

# Ardmore refinery sues chemical manufacturers for toxic 'forever chemical'



Texas Man Files PFAS Lawsuit Against 3M, Others Over Firefighting Foam



## Per and Polyfluoroalkyl Substances (PFAS) Awareness and Management for Texas

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# Safety Moment - US Fire Administration (USFA) Recommendations

- Protection against exposure
- PFAS/PFOA/PFOS may be orally ingested, absorbed through the skin or inhaled through exposure in the atmosphere. Personnel at departments that use firefighting AFFFs with PFAS/PFOA/PFOS should practice the following controls to stay safe from exposure:
  - Replace older AFFF stocks with fluorine-free foam solutions
  - Contain and manage AFFF and water runoff
  - Wear personal protective equipment (PPE) and a self-contained breathing apparatus (SCBA) whenever handling AFFF
  - Properly remove and bag contaminated PPE prior to transporting
  - Use cleaning wipes on your face, neck and hands immediately after exposure
  - Clean contaminated PPE and SCBA before its next use
  - Shower within one hour of returning to the station or home



# Presentation Overview

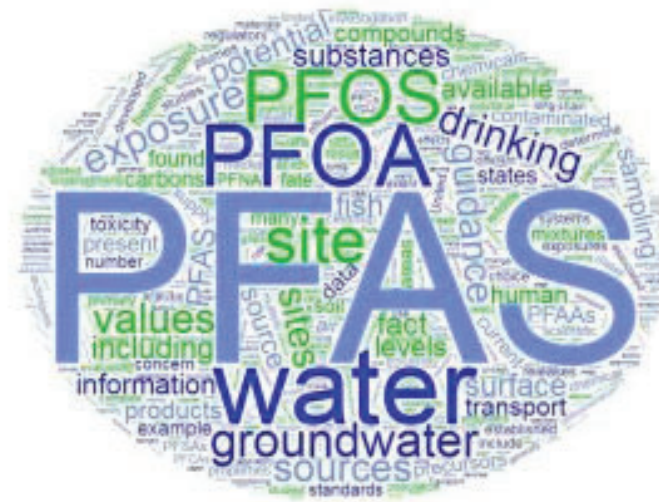


- What are PFAS?
  - PFAS Chemistry
  - PFAS Uses
  - History of PFAS
- PFAS Health Risks
- PFAS Regulatory Framework
- PFAS Sampling Strategies
  - Analytical Methods
  - PFAS Forensics
- PFAS Remedial Options
- Texas Mitigation and Response
  - Evaluation of alternatives
  - Transition to different chains
  - Retrofitting and upgrading systems
  - Future compliance planning and management through operations and physical controls

