

The PFAS Crystal Ball: An Update

A New Administration, a New Vision for the Future of PFAS



Speakers



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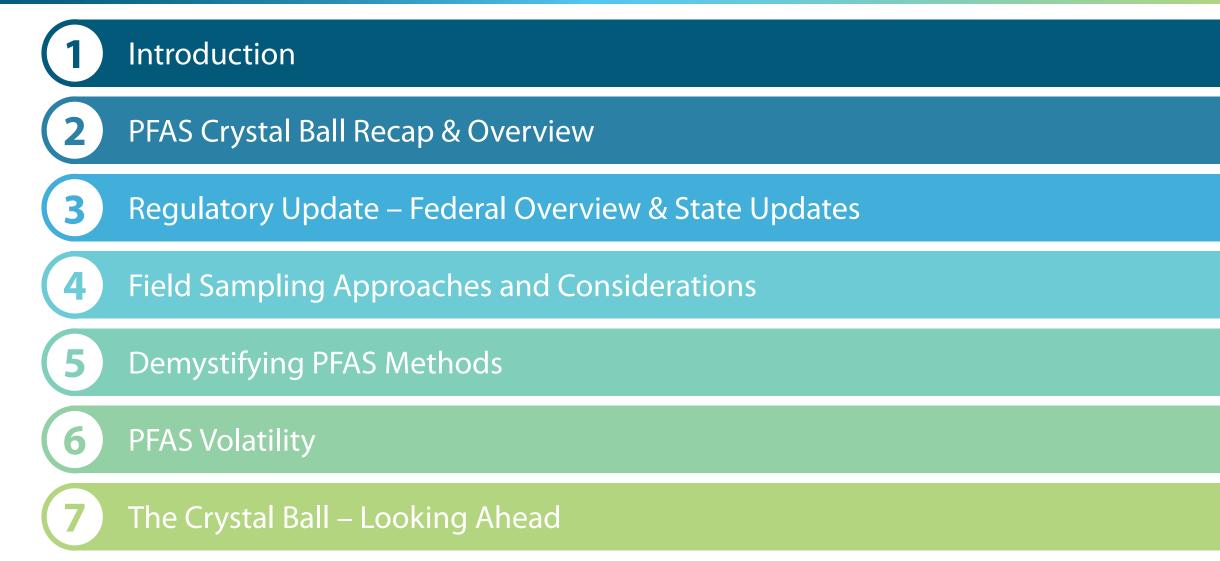
Julia Roth Featured Speaker Air Services Portfolio Lead



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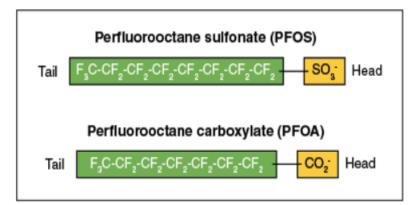


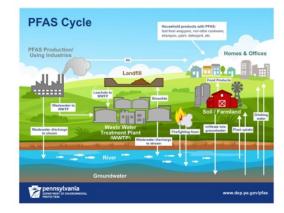






- PFAS—industry term for Per- and Polyfluoroalkyl substances.
- 6,000 man-made compounds engineered to resist heat, oil, staining, grease & water.
- Perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic (PFOS) acid—most common.
- Widely used due to their unique surface tension/leveling properties
- Persistent in the environment & tend to bioaccumulate ("forever chemicals")
- Technology developed in the 1940s—production reached its peak in the 80s.
- First PFAS Health Advisory issued by Minnesota DOH in 2002





Common PFAS hiding places:

- Metal plating/metal finishers
- Textile and leather processors
- Carpet manufacturing
- Paper mills
- Wire manufacturers
- Surfactants use in industrial processes
- Airport
- Military facilities
- Bulk fuel terminals & refineries
- Class B Fluorine-Containing Firefighting Foams
- Waste disposal facilities
- Wastewater treatment plants



Source: ITRC

EPA Regulations Forecast – What Apex Said Last October



- MCLs for PFOA and PFOS, potentially others
- Listing PFOA and PFOS as hazardous substances under CERCLA/RCRA
- Industrial discharge regulation water, air, sludges
- Monitoring and regulating PFAS manufacturing, importation, releases
- Additional ongoing research will drive future requirements
- Enforcement, remediation cost recovery

Regulatory Update



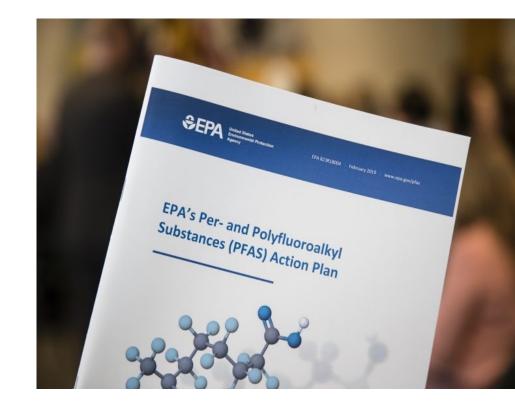
EPA Update

Interim Guidance Document Published December 2020

- Public comment period through February 2021
- Offers options for treatment and disposal & reiterates common PFAS sources

Press Release Issued February 22, 2021

- Reproposing the Fifth Unregulated Contaminant Monitoring Rule (UCMR 5) to collect new data on PFAS in drinking water and reissuing final regulatory determinations for perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) under the Safe Drinking Water Act (SDWA).
- With final regulatory determinations, EPA will move forward to implement the national primary drinking water regulation development process for these two PFAS.





