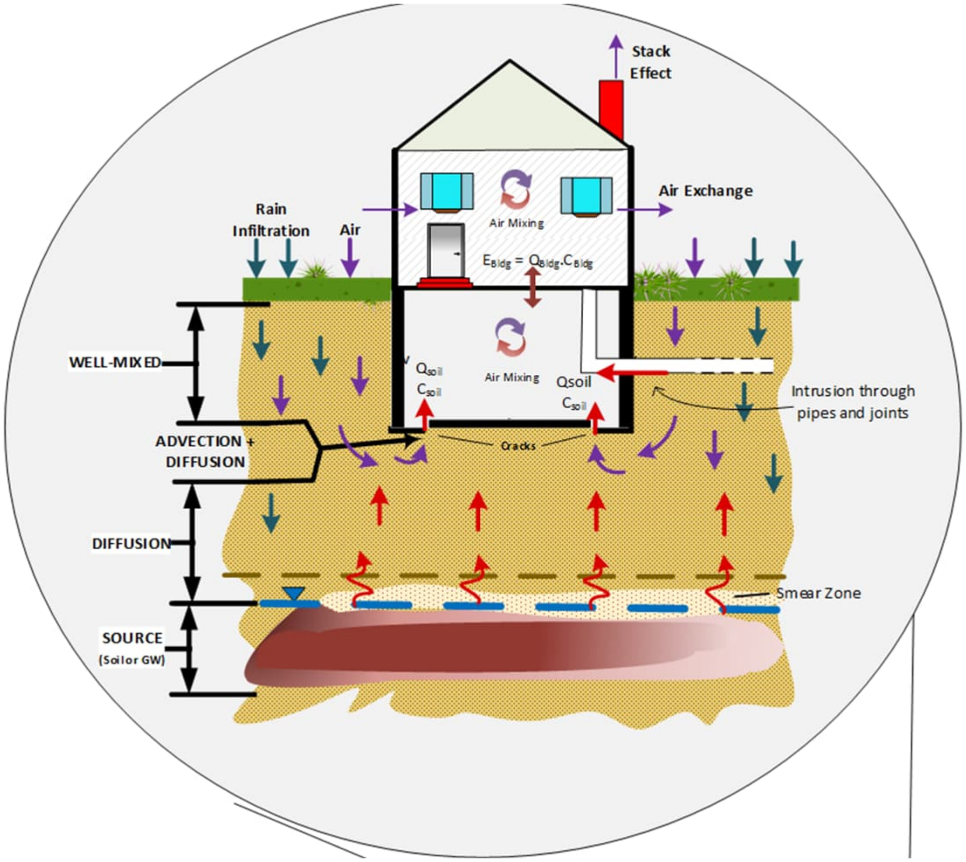
Short chain (C4 to C7) and C8 Perfluorocarboxylic acids (PFCAs)

Key Points: Some PFAS are sufficiently volatile to qualify as “vapor forming chemicals” warranting further evaluation for Vapor Intrusion. Growing interest in assessing PFAS as potential vapor intrusion sources.

Compound	Vapor Pressure (mmHg)	Henry's Constant (atm m^3 /mol)	Acid Dissociation Constant pKa
Perfluorooctane sulfonamide (FOSA)	0.11 to 0.25	1.3E-9 to 6E+2 (most values over)	6.2 to 6.5
N-Methyl perfluorooctane sulfonamide (MeFOSA)	0.08	1.3E-9 to 5E+3 (most values over)	Not available
N-Ethyl perfluorooctane sulfonamide (EtFOSA)	4.3E-7 to 10	1.6E-10 to 4.7E+3 (Most values over)	9.5
4:2 Fluorotelomer alcohol (4:2 FTOH)	0.79 to 13	7.4e-4 and 1.5E-3	Not available
6:2 Fluorotelomer alcohol (6:2 FTOH)	0.14 to 6.6	8.2E-4 to 6E-2	Not available
8.2 Fluorotelomer alcohol (8:2 FTOH)	0.02 to 1.9	3.7E-4 to 5E-2	14.2
10.2 Fluorotelomer alcohol (10:2 FTOH)	0.0014 to 0.04	8E-2	Not available
Perfluorooctanoic acid (PFOA)	0.02 to 13	3.6E-6 to 2.0E-4	0.5 to 2.8
EPA definition of volatile	>1	>1E-5	Lower pKa = stronger acid

PFAS Conceptual Site Model for VI – What's Different?