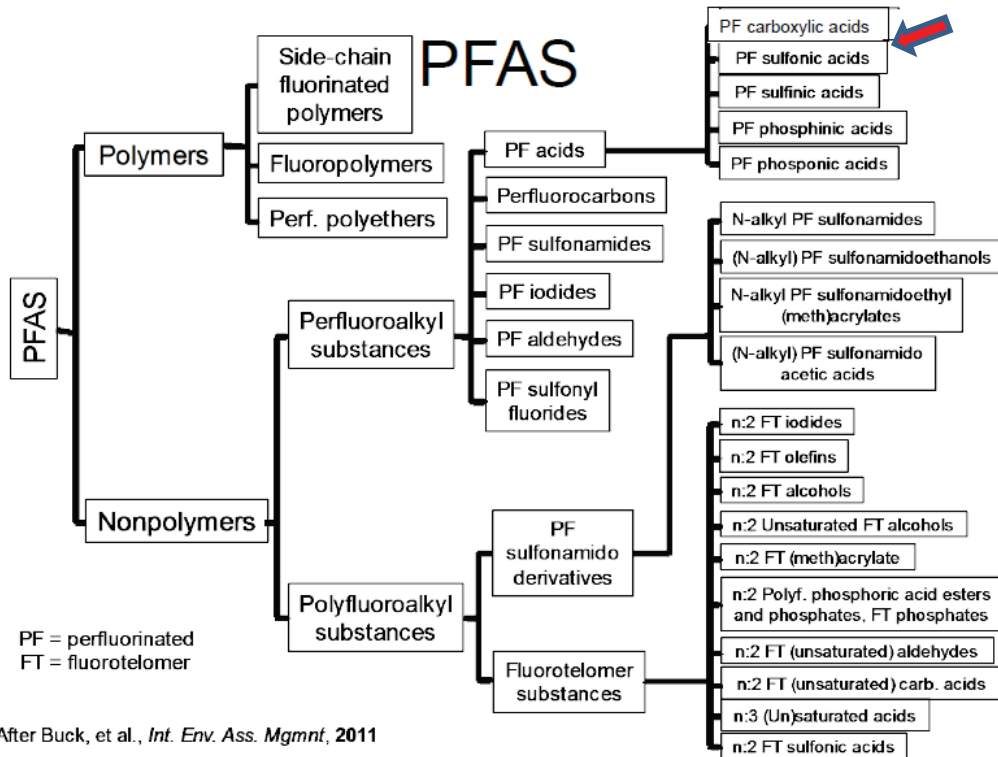


# PFAS Nomenclature

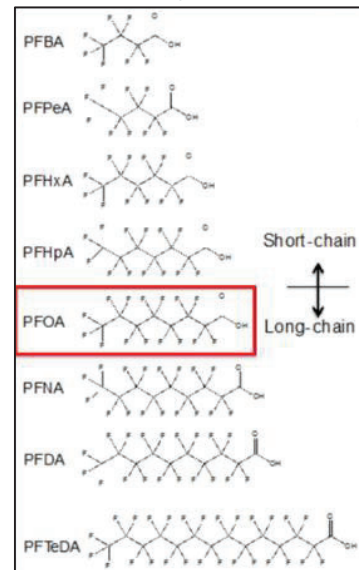
- **PFAS – Per- and Polyfluoroalkyl Substances (also written as PFASs)**
  - Perfluoroalkyl substance – All carbon atoms are bonded to fluorene atoms
  - Polyfluoroalkyl substance – At least one carbon is bonded to something other than a fluorene atom
- **PFCs – List of 6 perfluorinated compounds analyzed for in UCMR3**
  - PFOS – Perfluorooctane sulfonate
  - PFOA – Perfluorooctanoic acid
  - PFNA – Perfluorononanoic acid
  - PFHxS – Perfluorohexanesulfonic acid
  - PFHpA – Perfluoroheptonic acid
  - PFBS – Perfluorobutanesulfonic acid
- **PFAA - perfluoroalkyl acids**
  - PFSAs - Perfluorosulfonic acids
  - PFCAs - Perfluorocarboxylic acids
- **Types of PFAS**
  - Monomers – smaller molecules with no repeating units
  - Polymers – Bigger molecules with repeating sections
  - Oligomers – “small” polymers



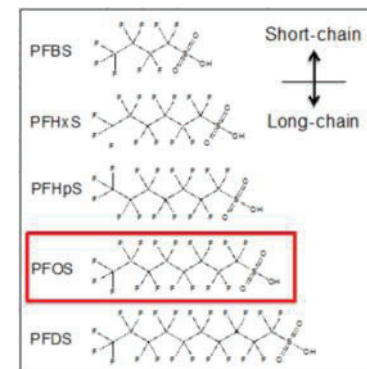
# PFAS Family Tree



## Carboxylic Acids



## Sulfonic Acids



After Buck, et al., *Int. Env. Ass. Mgmt.*, 2011

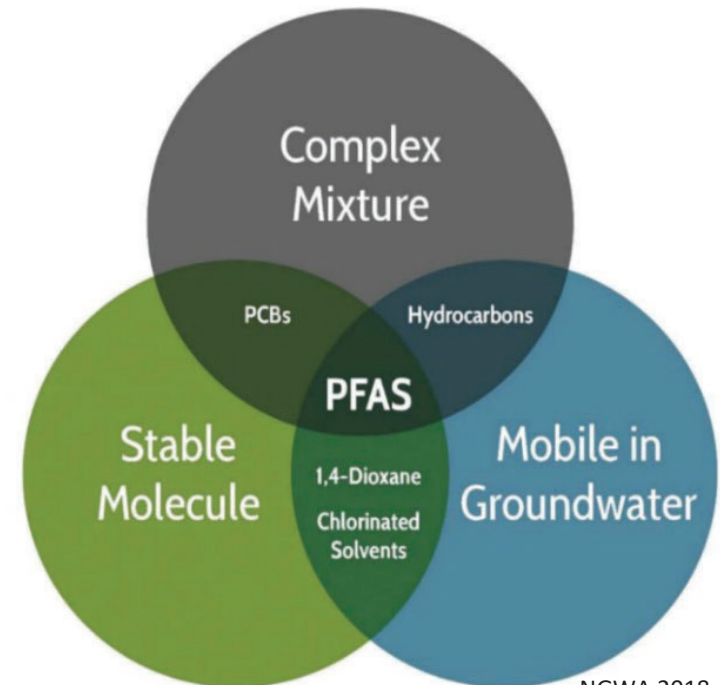
Adapted from: SERDP & ESTCP Webinar Series (#59)



