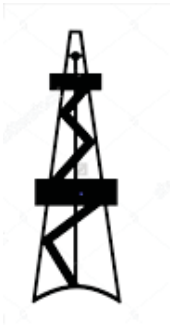
Introduction to Per- and Polyfluoroalkyl Substances (PFAS)

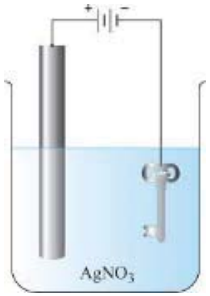
Presentation Outline

1. History and Regulations
   - ✓ What are PFAS? Why should you care?
   - ✓ Regulatory Status
2. Challenges and State of the Practice
   - ✓ Sampling and Analysis
   - ✓ Regulatory Considerations
   - ✓ Analytical Considerations

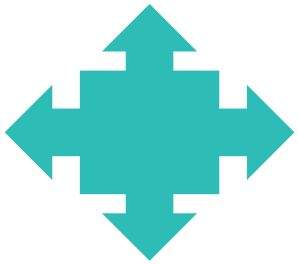
What are PFAS? Sources/Uses



Oil and Gas Extraction

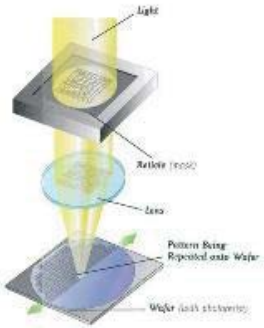


Electroplating
(mist suppressants)