- In addition to storage in aqueous, vapor and solid phases; adsorption of PFAS at air-water interface is also very important
- Even greater importance of indoor sources – impossible to just remove because….
- FTOHs have been used as part of a wide range of products including paints, cleaners, adhesives, waxes, polishes, electronics, carpets, paper goods and caulks.
- So source identification will require multiple lines of evidence along the flow path



- Source identification (i.e. release or historical production of materials that may contain PFAS; current products, building materials)
- PFAS concentrations in groundwater
- Water table depth
- Type and permeability of the vadose zone
- PFAS concentration in soil gas
- Presence of sewers and utility lines
- Compound ratios across matrices
- Tracers, potentially controlled pressure method testing

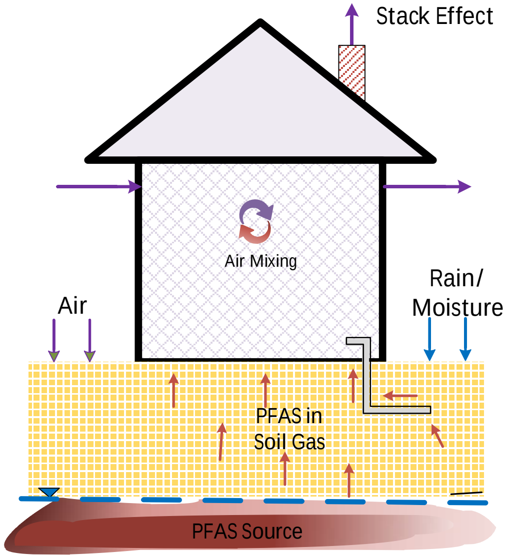
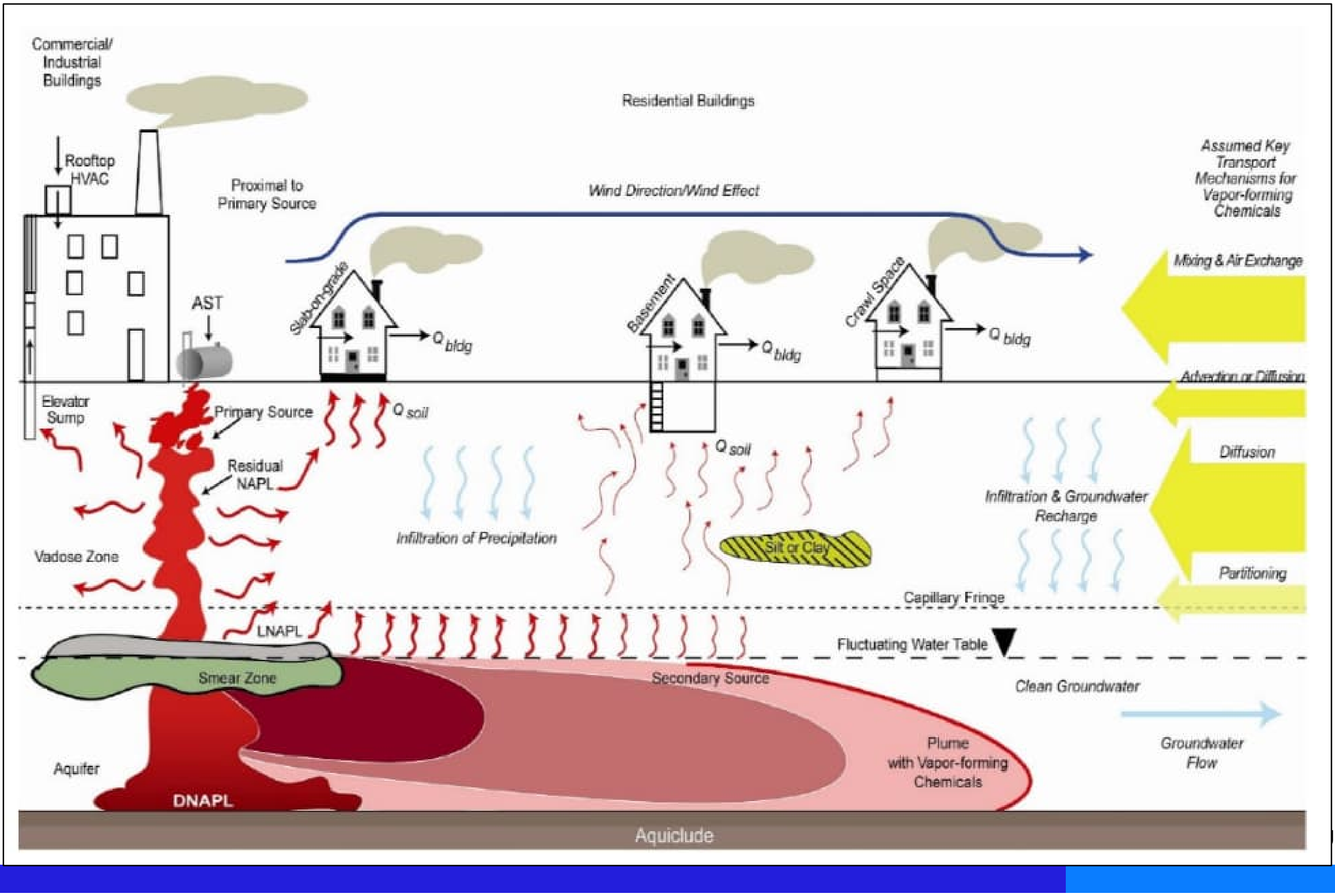


Photo Source: https://www.floorstores.com/flooring/carpeting/

An Overview of Important VI Pathways

Figure source: US EPA 2015.