# PFAS Challenges

- No natural sources
- Mobile in groundwater and surface water
- Atmospheric transport / deposition
- Stable molecules
  - Resists heat, water or grease
  - Resistant to natural biotic or abiotic degradation
- Complex mixture
  - PFAS mixtures
  - Often mixed with other contaminants
- Bioaccumulates

Figure 4.2. PFAS comparison to other contaminant classes.



NGWA 2018



# Aqueous Film Forming Foams (AFFF)

- Aqueous film forming foams (AFFF)
  - Bulk storage facilities, terminals, refining, petrochemical and chemical
  - Airports
  - Fire training facilities
  - Building/gas station fire suppression systems
  - Military facilities
  - Mining and landfills (odor and dust control)
  - 5% of PFAS



**“The only places we’re not finding PFAS are places we’re not looking”**

Heidi Grether, Director, Michigan Department of Environmental Quality

# Performance Chemicals and Industrial Uses

- Aerospace
- Alternative energy
- Automotive
- Chemical manufacturing
- Electronics
- Medical supplies
  - Fluid resistant clothing
  - Implants, patches and grafts
  - Low friction coatings
- Photolithography
- Performance chemicals
  - Building and construction – weather resistant coatings
  - Hydraulic fluids
  - Fuels
  - Industrial surfactants
- Oil and gas – enhanced recovery
- Metal plating and etching
- Paints, varnishes, sealants, waxes and polishes
- Plastics
  - Polymer manufacturing, Resins
- Semiconductors
- Wire manufacturing and coating







- Leather and products
- Paper coatings
- Stain repellants
- Weather resistant apparel and equipment



- Cosmetics
  - Foundation
  - Concealer
- Insect repellent
- Sunscreen
- Dental floss
- Shampoo
- Body wash



# PFAS Usage Timeline

- 1930's – PTFE (Teflon) discovered
- 1940's – Use in consumer products begins
- 1950's – Stain resistant products
- 1960's – AFFF, packaging
- 1970's – Detected in the blood serum of workers and consumers
- 1990's – Chromium plating dust suppressant
- 2000's – C8 Study demonstrates human toxicity
- 2006 – 2015 – Voluntary Stewardship Program phases out manufacture of PFOA and PFOS in the United States
- 2020 – PFOA and PFOS no longer manufactured in US, but present in imported raw, finished, and waste materials





## Health Study (C8)

- High cholesterol, testicular and kidney cancer, ulcerative colitis, thyroid disease, pregnancy-induced hypertension, and reduced antibody titer rise

## Cancer Incidence rates

- One study estimated that the odds of testicular cancer and kidney cancer in Little Hocking County, OH increased by 5.1 and 1.7 respectively

- 80-90% of human exposure to PFOS and PFOA through ingestion

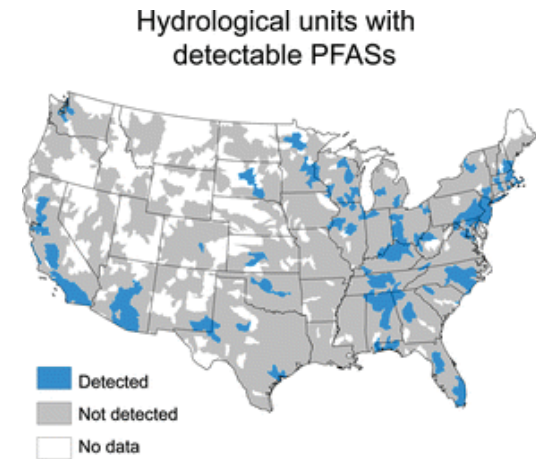
Perfluorooctanoic Acid Exposure and Cancer Outcomes in a Contaminated Community: A Geographic Analysis