Manufacturing Processes/
Intermediates/ By-products

Consumer Products



Semiconductor
Industry

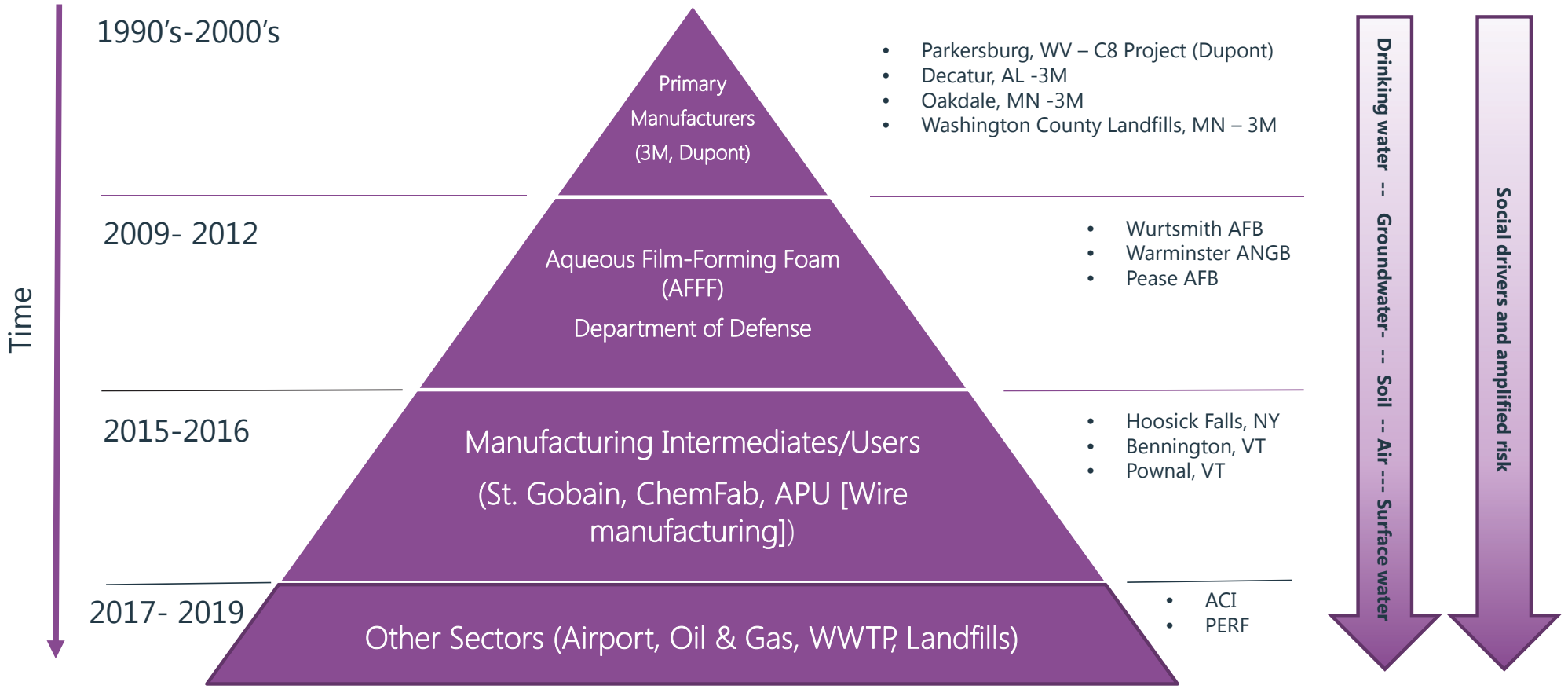
Aqueous film forming
foams

How are PFAS different? Characteristics

Chemical Properties	PCB (Arochlor 1260)	PFOA	PFOS	TCE	Benzene
Molecular Weight	357.7	414.07	538	131.5	78.11
Solubility	0.0027 mg/L @24°C	3400–9500 mg/L @25°C	519 mg/L @20°C	1100 mg/L @ 20°C	1780 mg/L @20°C
Vapor Pressure (25°C)	4.05×10^{-5} mmHg	0.5-10 mmHg	2.48×10^{-6} mmHg	77.5 mmHg	97 mmHg
Henry's Constant	4.6×10^{-3} atm-m^3/mol	0.0908 atm-m^3/mol	3.05×10^{-6} atm-m^3/mol	0.0103 atm-m^3/mol	0.0056 atm-m^3/mol
Organic Carbon Part. Coeff. (Log K_{oc})	4.8-6.8	2.06	2.57	2.42	2.15

- High solubility, low volatility in water
- High detection frequency in soil and sediment

A Moving Target; Why the Concern?



Where are we now? Regulatory Criteria (µg/l)

Federal		PFOA	PFOS
USEPA	DW	0.07	0.07
USEPA	GW	0.4	0.4
US States			
Alabama (AL)	DW	0.07	0.07
Alaska (AK)	GW	0.40	0.40
Arizona (AZ)	DW	0.07	0.07
California (CA)	DW	0.014	0.013
Colorado (CO)	DW	0.07	0.07
	GW	0.07	0.07
Connecticut (CT)	DW/GW	0.07	0.07
Delaware (DE)	GW	0.07	0.07
Iowa (IA)	GW	0.07	0.07
Maine (ME)	DW	0.07	0.07
	GW	0.13	0.56
	RW	0.05	1.2
Massachusetts (MA)	DW	0.07	0.07
Michigan (MI)	SW	0.42	0.011
	DW/GW	0.07	0.07
Minnesota (MN)	DW/GW	0.035	0.027
Nevada (NV)	DW	0.667	0.667
New Hampshire (NH)	GW	0.07	0.07
New Jersey (NJ)	DW	0.014	0.013
North Carolina (NC)	GW	2	NA
Oregon (OR)	SW	24	300
Pennsylvania (PA)	GW	0.07	0.07
Rhode Island	DW/GW	0.07	0.07
Texas (TX)	GW	0.29	0.56
Vermont (VT)	DW/GW	0.02	0.02
West Virginia (WV)	DW	0.07	0.07

NOTABLES

- ✓ 22 States with some form of water criteria, over 70% in the last 2 years
- ✓ Over half of the states have adopted EPA Lifetime Health Advisories
- ✓ NJ (and now CA) with lowest criteria for PFOS and PFOA
- ✓ Promulgated rule in a dozen states
- ✓ Ten states have adopted criteria for other PFAS
- ✓ Trend to add PFAS analytes together and compare to criteria
- ✓ Globally, nearly a dozen countries with criteria