EPA Update

Updated Toxicity Assessment for PFBS – April 2021

- Key goal of the EPA's PFAS Action Plan.
- EPA, states, local governments and tribal communities may use this toxicity assessment to determine whether to take action on PFBS to address human health risks in their communities.
- PFBS was used as a replacement chemical for PFOS, which was phased out of US manufacturing by 2002. PFBS has been identified in many products as well as in the environment across the US.

New "EPA Council on PFAS" – April 27, 2021

- Develop "PFAS 2021-2025 Safeguarding America's Waters, Air and Land," a multi-year strategy to deliver critical public health protections to the American public.
- Work with various state and local agencies to address technical challenges, funding and ensure a consistent approach to communication and remediation.

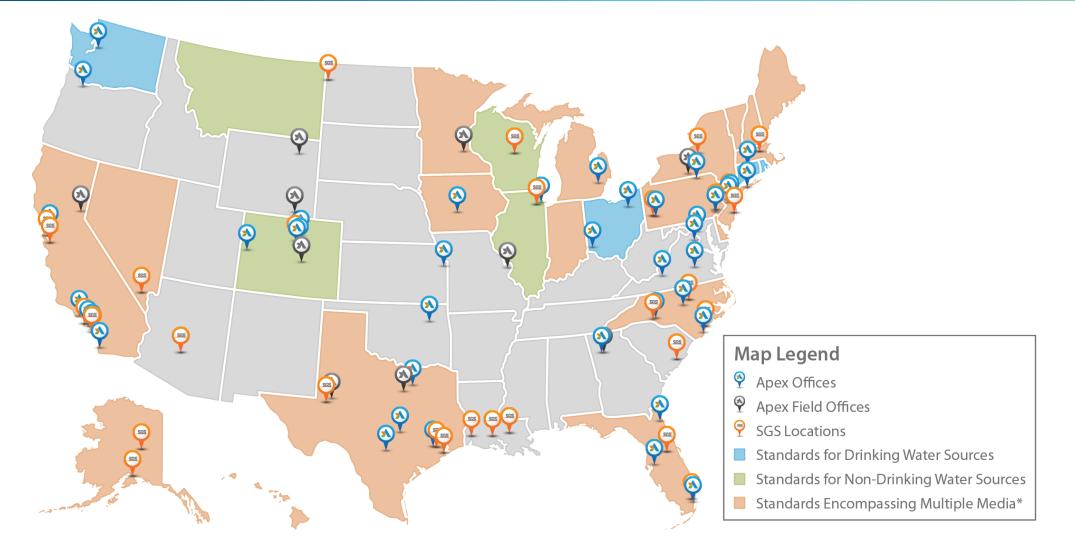
EPA Drinking Water Treatability Database – May 2021

• Added references and treatment options for 11 PFAS (bringing total # to 37 in the database).





PFAS Screening Criteria Nationwide At-a-Glance



Federal – USEPA – Drinking Water: Health Advisory Level for PFOS and PFOA = 70 ppt; Interim Recommendation Screening Levels for PFOA and PFOS = 40 ppt Federal – USEPA – Soil: Regional Screening Levels for Residential, Industrial, and Protection of Groundwater

* Multiple media to include drinking water, non-drinking water (groundwater/surface water), and soil/sediment.

Note: States referenced in the Map Legend have formal standards, proposed standards, and/or guidance screening values.



California Update

Targeted Industries

- Airports Order WQ 2019-0005-DWQ
- Landfills Order WQ 2019-006-DWQ
- **Chrome Platers** Order WQ 2019-0045-DWQ
- Publicly Owned Treatment Works (POTWs) Order WQ 2020-0015-DWQ
- **Bulk Refineries** Issued March 2021 Order WQ 2021-0006-DWQ; as of May 2021, 90-day extension applied

Submit a Work Plan

- Conduct an investigation based on an approved work plan
- Submit final results to the Water Board
- Respond to questionnaire

https://geotracker.waterboards.ca.gov/map/pfas_map

Operator/Principal Name			
Name of Facility			
Address of Landfill			
City	County	Zip	
Phone number	Email Address		
PER- AND POLY-FLUOR	DALKYL SUBSTANCES (PFAS) - CONSTITUENT SC	REEN	ING
concerning the presence and/or groundwater?	ata or information produced by your facility of PFAS in soil, soil-gas, storm water, leachate, v attachment and include method of analysis, a	YES	NC
	cal results, as well as the laboratory analytical		
2. Has any waste generator supplied data or information that you possess concerning the presence of PFAS in off-site generated waste at your facility?			NC
If yes, please describe by	y attachment.		
3. Do you possess any data or information that was produced by your facility concerning the presence of PFAS in off-site generated waste at your facility?			NC
If yes, please describe by	/ attachment.		
discharge, spill, release already conducted sam	ed to be completed if your facility did not acce a in any way, or dispose PFAS materials or you pling for PFAS materials. This form and supp e uploaded to GeoTracker by the date specified	i have orting	
and all attachments we the information submitte	, certify under penalty of law that this re prepared by me, or under my direction or super ed is, to the best of my knowledge and belief, true, are that there are significant civil penalties for subr	vision, , accur	, and rate,
Signature: Title: Date:			