Verónica M. Vieira,<sup>1,2</sup> Kate Hoffman,<sup>1,3</sup> Hyeong-Moo Shin,<sup>4,5</sup> Janice M. Weinberg,<sup>6</sup> Thomas F. Webster,<sup>1</sup> and Tony Fletcher<sup>7</sup>



# Federal Regulatory Framework

- **Safe Drinking Water Act (SDWA)**
  - UCMR3
  - Health Advisory
  - Current USEPA Authority
- **Comprehensive Environmental Response Compensation and Liability Act (CERCLA)**
  - Part 102
  - Part 107
- **Toxic Substances Control Act (TSCA)**
  - As of 2015, 73,757 chemicals are approved for use
  - EPA reviewed over 900 new PFAS in the last 12 years based on CBI provided by the manufacturer
  - 2015 TSCA Amendments require EPA to prioritize chemicals and review risk (3-year clock), but the clock doesn't start until there is enough data to designate "unreasonable risk"
  - 3-year clock doesn't start until EPA "has all the data they need for the review"
- **Emergency Planning and Community Right to Know Act (EPCRA)**
  - 767 chemicals on EPA Toxic Release Inventory (TRI); 100 PFAS included for 2020 reporting year



# Food and Drug Administration (FDA):

- **Focused on generating, applying, and evaluating the science that is needed to begin to estimate PFAS exposure from food**
  - The FDA currently uses the EPA's reference doses (RfD) for PFOA and PFOS of **20 ng/kg bw/day** as the most appropriate toxicity reference value (TRV).
- **Two major vectors being evaluated by FDA**
  - PFAS in foods from specific areas affected by PFAS contamination
  - PFAS in foods from uses of food contact applications
    - PFAS in non-stick coatings on cookware and processing equipment generally do not transfer to food
    - PFAS in oil- and water-resistant packaging may transfer to food



<https://www.fda.gov/food/chemicals-and-polyfluoroalkyl-substances-pfas>; <http://blogs.edf.org/health/files/2019/06/FDA-PFAS-in-food-poster-presentation-2-5-30-19.pdf>  
<https://www.fda.gov/news-events/press-announcements/statement-fdas-scientific-work-understand-and-polyfluoroalkyl-substances-pfas-food-and-findings>



# States Taking the Lead - PFAS Drinking Water Standards and Guidance (ng/L)

	PFOS	PFOA	PFNA	PFBS	PFBA	PFHxS	PFHpA	GEN-X
TX	560	290	290	34,000	71,000	93	560	
USEPA, AK, AL, AZ, DE, PA, WV	70	70						
CO, IA, MI, MT, NH, RI	70	70						
CA	13	14						
CT	70	70	70			70	70	
FL*		70						
MA	20	20	20			20	20	
ME	400	400						
MN	300	35		7,000	7,000			
NV	667	667		667,000				
NH	70	70						
NJ	13	14	13					
NY	10	10						
OH*	70	70	21	140,000		140		
VT	20	20	20			20	20	
NC		2,000						140