Work Completed/Published to Date

Results of initial methods development activities and field testing at a NJ manufacturing facility and GA landfill reported in:

- Hayes, H., et al. "*Laboratory Development and Validation of Vapor Phase PFAS Methods for Soil Gas, Sewer Gas, and Indoor Air*"; Environmental Science Atmospheres, November 2024. https://pubs.rsc.org/en/content/articlepdf/2024/ea/d4ea00084f
- Schumacher, Brian et al. "*Distribution of Select Per- and Polyfluoroalkyl Substances at a Chemical Manufacturing Plant*" Journal of Hazardous Materials 464 (2024): 133025 https://www.sciencedirect.com/science/article/pii/S0304389423023099
- Bronstein, K., R. Warrier and C.C. Lutes; Subsurface Per- and Polyfluoroalkyl Substances (PFAS) Distribution at Two Contaminated Sites; EPA 600/R-23/294 I November 2023 https://clu-in.org/download/contaminantfocus/pfas/Subsurface-PFAS-Distribution-Two-Contaminated-Sites.pdf

See also:

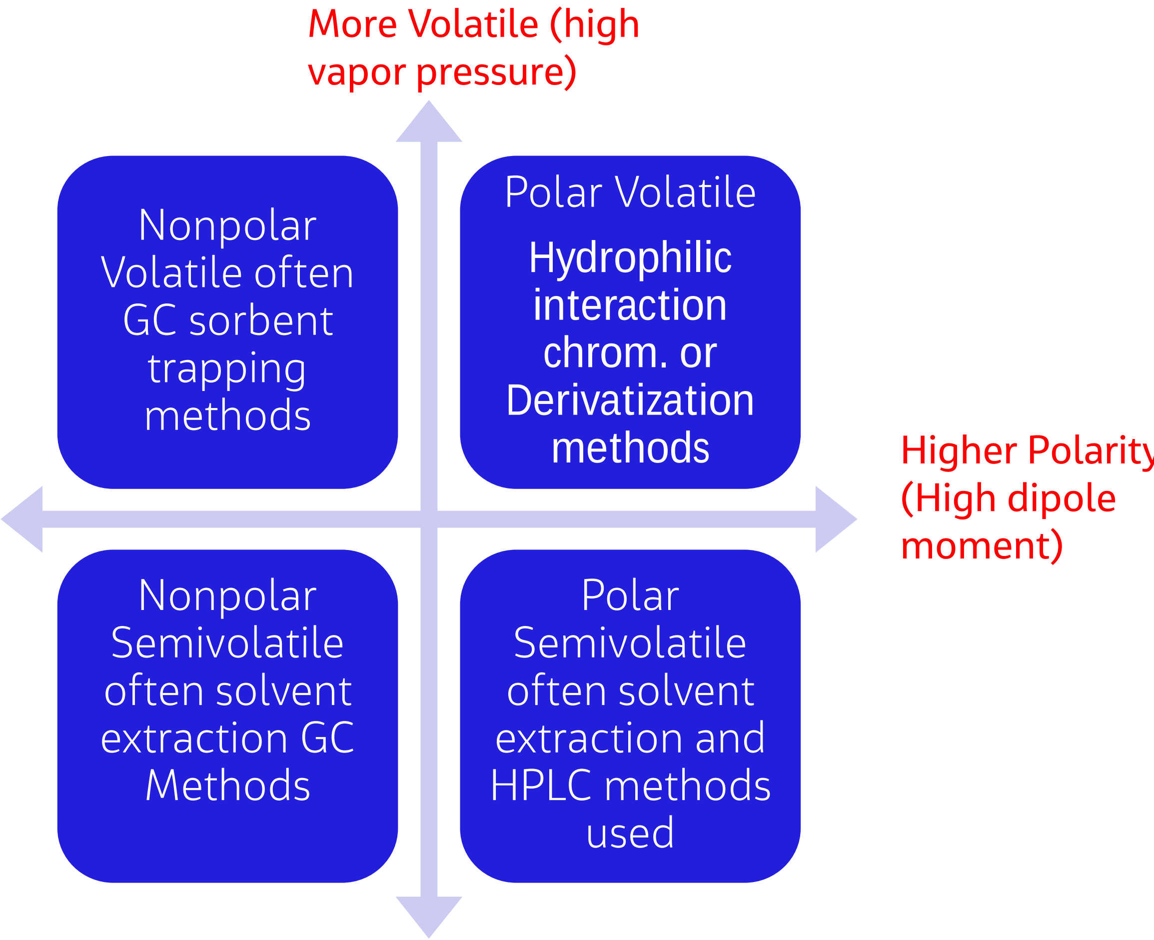
- Titaley, Ivan A., et al. "Neutral per-and polyfluoroalkyl substances, butyl carbitol, and organic corrosion inhibitors in aqueous film-forming foams: Implications for vapor intrusion and the environment." *Environmental Science & Technology* 56, no. 15 (2022): 10785-10797.
- Kapuscinski, Richard B. "Research Needs Regarding the Vapor Intrusion Potential of Volatile Per-and Polyfluoroalkyl Substances." *Environmental Science & Technology* 58.9 (2024): 4056-4059.