FDEP = Currently has set provisional Clean Up Target Levels (CTLs)

	Residential	Commercial/Industrial	Leachability
PFOA	1.3 mg/kg	25 mg/kg	0.002 mg/kg
PFOS	1.3 mg/kg	25 mg/kg	0.007 mg/kg

- Groundwater at Federal MCL of 70 ppt; provisional surface water and irrigation water screening levels
- FDEP PFAS Dynamic Plan, February 2021
 - Objectives include FDEP national leader with respect to PFAS concerns; implement response strategy that minimizes risks to human health and natural resources
 - Plan to develop GIS database layer to identify locations of PFAS investigations and areas of known groundwater contamination
 - FDEP will provide WMDs areas with groundwater CTL exceedances, for use during well construction permitting
 - Investigation of PFAS sources: Solid waste facilities (C&D, untreated MSW leachate); textile, wiring & plating manufacture; paper mills



PFAS at Dry Cleaning Sites

- Looked at 15 sites in FL; 10 had elevated levels of PFAS
- Waste stream sampling indicated that dry cleaning and wet laundering processes cause leaching of PFAS from fabrics

FDEP Technical Developments

Investigate PFAS impacts to air quality and landfill leachate

Proposed Legislation

- Fund a study by FDEP to determine parameters and costs for a state cleanup program
- Closure of large areas with multiple properties using non-recorded Institutional Controls (ICs)
- Closure mechanisms:
 - Municipal ordinances that require connection to municipal water
 - GIS layer through WMD consumptive water use permitting
 - Modify statutes to include delineated areas (previously done for EDB)
 - Noticing



Notables

State	Date	Action	
Massachusetts	October 2, 2020	Formally adopted the proposed MCLs	
Wisconsin	November 2020	Published recommended groundwater standards for PFAS. Included several compounds other states have not yet considered	
Michigan	December 2020	Updated their PFAS cleanup standards for drinking water.	
Hawaii	December 2020	Published Environmental Action Levels for soil and groundwater, list of 18 PFAS	
Mississippi	December 2020	State lawsuit filed against major PFAS manufacturers	
New Jersey	January 2021	State lawsuit filed against the federal government, for PFAS at military bases polluting drinking water sources.	
NewYork	January 2021	Published a revised sampling and assessment plan for PFAS	
New York	February 2021	Published an ambient air annual guideline concentration for PFOA, 0.0053 μ g/m3	
New Mexico	February 2021	Petitioned US Court of Appeals to advance PFAS litigation against US DoD	
Alaska	April 2021	State lawsuit filed against over 30 companies	
Minnesota	Spring 2021	Expected to finalize drinking water sampling plan related to 3M settlement	
Connecticut	April 2021	Launched an AFFF take-back program	
Pennsylvania	May 2021	Delaware County lawsuit filed against over 20 PFAS manufacturers	
Vermont	May 2021	New law restricting the use, manufacture, and sale of products containing PFAS	
Indiana	Spring/Summer 2021	Starting drinking water sampling program in 3 phases	
Illinois	2022 Results Expected	Currently sampling all 1,749 community drinking water supplies. Accepting public comment on draft groundwater quality standards for 5 PFAS.	











Wet Laundry/ Dry Cleaners

Car Washes

Janitorial Supplies

Septic Systems



4 Field Sampling Approaches and Considerations

APEX

Site Investigation – Sampling Techniques

- Extensive requirements, avoid anything that contains PFAS
- EPA approved labs
- Sampling equipment must be PFAS-free.
- Decontamination and blank water—obtain certified PFAS-free from laboratory
- Use HDPE and silicone materials, nitriles, Alconox or Liquinox, and laboratory-supplied PFAS-free materials
- Use cotton textiles, laundered at least 6 times, not with fabric softener



Sources of Potential Sampling/Analytical Bias

- A 2020 study indicated that field sampling materials are unlikely sources of cross contamination in field samples, mainly because a good sampler isn't putting notes, ice packs, markers, etc. in the sample bottles; there's not meaningful direct contact with samples and the field materials. <u>https://pubs.acs.org/doi/pdf/10.1021/acs.estlett.0c00036</u>
- Storage and analysis concerns due to stratification, filtration, sorption to containers (negative bias; research is ongoing)
 - Air-water interface (currently being studied—affects how we should sample surface water, groundwater, sample bottles, autosampler vials).
 - There are weak van der Waal forces in PFAS which partitions them out of water to the interfaces.
 - This results in bias especially when sampling surface water and groundwater, during sample storage, and also possibly during the analysis.