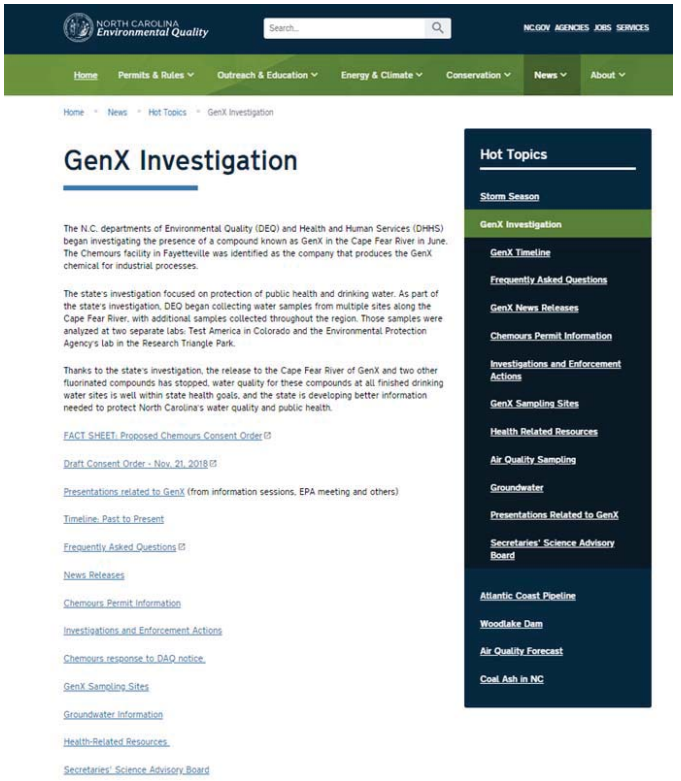
NOTES

DW= drinking water
GW= groundwater
RW= recreational water
SW= surface water

ITRC, 2018. PFAS Fact sheets.
https://pfas-1.itrcweb.org/fact-sheets/

North Carolina – More than just GenX

- ✓ "GenX" is trade name for processing aid technology, not the chemical name
  - ✓ Hexafluoropropylene oxide dimer acid (HFPO-DA)
  - ✓ Short Chain PFAS
- ✓ NCDEQ evaluating PFAS as a class of compounds, GenX no longer the only PFAS compound of concern
- ✓ NCDEQ deferring to USEPA for toxicology and other risk evaluations
- ✓ NCDEQ reviewing methodologies to evaluate ambient concentrations of PFASs to differentiate between background and source concentrations
- ✓ NCDEQ has developed air emissions testing methods using rainwater collection



Federal Updates

USEPA

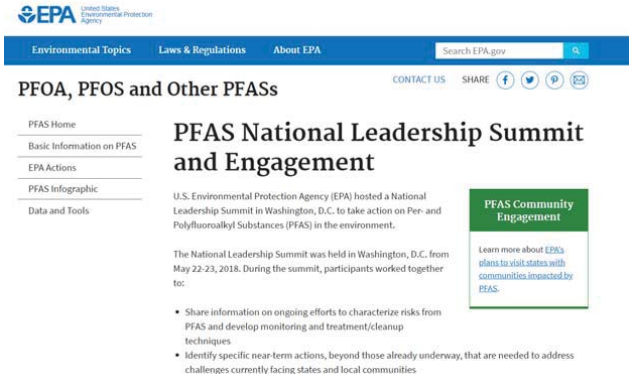
- ✓ PFAS Leadership Summit – May 22-23, 2018
- ✓ GenX and PFBS toxicity assessments released
- ✓ Five more PFAS toxicity values currently being evaluated
- ✓ National PFAS Management Plan to be released early 2019
- ✓ Evaluation of MCLs for PFOS and PFOA

ATSDR – June 2018

- ✓ Released toxicity profile for PFOA and PFOS
- ✓ MRLs 10x lower than EPAs RfDs
- ✓ Profiles released for PNFA and PFHxS

ITRC/ECOS

- ✓ AFFF Fact Sheet
- ✓ ITRC PFAS Training



Challenges and the State of Practice

- ✓ Sampling and Analysis
- ✓ Regulatory Considerations
- ✓ Analytical Considerations

Wood – The basis for our lessons learned

Sampling Considerations

Have SOPs designed to minimize false positive results:

- ✓ No Teflon in sampling pumps, equipment, or sample containers
- ✓ No Gore-Tex, Tyvek, waterproof clothing
- ✓ Natural-based products for sunscreens, bug spray, personal care products
- ✓ Use vegetable oil instead of standard drilling equipment grease
- ✓ Adequate numbers of blanks to monitor contamination
- ✓ Well planned & executed programs can avoid the problems.