Matrices Studied, Challenges and Solutions

Matrix	Challenge	Solutions
Indoor Air (and Outdoor Air)	Need for low detection limits and thus high sample volumes. High sample volume leads to significant humidity/water and nontarget interferences.	Multiple sorbent tube (Camsco PFAS proprietary) tailors binding strength and thus desorption requirements to particular target compounds, manages water.
Soil Gas	Limited feasible sampling flow rate. Near 100% humidity. Temperature difference between soil and sampling area could lead to condensation. Potential interference from other organics.	Thermal desorption delivers maximum amount of sample to instrument. Tandem MS and multiple reaction monitoring (MRM) minimizes interferences. MRM relies on a series of ionization and mass filtering steps optimized for each target compound to minimize or eliminate background noise and matrix interference Recollection of tube allows follow up analysis to adjust loading to instrument.
Sewer Gas	Near 100% humidity. Temperature difference between sewer and sampling area could lead to condensation. Potential interference from other organics, H_2S etc..	

Classification of Air Methods

- EPA VI guide defines volatile as “1) Vapor pressure is greater than 1 millimeter of mercury (mm Hg), or 2) Henry’s law constant (ratio of a chemical’s vapor pressure in air to its solubility in water) is greater than 10^{-5} atmosphere-meter cubed per mole (atm m^3 mol-1).
- Polarity is linked to reactivity and water solubility. Generally polar analytes are more difficult to sample/analyze from air samples and want to stay with moisture.
- Tail of PFAS molecules are nonpolar; head is more polar.



More Volatile (high vapor pressure)

Higher Polarity (High dipole moment)

Nonpolar Volatile often GC sorbent trapping methods

Polar Volatile

Hydrophilic interaction chrom. or Derivatization methods

Nonpolar Semivolatile often solvent extraction GC Methods

Polar Semivolatile often solvent extraction and HPLC methods used

Relationship between polarity, reactivity and solubility from Kelly, Thomas J., et al. "Method development and field measurements for polar volatile organic compounds in ambient air." *Environmental science & technology* 27.6 (1993): 1146-1153. Figure concept after Wallace, 2023; Per- and Polyfluorinated Alkyl Substances (PFAS) Detected in Source Samples Using Thermal Desorption-Gas Chromatography/Mass Spectrometry

Establishing Target Concentration Range

- Inhalation risk based screening values do not exist for most PFAS compounds yet.
- Ambient air background concentrations and indoor air concentrations at background houses taken as a jumping off point.
- Conservative attenuation factor of 0.03 assumed

Compound	Max Global Remote Vapor background, (pg/m^3)	Indoor Vapor background, typical (pg/m^3)	Desired Soil Gas or Sewer Gas Reporting Limit (ng/m^3)
N-Methyl perfluorooctane sulfonamide (MeFOSA)	0.6	65	2
N-Ethyl perfluorooctane sulfonamide (EtFOSA)	0.9	40	1.3
6:2 Fluorotelomer alcohol (6:2 FTOH)	12	2440	81
8:2 Fluorotelomer alcohol (8:2 FTOH)	286	3790	126
10:2 Fluorotelomer alcohol (10:2 FTOH)	153	1420	47
Perflourooctanoioc acid (PFOA)	1	113	3.7

Shoeib et al. 2011. Indoor Sources of Poly- and Perfluorinated Compounds (PFCS) in Vancouver, Canada: Implications for Human Exposure. ES&T. 45:7999-8005.