NOTES:  
**Promulgated**

\* Pending

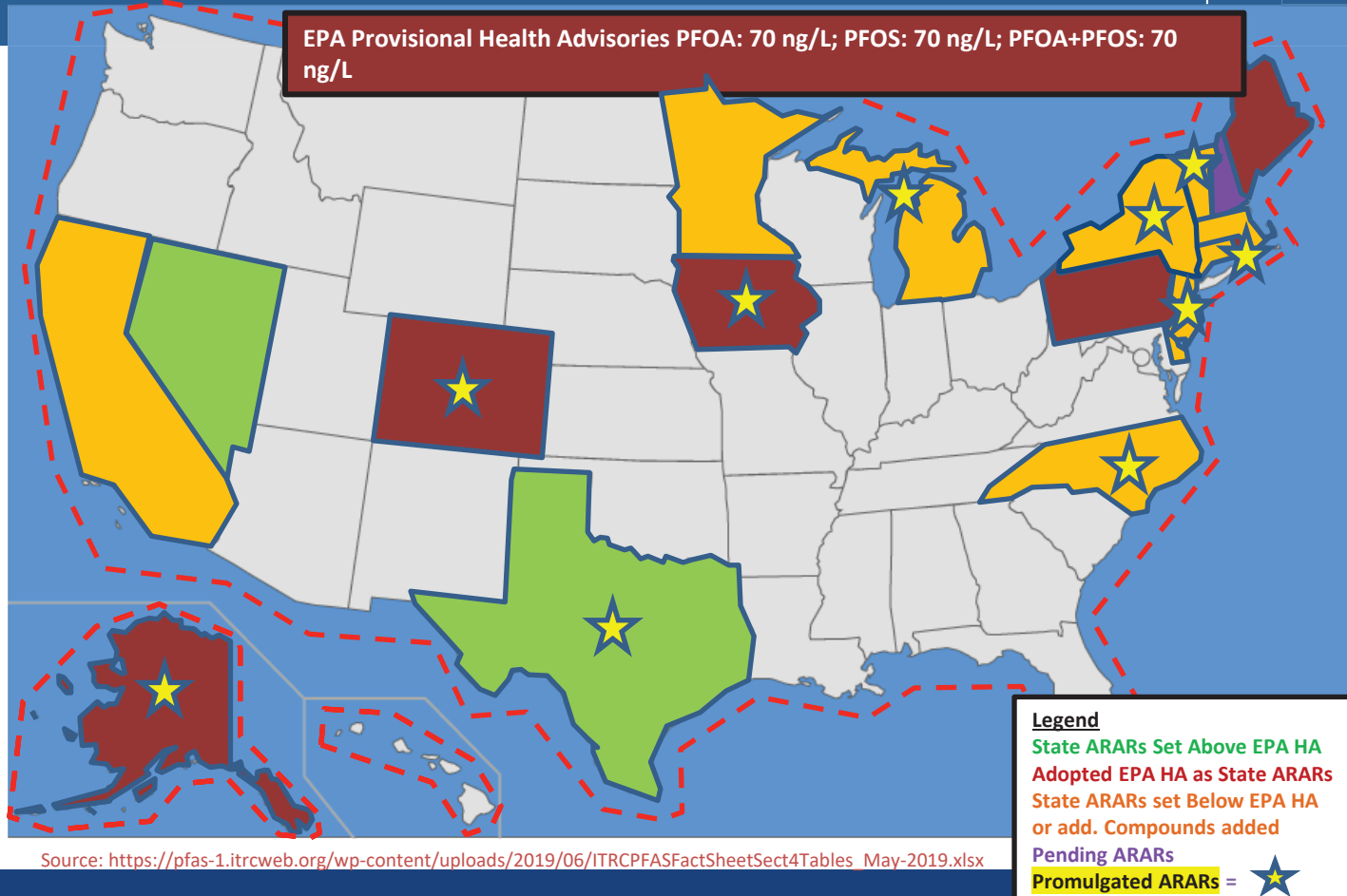
Also have soil criteria

Use EPA HA without State ARARs

ITRC, January 2020



# Implications of Varying ARARs



# Sampling Challenges



- Lack of environmental background
- Use of/contact with materials that may contain PFAS
  - Clothing
  - Sampling equipment
  - Food packaging
  - Vehicle carpeting
  - Cosmetics, sunscreen, bug spray
  - Personal protective equipment
- Cross Contamination
  - PFAS are found in many of the items we use in the field
  - Often analyzing for trace amounts of PFAS (ppt)
- Health and Safety
  - Many protective products contain PFAS





# Environmental Sampling: Laboratory Considerations

- Difficulties associated with high and low concentration samples
  - Micelles and foaming
  - Reproducibility
    - TOP pre-treatment samples compared to standard analyses
  - What is non-detect?
- Atypical Matrices
  - There may be best practices out there...but they may require significant research to find.
- Aqueous Fire Fighting Foam Concentrate
  - US EPA Method: 537.1 Modified
  - DoD Method: PFAS by LCMSMS Compliant with Table B-15 of QSM 5.3
  - International Methods: S.R. CEN/TS 15968:2010 & others
  - Sampling Complications
- When is the Total Oxidizable Precursor Assay useful?