PFAS Background levels

• Atmospheric Deposition

Forensics

- Site history review
- Manufacturing processes—electrochemical fluorination (ECF) and fluorotelemerization provide different PFAS signatures
- Extended PFAS list to review for various PFAS signatures
 - Examples: Legacy ECF signatures are high in PFOS, PFHxS; fluorotelomer foams have short chain carboxylate pattern, 6:2 FTS, 8:2 FTS
- Indicator Compounds
- Linear vs. Branched speciation for select PFAS
 - Tells you whether ECF foam was used
- TOP Assay
 - Can provide info on possible sources



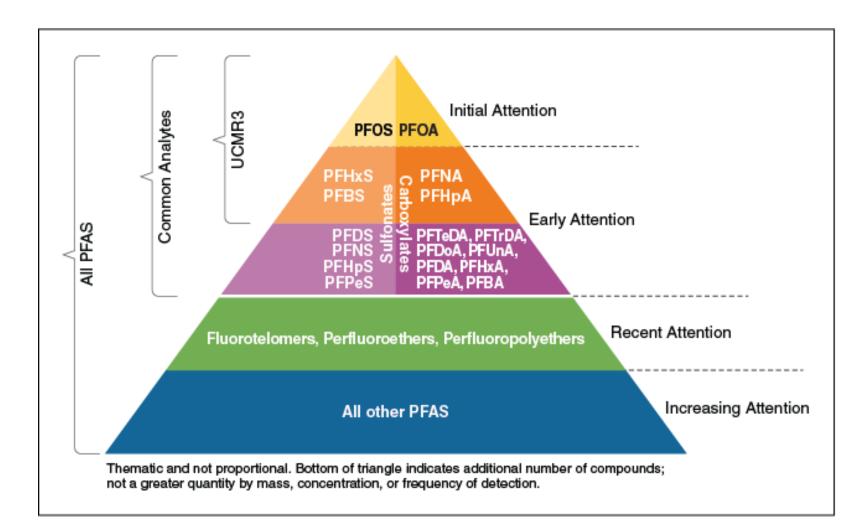


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North American PFAS Attention



Source: ITRC: 2.3 Emerging Health and Environmental Concerns – PFAS — Per- and Polyfluoroalkyl Substances (itrcweb.org)

- Targeted analysis has grown from 1-2 PFAS to 40+
- Occurrence and trend information are way ahead of toxicology and regulation
- Expect increasing use of non-target high resolution discovery work to exacerbate this difference



*15+ years of PFAS experience, lessons learned, mistakes and a whole PFAS methods course fit in one slide

Extraction

- Spike with isotopically labeled standards
- Solids:, Sequential basic methanol* extraction
- Aqueous: whole water pH Adjustment
- Tissue: Sequential/extended basic extraction

Cleanup

- Weak Anion Exchange
- Carbon

LC-MS/MS Analysis with Isotope Dilution/Surrogate Standard Quantitation

- Transition ratios
- Branched/linear quantitation



PFAS Targets Currently Supported at SGS

Analyte Groups

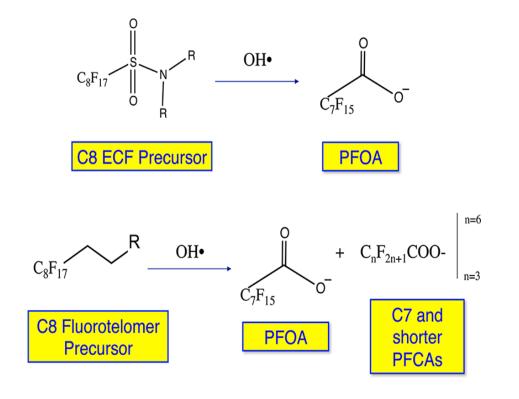
- Perfluoroalkyl carboxylates (C_4 - C_{14} , C_{16} , C_{18})
- Perfluoroalkyl sulfonates (C₄-C₁₀, C₁₂)
- Fluorotelomer sulfonates (4:2, 6:2, 8:2 and 10:2)
- Fluorotelomer carboxylates (3:3, 5:3 and 7:3)
- Perfluorooctane sulfonamides (FOSA, MeFOSA and EtFOSA)
- Perfluorooctane sulfonamidoacetic acids (MeFOSAA and EtFOSAA)
- Perfluorooctane sulfonamide ethanols (MeFOSE and EtFOSE)
- Per- and polyfluoroether carboxylates (HFPO-DA, ADONA, PFMBA, PFMPA, NFDHA)

Ether sulfonates (F-53B, PFEESA)

- Reporting limits as low as 0.4 ng/L PFOA/PFOS
- Coverage of all statespecific lists
- **NEW:** Fluorotelomer alcohols in water