Method Development Steps Completed

1. Determine target retention time, spectra
2. Establish parent and product ions (using MRM)
3. Generate initial calibration curve (ICC) to establish linearity (Method Criterion < 30%RSD)   Range 0.1 to 10 ng per tube.
4. Assess desorption efficiency (Method Criterion >95%)
5. Verify accuracy (second source verification) (70-130%)
6. Complete method detection limit study (~0.05 ng)
7. Determine initial demonstration of capability – accuracy and precision based on replicate spikes
8. Confirm storage stability on tubes over 28 days

Thermal Desorption – Two Instrument Designs Tested

- The analytical method was set up using two commercially available TD introduction systems, with different secondary trap design used to focus the thermally desorbed compounds:
- Gerstel TD 3.5+ system with a cryogenically cooled trap with quartz wool and forward flush of compounds to the GC column, which is a non-selective approach useful for method development.
- Markes TD100-xr system configured with a back flush multi-bed sorbent trap in which the sample is focused in one direction and desorbed and injected onto the GC in the opposite direction to allow for sample split and re-collection for re-analysis.
- Initial calibration, desorption efficiency, second source verification, initial demonstration of capability, and method detection limit studies were conducted using both systems

Images Gerstel (top) Markes (bottom)

reprinted from https://gerstel.com/en/td-35 and https://markes.com/thermal-desorption-instrumentation/sorbent-tube/td100-xr

Linearity and Sensitivity

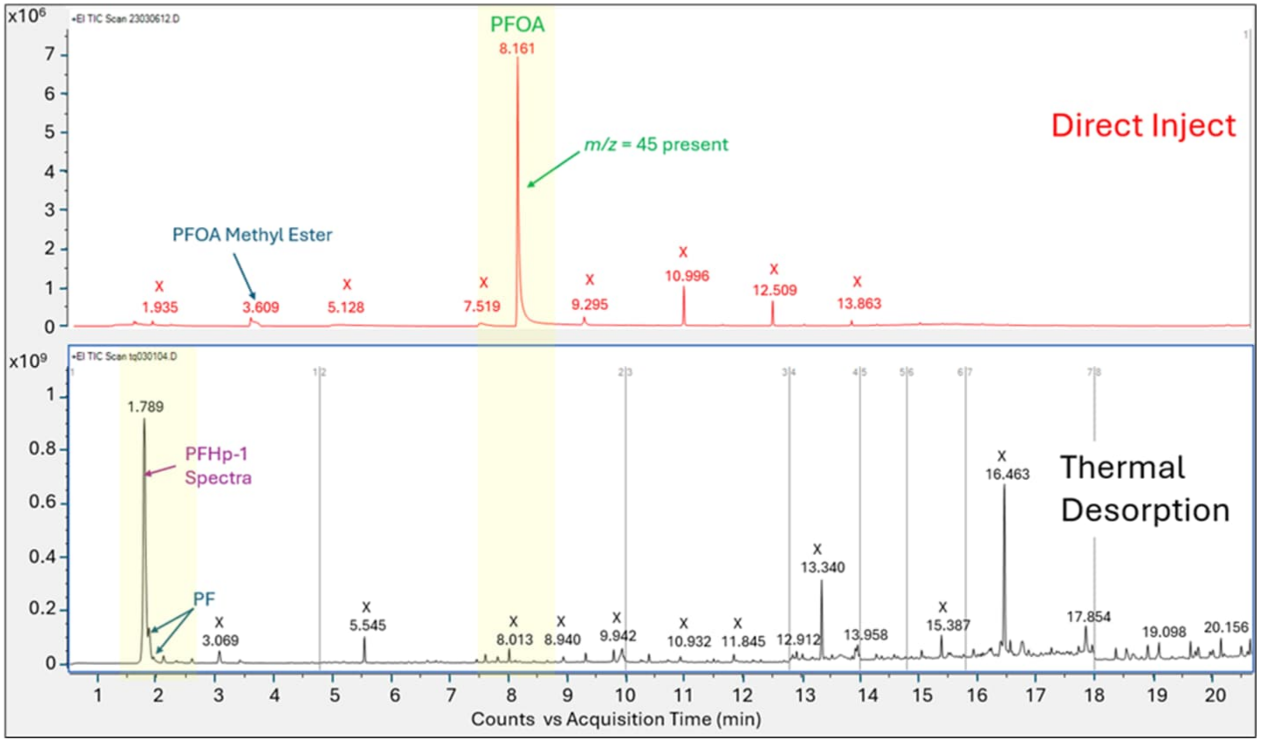
Analyte	Gerstel 3.5+			Markes TD100-xr		
	Linearity (%RSD)	Method Detection Limit (ng)	Indoor MDL, 288 liter sample (pg/m^3)	Linearity (%RSD)	Method Detection Limit (ng)	Indoor MDL 288 liter sample (pg/m^3)
4:2 FTOH	8.2	0.029	100	5.3	0.011	38
5:2s FTOH	13	0.045	160	5.9	0.028	97
6:2 FTOH	6.4	0.047	160	9.2	0.12	416
7:2s FTOH	6.7	0.045	160	6.1	0.022	76
8:2 FTOH	13	0.032	110	8.9	0.051	180
10:2 FTOH	13	0.062	210	5.4	0.027	94
12:2 FTOH	13	0.041	140	3.8	0.030	100
n-MeFOSA	10	NA	NA	12	0.043	150
n-EtFOSA	12	NA	NA	12	0.035	121

Key Point: MDL below indoor background for FTOHs, somewhat above background for FOSAs

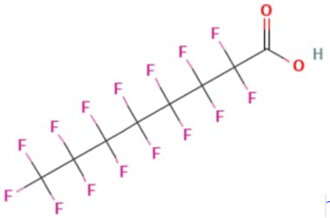
Can This Method Be Used for Acids (PFCAs?)