## Analytical Options

- USEPA Method 537 Rev 1.1
- USEPA Method 533
- ASTM D7979-16
- Total Oxidizable Precursor (TOP) Assay
- Particle Induced Gamma-Ray Emission (PIGE) Analysis)
- Adsorbable Organic Fluorine (AOF) Analysis

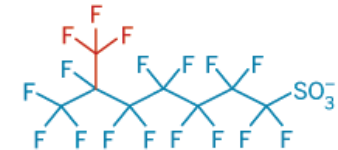


# Environmental Sampling: Laboratory Considerations (Continued)

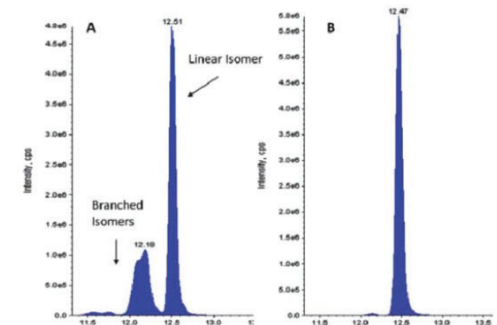
- Verify your lab has the correct certification(s)
- Verify method(s) to be used for different media
  - EPA Method 537
    - Drinking Water/Groundwater
  - EPA Method 537.1 Modified
    - Groundwater/Soil
    - Modified method uses isotope dilution
- Verify MDLs, TATs, and the analyte list(s) to be reported with regulator(s) and the laboratory
- Verify your lab can quantify branched and linear isomers
- Both high and low conc. can be problematic



PFOS linear isomer



PFOS branched isomer



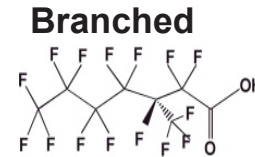
- Sorption generally increases with number of carbons
- Transport related to charged state of PFAS
  - Anions > zwitterions > cations
  - Shorter chain lengths generally move faster
- Polyfluorinated substances
  - Potential to form PFSAs and PFCAs (abiotically and biotically)
  - Variable transport properties
- PFSAs and PFCAs
  - Not readily biodegradable
  - Not readily transformed abiotically
  - Generally have high mobility

Mobile & Persistent

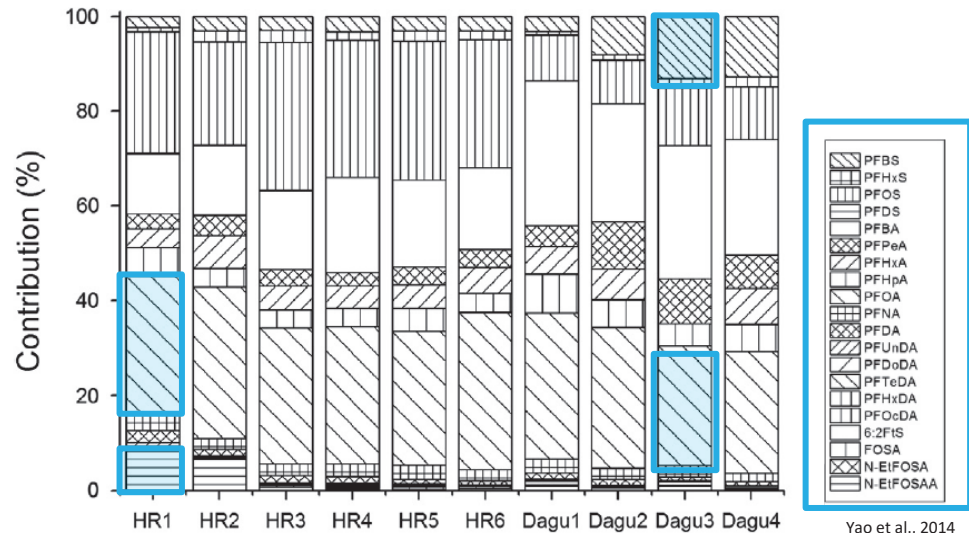
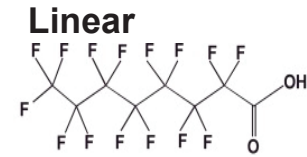


# Manufacturing and Forensics

- 1950s-2002:
  - 3M major producer, uses Electrochemical Fluorination (ECF) manufacturing process
  - PFOS produced in United States
- 2002-present:
  - Telomerization becomes dominant manufacturing process
  - Shorter chain PFAS (GenX, PFBS, PFBA) used as substitutes
- Multiple compound evaluation
  - Ratios can indicate multiple sources or distance from a source
  - More PFAS analytes make analysis more meaningful