TOP: Perfluorinated Potential

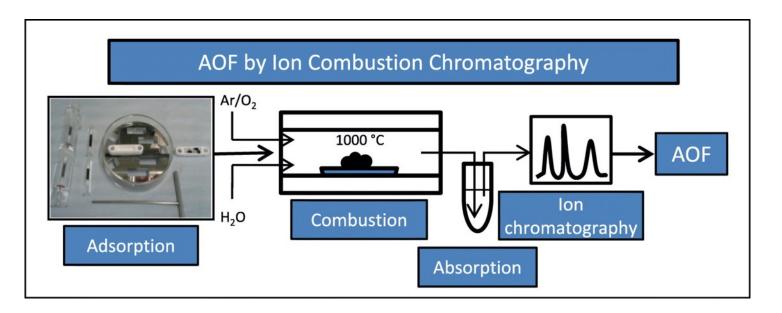


- The total oxidizable precursor assay (TOP) is a technique to transform thousands of potential "precursors" into a small number of terminal acids for easier measurement
- Measure PFCAs/PFSAs in sample before and after to report conversion rates
- Interpretation: TOP is to be considered a lowerbound estimate for certain types of PFAS, and chain length information as well

Houtz & Sedlak, D. L. (2012). Environmental Science & Technology, 46(17), 9342–9349.



Emerging technique for estimating organic fluorine in a sample by combustion ion chromatography.



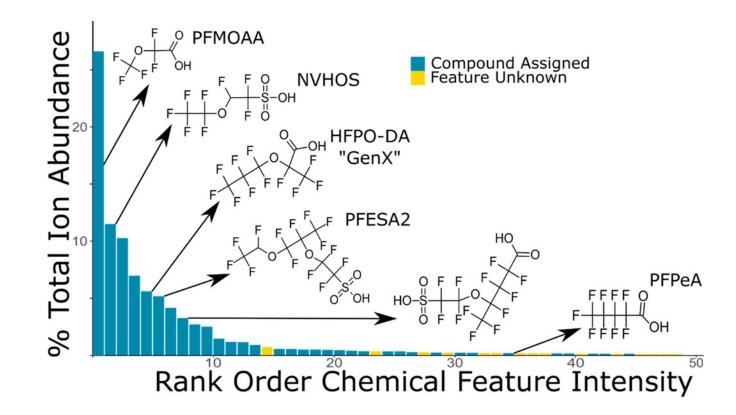
Science of The Total Environment 673, 384–391 (2019).

- Good potential for quickly understanding total fluorine, EPA methods in progress
- Challenges
 - Fluorine background
 - Reporting limits 100-1000 times higher than LC-MS/MS
 - No chain length information



Identification of Per- and Polyfluoroalkyl Substances in the Cape Fear River by High Resolution Mass Spectrometry and Nontargeted Screening

James McCord[†][©] and Mark Strynar^{*,‡}[©]



- The wider availability of mass spectrometers that can scan samples at high-resolution unlocks another tool to understand and characterize unknown PFAS
- Lots of promise and widely available with academic and some government institutions
- Major questions on data workflow, quality and more
- Commercial availability for environmental analysis limited