- Several manufactures/authors have suggested TD-GC MS works for PFCAs
- For the five PFCA tested, TO-17 calibration criteria can be met for TD-GC/MS/MS, but evidence suggested that the thermal desorption introduction step may cause inadvertent breakdown of these compounds.
- Perfluorooctanoic acid met TO-17 calibration requirements when calibrated using NIST traceable standard solutions introduced through the thermal desorption system followed by analysis using GC/MS/MS.
- Subsequent detailed studies comparing direct injection of PFOA standards into the GC inlet to PFOA standards thermally desorbed from a multi-bed sorbent tube suggested that PFOA was breaking down during the thermal desorption step.
- The primary peak resulting from the thermal desorption of PFOA standard loaded onto the multi-bed sorbent tube exhibited spectra consistent with perfluoro-1-heptene (PFHp-1). Therefore, the identification of the PFCA compounds in this method is currently subject to a potential positive interference from the corresponding perfluoroalkene and potentially other thermally labile PFAS that may generate products with common spectra and retention time.
- Alternate approaches using either a solvent extraction method for the PFCAs or an alternate thermally desorbed sorbent system should be explored.

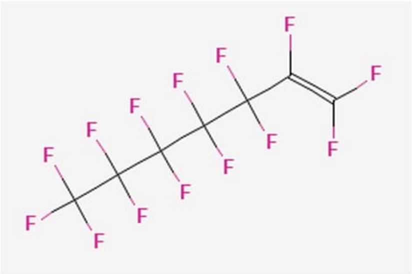
Degradation of PFOA in Thermal Desorption



- Total Ion Chromatograms for PFOA Analysis on HP-5MS Column with Direct Injection (top panel) vs. Thermal Desorption (bottom panel)
- Area counts on Y axis, and retention time in minutes on the x axis
- X = Non-Perfluorinated compound;
- PF = Perfluorinated compound, identified structures labeled
- m/z 45 ($COOH^+$) is diagnostic for the acid



Perfluorooctanoic acid (PFOA)



Perfluoro-1-heptene (PFHp-1)

Structure diagrams https://pubchem.ncbi.nlm.nih.gov/compound/9554
https://pubchem.ncbi.nlm.nih.gov/compound/67737#section=2D-Structure

Performance Test Matrix

Matrix	Description	Temperature (T)	% Relative Humidity (% RH)	Flow Rate (F) and Volume (V)
Indoor air	Office air at lab facility; with and without target analyte spikes < 5 ng per tube	20–25°C	30–50%	F = 50 to 200 ml/min V = 72 to 288 L
		20–25°C	> 65%	F = 50 ml/min V = 72 L
Soil gas	Humidified zero air prepared in a canister; with target analyte spikes in the 50–300 ng range	T_1 = inlet gas and tube at room temp (20–25°C)	≥ 80% RH	F = 200 ml/min V = 1.0 L
		T_2 = tube cooled to < 10°C to simulate winter sampling from soil gas	> 80%RH	F = 200 ml/min V = 1.0 L
Sewer gas	Field sewer gas collected local to the lab; with and without target analyte spikes in the 50–300 ng range	20–25°C	> 50%RH	F = 200 ml/min V = 1.0 L