Overview of Analytical Methods

- ✓ EPA Method 537
  - ✓ Developed for finished/treated drinking water
- ✓ Modified EPA Method 537
  - ✓ Typically used by commercial laboratories
- ✓ ASTM Method 7979-17
  - ✓ Analysis of environmental solids (soil, sediment, sludge)
- ✓ ASTM Method D7968
  - ✓ Analysis of environmental waters (other than drinking water)
- ✓ Specialty Analyses
  - ✓ Source Fingerprinting
  - ✓ Non-targeted methods to explore unknown compounds
  - ✓ Total Oxidizable Precursors (TOP) Assay

Regulatory Considerations and Challenges

Official EPA Position –

"Currently, there are no standard EPA methods for analyzing PFAS in groundwater, surface water, wastewater, or solids. Some U.S. laboratories are using modified methods for non-drinking water samples based on EPA Method 537. These modified methods have no consistent sample collection guidelines and have not been validated nor systematically assessed for data quality."

(EPA/600/F-17/022, March 2017)

EPA Technical BRIEF

INNOVATIVE RESEARCH FOR A SUSTAINABLE FUTURE

www.epa.gov/research

Per- and Polyfluoroalkyl Substances (PFAS)

Sampling studies and methods development for water and other environmental media

Background

Per- and polyfluoroalkyl substances (PFAS) are a large group of manufactured compounds used in a variety of industries, such as aerospace, automotive, textiles, and electronics, and are used in some food packaging and firefighting materials. For example, they may be used to make products more resistant to stains, grease and water. In the environment, some PFAS break down very slowly, if at all, allowing bioaccumulation (concentration) to occur in humans and wildlife. Some have been found to be toxic to laboratory animals, producing reproductive, developmental, and systemic effects in laboratory tests.

The U.S. Environmental Protection Agency's (EPA) methods for analyzing PFAS in environmental media are in various stages of development. EPA is working to develop robust analytical methods for groundwater, surface water, wastewater, and solids, including soils, sediments, and biosolids.

Drinking Water

Analysis using EPA Method 537

To assess for potential human exposure to PFAS in drinking water, EPA-approved commercial drinking water laboratories successfully analyzed finished (treated) drinking water samples for six PFAS monitored under the third Unregulated Contaminant Monitoring Rule (UCMR3). For the UCMR3 analyses, laboratories used EPA Method 537, which also includes eight additional PFAS analytes not listed on the UCMR3.

Health Advisories

In May 2016, EPA issued drinking water health advisories for two types of PFAS – perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS). EPA's health advisories are non-enforceable and non-regulatory, and provide technical information to state agencies and other public health officials on health effects, analytical methodologies, and treatment technologies associated with drinking water contamination.

EPA expects to have draft methods for water and solids by fall 2017.

Method Development and Validation

Currently, there are no standard EPA methods for analyzing PFAS in groundwater, surface water, wastewater, or solids. Some U.S. laboratories are using modified methods for non-drinking water samples based on EPA Method 537. These modified methods have no consistent sample collection guidelines and have not been validated nor systematically assessed for data quality.

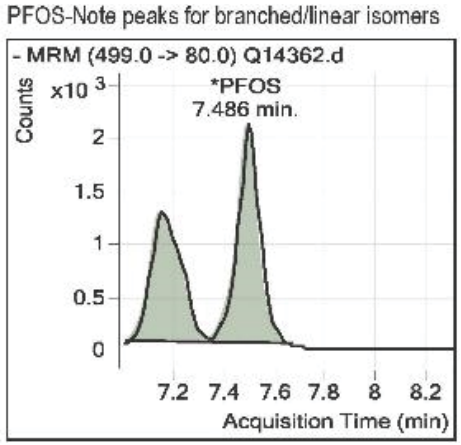
To provide validated methods for sample types other than drinking water, which will fill this sampling and analytical gap, EPA formed a cross-Agency method development and validation workgroup. The workgroup will develop analytical methods for quantifying 24 PFAS analytes. The method development process will occur in a phased approach:

Phase I EPA labs will test three existing analytical protocols for preparing and analyzing 24 PFAS analytes in surface water, groundwater, and wastewater.

Phase II Several external labs will validate the most promising protocol(s) based on the Phase I results.