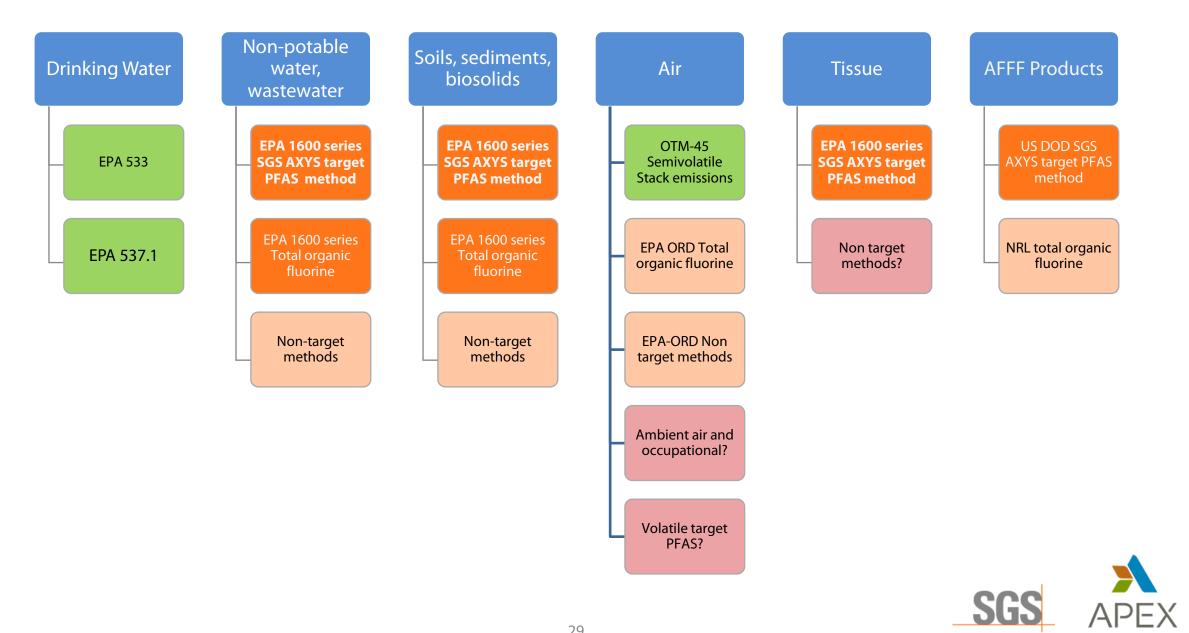


Fingerprinting and Source Tracking Lines of Evidence

Site model and specific plan	
Long list of targets	 Add targets relevant to specific sources Multivariate analysis of patterns HFPO-DA (GenX), FTCAs (landfills), sulfonamides (legacy waterproofing)
Branched characterization	Additional lines of evidence on manufacturing
TOP, TOF, other Total methods	 TOP provides chain length information on precursors TOP patterns point to different sources Organic fluorine by CIC emerging commercially
Non target analysis	 Provides distinct fingerprints Commercial availability limited, data workflows a challenge. Future liability?
Statistical analysis, both exploratory and predictive	



EPA and US Federal Methods Status May 2021



Parting Thoughts on Data Usability



- For any analysis other than prescriptive drinking water analysis by EPA 537.1, insist on isotope dilution analysis
- Pay attention to blank data, have a conversation with the lab about their background levels and cleaning processes before selection
- Pay attention to performance, check the lab's participation in proficiency testing and benchmarking
- While LC-MS/MS analysis is getting a bit easier, people and experience still matter a lot, work with trusted partners
- Lab flags vary, check reports as needed



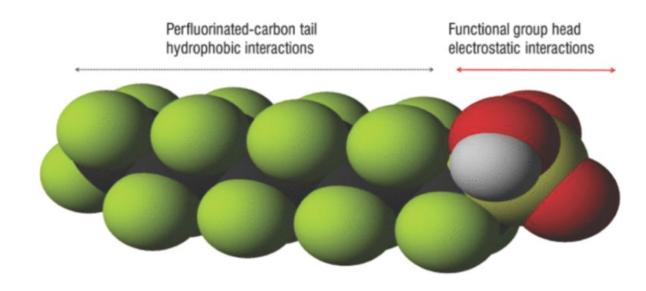


PFAS Volatility Market

- Remediation
 - Emergency Response Sites
 - Firefighter Training Facilities
 - Former Manufacturing Sites
- Emissions
 - Product Manufacturers
 - Incinerator Facilities
 - Landfill Sites
- Occupational Health/Personal Monitoring
 - Wastewater Treatment Facility
 - Firefighter Training area

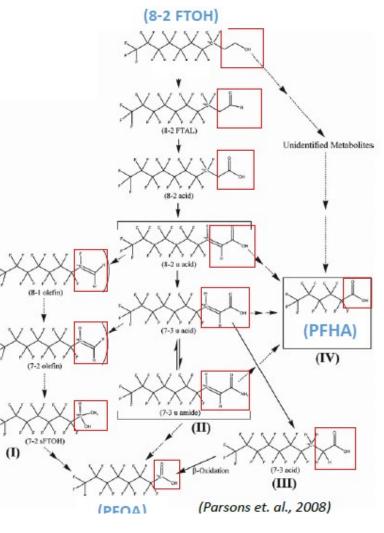


Background



(National Academies of Sciences, Engineering, and Medicine, 2017)

Key Takeaway	The functional group determines volatility.
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Terminology

- PFAS Precursor Subgroup:
 - FASAs: Perfluoroalkyl Sulfonamido Substances
 - **FTOHs**: Fluorotelomer Alcohols
 - FTSs: Fluorotelomer Sulfonic Acids
- PFAS Production Methods:
 - ECF: Electrochemical Fluorination
 - **FT**: Telomerization

	Sub-Type	Individual Chemical Name and Acronym
	Perfluoroalkyl carboxylic acids (PFCAs)	Perfluorobutanoic acid—PFBA
		Perfluoropentanoic acid—PFPeA
		Perfluorohexanoic acid—PFHxA
		Perfluoroheptanoic acid—PFHpA
		Perfluorooctanoic acid—PFOA
		Perfluorononanoic acid—PFNA
		Perfluorodecanoic acid—PFDA
		Perfluoroundecanoic acid—PFUnA
		Perfluorododecanoic acid—PFDoA
Perfluoroalkyl acids (PFAAs)		Perfluorotridecanoic acid—PFTrDA
2		Perfluorohexadecanoic acid—PFHxDA
		Perfluorooctadecanoic acid—PFOcDA
	Perfluoroalkyl sulfonic acids (PFSAs)	Perfluorobutane sulfonic acid—PFBS
		Perfluoropentane sulfonic acid—PFPeS
		Perfluorohexane sulfonic acid—PFHxS
		Perfluoroheptane sulfonic acid—PFHpS
		Perfluorooctane sulfonic acid—PFOS
		Perfluorononane sulfonic acid—PFNS
	Perfluoroalkyl sulfamido substances (FASAs) Precursor to PFSAs	N-Ethyl-perfluorooctane sulfonamido ethanol—N-EtFOSE
Perfluoroalkyl sulfamido		N-Methyl-perfluorooctane sulfonamido ethanol-N-MeFOSE
		N-Ethyl-perfluorooctane sulfonamido acetic acid—N-Et-PFOSA-AcOH
substances (FASAs) Precursor to PFSAs		N-Methyl-perfluorooctane sulfonamido acetic acid-N-Me-PFOSA-AcO
		Perfluorooctane sulfonamide—PFOSA
Fluorotelomer	Fluorotelomer alcohols	6:2 Fluorotelomer alcohol—6:2 FTOH
alcohols (FTOHs) Precursor to PFCAs	(FTOHs) Precursor to PFCAs	8:2 Fluorotelomer alcohol—8:2 FTOH
Fluorotelomer	Fluorotelomer sulfonic	6:2 Fluorotelomer sulfonic acid—6:2 FTS
sulfonic acids (FTSs) Precursor to PFCAs and PFSAs	acids (FTSs) Precursor to PFCAs and PFSAs	8:2 Fluorotelomer sulfonic acid—8:2 FTS