Office Indoor Air Test Setup

Office Air Performance Test

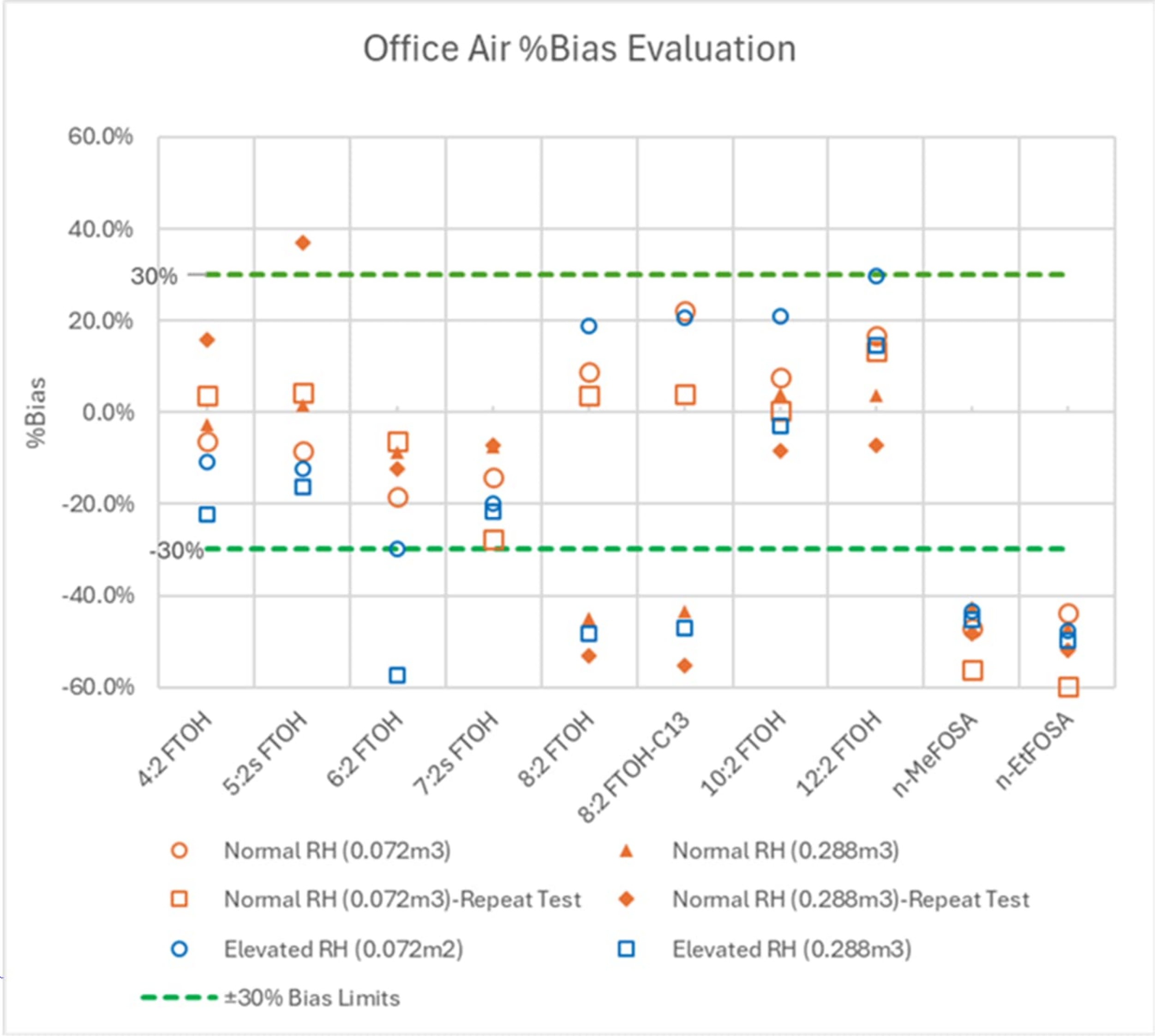
Percent bias for two humidity conditions and two volumes calculated vs. tube spiked at the same time but not sampled.

Good precision for all analytes

Several analytes exceeded the +/- 30% bias criteria

n- MeFOSA and n-EtFOSA %bias exceeding -30% regardless of the sample volume or the humidity condition. Isotopically labeled FOSA standard should be considered for future studies.

8:2 FTOH bias exceeds -30% at high at elevated volumes and humidities.