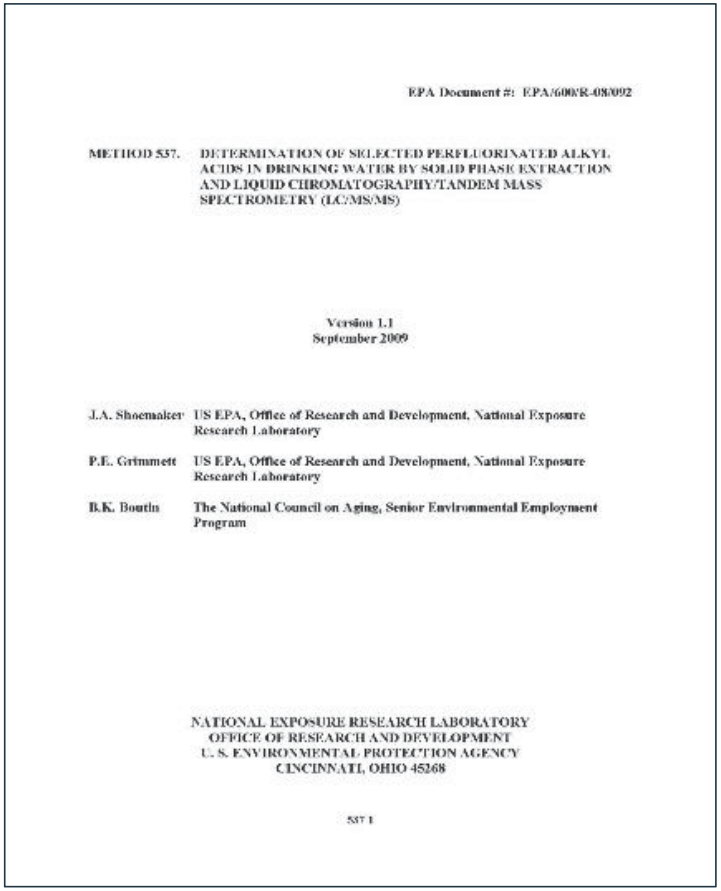
Regulatory Considerations and Challenges

- ✓ EPA Method 537, is only a drinking water method
- ✓ Modifications vary widely between labs
- ✓ Regulator concerns - accuracy and interlab agreement
- ✓ Interagency work group on PFAS methods
- ✓ EPA and DoD disagree on method details
- ✓ Some EPA Regions (e.g. R3) require unmodified Method 537
- ✓ Regional EPA developing/updating ASTM method



Current Laboratory Capabilities

- ✓ Analysis available for maximum of 20-30 PFAS compounds
- ✓ Most labs can analyze fewer than that (10-15)
- ✓ Laboratory DLs and overall capability at ng/L or lower concentrations varies widely
- ✓ Very few labs can analyze newer PFAS components (e.g. GenX™), which are coming under increased regulatory scrutiny
- ✓ The situation is constantly evolving
- ✓ Proceed with CAUTION: Verify all capability claims



EPA Document #: EPA/600/R-08/092

METHOD 537. DETERMINATION OF SELECTED PERFLUORINATED ALKYL ACIDS IN DRINKING WATER BY SOLID PHASE EXTRACTION AND LIQUID CHROMATOGRAPHY/TANDEM MASS SPECTROMETRY (LC/MS/MS)

Version 1.1
September 2009

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P.E. Grimmett — US EPA, Office of Research and Development, National Exposure Research Laboratory

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CINCINNATI, OHIO 45268

537.1

Selecting a PFAS Laboratory

Use the following criteria for laboratory selection:

- ✓ Determine experience with PFAS (multiple years and hundreds of samples?)
- ✓ Review operating procedures, proficiency test results, and QC and performance record on PFAS projects
- ✓ Consider conducting a lab audit before submitting samples
- ✓ Determine if lab is accredited in the State where the project site is located
- ✓ Determine if the laboratory has capacity to accommodate demand

Laboratory accreditation

Verify lab meets DQOs

EPA Development of New Analytical Methods

- ✓ EPA Method 537 – Recently updated to include:
  - ✓New Drinking Water method coming
  - ✓SW-846 Method 8327 – direct aqueous injection for noncomplex aqueous matrices
  - ✓SW-846 Method 8328 – SPE and isotope dilution for more complex aqueous matrices, soils, sediments and sludges
  - ✓SW-846 Method 8329 – Under development; reportedly to be applicable to biological matrices

These methods will likely provide a more robust framework for analysis, and result in greater consistency between laboratories.