(National Academies of Sciences, Engineering, and Medicine, 2017)



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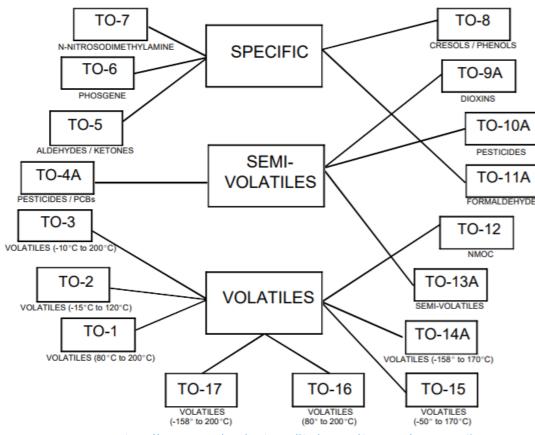
Meets USEPA's 2015 volatility criteria:

- Henry's Law Constant >10⁻⁵ atm*m³/mol
- 2. $P_{vapor} > 1 \text{ mm Hg}$

Substance	Aqueous Solubility (g/L)	P _{vapor} (PA)	Henry's Law Constant (atm m ³ mol ⁻¹)
PFOS (K ⁺)	5.19 E-1	3.31 E-4	3.4 E-9
PFOA (H+)	9.5	7.0 E1	4.6 E-6
PFOA (NH4+)	>5.00 E2	<1.3 E-3/9.2 E-3	<1.1 E-11/7.8 E-11
N-EtFOSE	1.51 E-4	5.4 E-1	1.9 E-2
N-EtFOSEA	8.9 E-4	N.A.	
6:2 FTOH	1.2-1.7 E-2	N.A.	1 E -2
8:2 FTOH	1.40 E-4	2.93	9.6 E-2

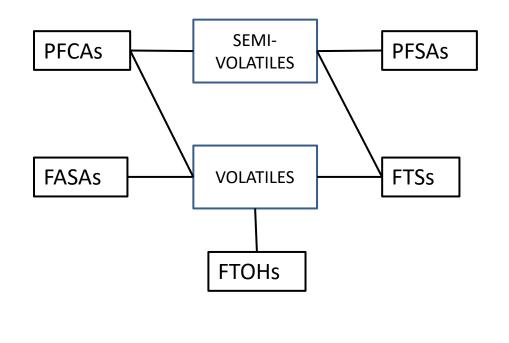
Key Takeaway Most FTOHs and FOSEs/FOSAs are considered volatile. Some theoretical calculations also suggest that some FTSs and PFCAs are volatile.





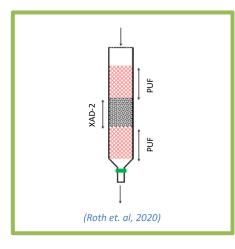
https://www.epa.gov/sites/production/files/2019-11/documents/tocomp99.pdfxt

Key Takeaway With thousands of PFAS compounds, there will likely need to be more than one analytical method to determine volatile and semi-volatile PFAS concentrations in air.



(Roth, 2021)