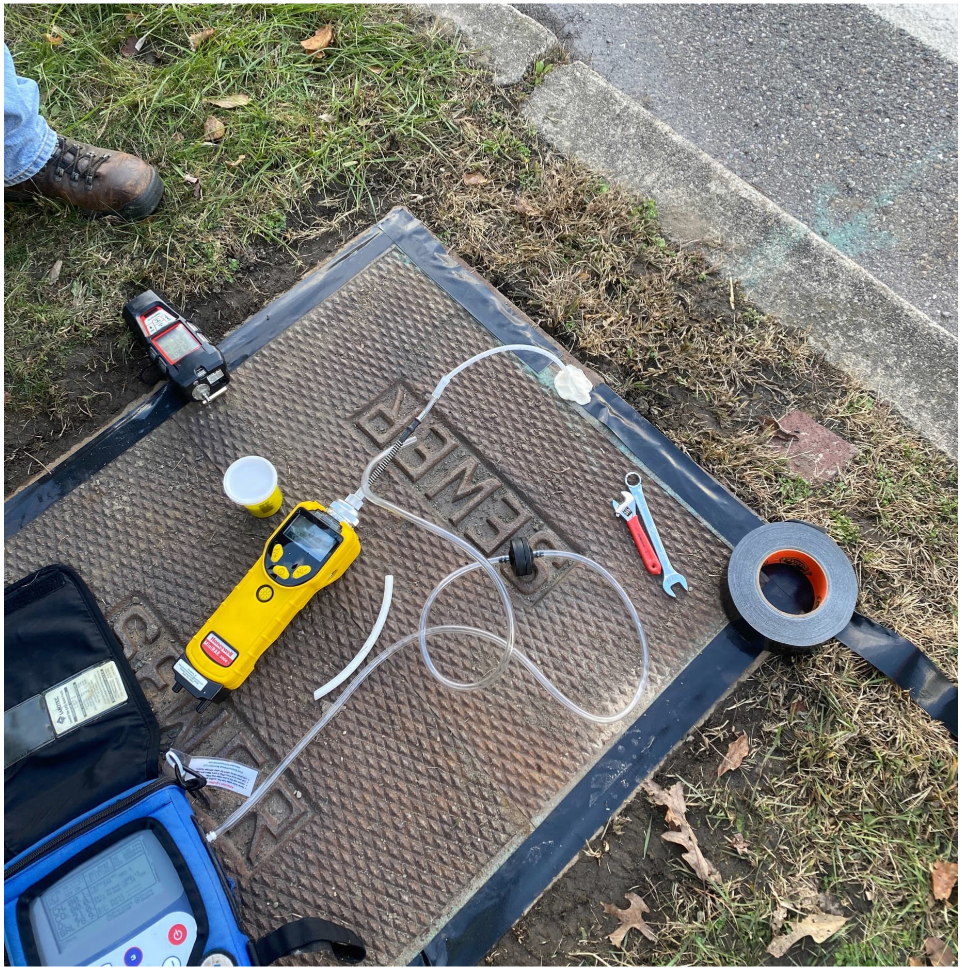


Soil Gas Results

- 1-liter volumes of soil gas perform well if the soil gas and sampling train temperatures are the same.
- Very low recoveries when there was a temperature difference (sample temperature less than soil gas temperature) and an extended sample storage time before the internal standards were spiked.
- This result was not replicated when the internal standard spiking and sample analysis was performed promptly after the simulated soil gas sampling.
- Previous tests without moisture have shown stability for long holding times for dry samples. Long term storage of samples with condensed water at ambient temperature may be the cause of low recoveries.
- Potential remedies: 1) avoiding collecting soil gas samples when the ambient temperature was significantly below the soil gas temperature OR 2)implementing more aggressive steps to remove water through dry purging prior to extended storage
- Potential condensation of water onto tubes during collection can negatively impact subsequent performance of tubes even after standard reconditioning protocols

Sewer Gas Results

- The two trial locations did not provide the high levels of background H_2S, ammonia, and methane typically associated with worst case sewer gas
- Acceptable recovery performance and precision for the fluorotelomer alcohols from 6:2 FTOH to 12:2 FTOH.
- Lower recoveries were observed for 4:2 FTOH and 5:2s FTOH. Poor precision was noted for n-MeFOSA and n-EtFOSA.



Conclusions

- TD-GC/MS/MS method exhibits good linearity, sensitivity, and sample stability for seven FTOH compounds for which at least one known standard is available, and FOSA compounds.
- Three additional FTOH compounds were incorporated based on retention time and structural similarities.
- Method evaluation was successfully conducted on two different manufacturer's instruments.
- Method generally performs with greater accuracy and precision for the FTOH compounds than the FOSA compounds.
- Method was easy to use in multiple field deployments.

Photo credit: Jacobs, NJ site, approved for release

Copyright notice

Important

Jacobs

Challenging today.
Reinventing tomorrow.

Compound	Vapor Pressure (mmHg)	Henry's Law Constant atm m^3 mol-1	Acid Dissociation Constant pKa
EPA definition of volatile	>1	>1E-5	Lower pKa = stronger acid
Trichlorethylene	60	9E-3	Not expected to be acidic
Chloroform	197	3.7E-3	Not expected to be acidic
1,3-Dibromopropane	1.36	8.8E-4	Not expected to be acidic
Naphthalene	0.05	4.4E-4	Not expected to be acidic
Formaldehyde	3980	3.3E-7	13.3
Benzo(a)pyrene	5.5E-9	4.5E-7	Not expected to be acidic

Validation Performance for PFCAs by TD-GC/MS/MS (Markes System)

Analyte	Linearity (%RSD)	Method Detection Limit (ng)	Initial Demonstration of Capability	
			Average Recovery	%RSD
PFBA	16	0.11	87%	7.2%
PFPeA	2.2	0.027	101%	3.4%
PFHxA	2.3	0.019	106%	3.5%
PFHpA	2.9	0.021	101%	5.4%
PFOA	11	0.049	95%	4.4%

Ambient Air, Remote Oceanic Sources

- Lai et al. 2016. Neutral polyfluoroalkyl substances in the atmosphere over the northern South China Sea. *Environmental Pollution*. 214: 449-455.
- Wang et al. 2015. Neutral Poly/Per-Fluoroalkyl Substances in Air from the Atlantic to the Southern Ocean and in Antarctic Snow. ES&T. 49: 7770-7775.
- Cai et al. 2012. Polyfluorinated compounds in the atmosphere along a cruise pathway from the Japan Sea to the Arctic Ocean. Chemosphere. 87 (9): 989-997.