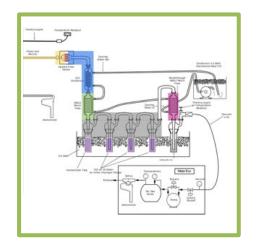


XAD/PUF Sampler

- Similar to TO-13
- 1-4 Days Sample Duration
- Most widely documented

Thermal Desorption

- Similar to TO-17
- 5-30 Minutes
 Sample Duration



OTM-45 Sampler

- Modified Method 5
 - Filter
 - XADs
 - Impingers



Other Methods

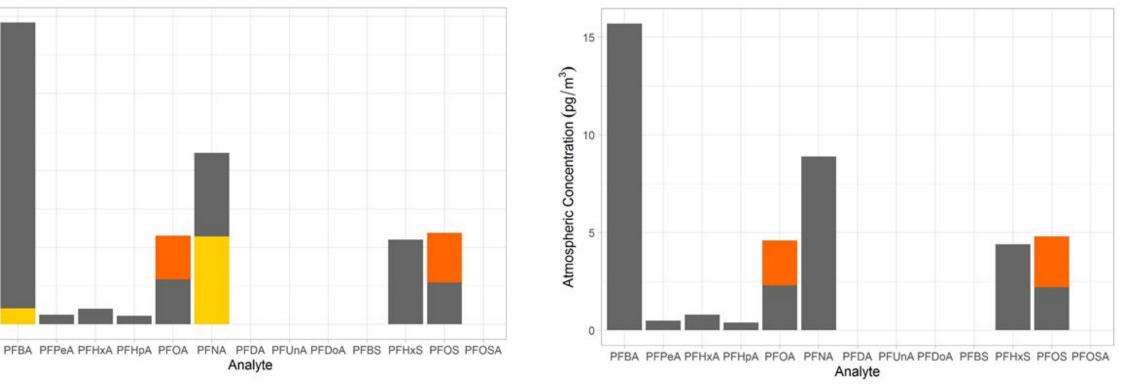
- SUMMA Canisters
- Diffusion denuder sampler
- Passive Sampler



Early Ambient Air Results Around Landfills

Matrix Filter Front PUF-XAD Back PUF

Matrix Particulate Gaseous



Key Takeaway

Reporting capabilities in pg/m³, lower than current air regulations in ng/m³.



https://www.pca.state.mn.us/sites/default/files/c-pfc1-02.pdf

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Concentration (ng/sample)

5

0

7 The Crystal Ball - What to look for?



- Formally promulgated PFAS screening criteria
 - CA, CO, FL, HI, IL, NH, NY, PA
- Investigation and inventorying of potential PFAS sources
 - IA, FL, KS, MA, ME, MD, MT, NC, ND, NH, NJ, NM, NY, OH, OR, PA, RI, SC, TN, VT, WA, WI
- Regulations of food, food packaging, agricultural products, worker exposure, AFFF use, storage, and disposal
 - CT, IA, ME, NC, VT, WA
- Ecological risk screening criteria (e.g. for fish tissue, surface water, sediment)
- Air/emissions monitoring
- Identifying new potential sources of PFAS (e.g. drycleaners, car washes, janitorial supplies, septic systems, etc.)
- July 1, 2021 TRI Reports due, includes 172 PFAS; expect additional guidance and regulation based on these results



Practical Considerations – Real Estate Transactions

- We don't fully know how PFAS plumes behave yet, since there aren't many widescale investigations
- The issue of PFAS is putting buyers and sellers at even more contentious odds with one another—people want to know what is on their site, but there is concern about exposure to malpractice claims and liability issues.
- A lot of buyers are seeking testing if a "source" property is in close proximity to their site
 - Concerns about migration
 - Some buyers are making assumptions when their site is downgradient and just assuming PFAS is there and are structuring their deals accordingly
 - Lenders don't really know what is going on or how this is going to impact their collateral



Changes to the ASTM Standard for Phase I ESAs are likely to change this



Practical Considerations – Litigation and Liability

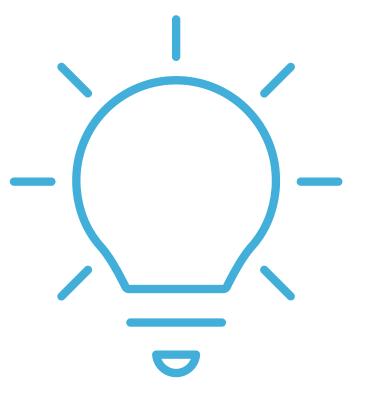
- We are seeing more exclusions for PFAS in the insurance world—most carriers are now excluding it
- There is the question on how will litigation be approached will most suits be carried out in pursuit of property damages, personal injury—or both?
- What about the current stockpiles of AFFF sitting out there in many facilities that can no longer be used?
- Do certain public benefits—i.e., immediate loss of life and property from fire damage—outweigh the issues that are associated with PFAS?
- States will likely look at creating programs similar to current LUST and Drycleaner programs—where certain products are taxed and that tax money is set aside for remedial efforts.





Your Knowledge is Power

- Have your processes used PFAS containing materials?
- Do any of your processes involve surfactants, wetting agents, PFAS containing materials?
- Experienced large fires on-site?
- Discharges or spills?
- What industries previously occupied your property?
- What industries are nearby?
- What are the regulations in your region?







Military Facilities



Metal Plating/Finishers



Airport



Wet Laundry/ **Dry Cleaners**



Bulk Fuel Terminals



Surfactants



Car Washes

Janitorial Supplies

Wire Manufacturer



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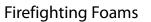
Paper Mills





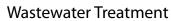
Textile/Leather Processors







Waste Disposal Facilities











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Septic Systems

Is Your Vision Clear? Or, Are You Guessing?

Thank you!

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