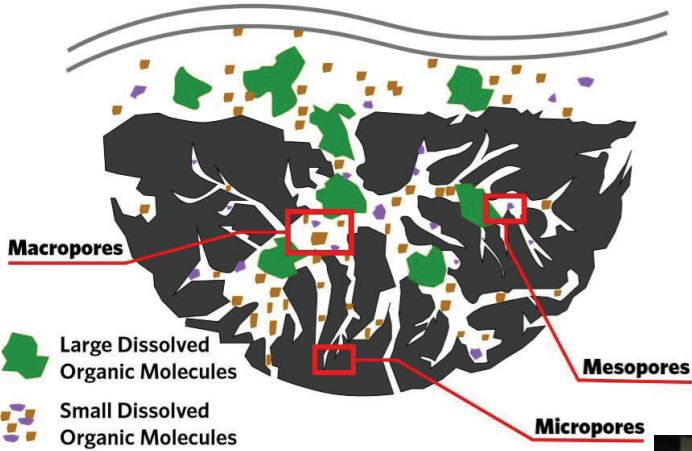
Naile, et al., 2016



Yao et al., 2014

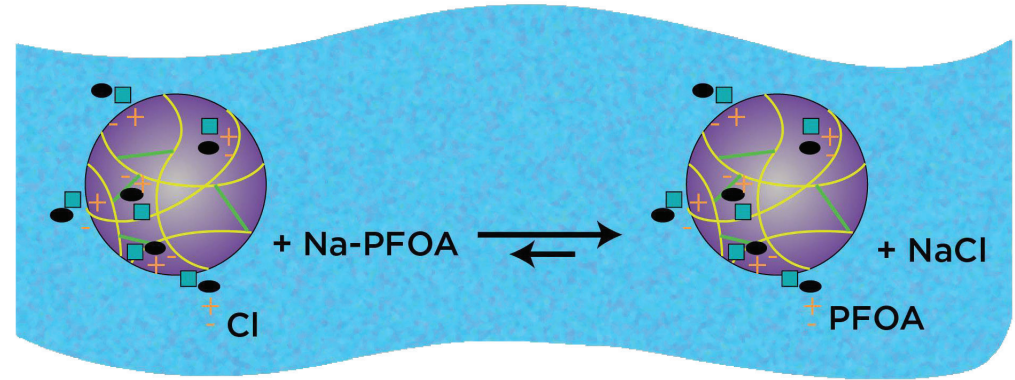


# Treatment Options



Granular Activated Carbon (GAC)

## Ion Exchange (IX) Resins



Reverse Osmosis (RO)

## When conducting a Phase I ESA, because states do not have enforceable regulatory limit, is PFAS...

- Business environmental risk? Risk which can have material environmental or environmentally-driven impact on the business
- *De minimis* condition? Does not present threat to human health or environment and generally not subject of an enforcement action
- Recognized environmental condition? Presence/likely presence of hazardous substance due to release or conditions pose material threat of release to environment

*\*\*\*PFOA/PFOS not currently listed as CERCLA hazardous substance but “in some circumstances could be responded to as CERCLA pollutants or contaminants”.*

- Consideration of historic operations, chemical storage and waste handling practices, and owner/occupant knowledge to ascertain potential for release of products containing PFAS



# AFFF Regulation and Guidance

- **Federal requirements**
  - FERC
  - PHMSA
  - FAA
  - OSHA
- **State fire and building codes**
  - International Building Code
  - International Fire Code (published by ICC)
  - Uniform Fire Code and Life Safety Code (published by NFPA)
- **Insurance requirements**
- **Internal risk tolerance for large loss events**
- **International guidance**



# Types of AFFF Systems

- Class B Foams
  - Low expansion
    - Open head
    - Closed head
  - High expansion foam
    - Deluge systems
    - Hose Stations
- Mobile rescue and fire fighting





# 2019 NATA Study Summary

- Performed by UMD funded by NATA
- 174 foam discharge incidents over 16 years
- 137 were accidental discharges
- 37 were actual fires – none of which were fuel spills
- Average cost per loss was \$0.74MM excluding cleanup costs

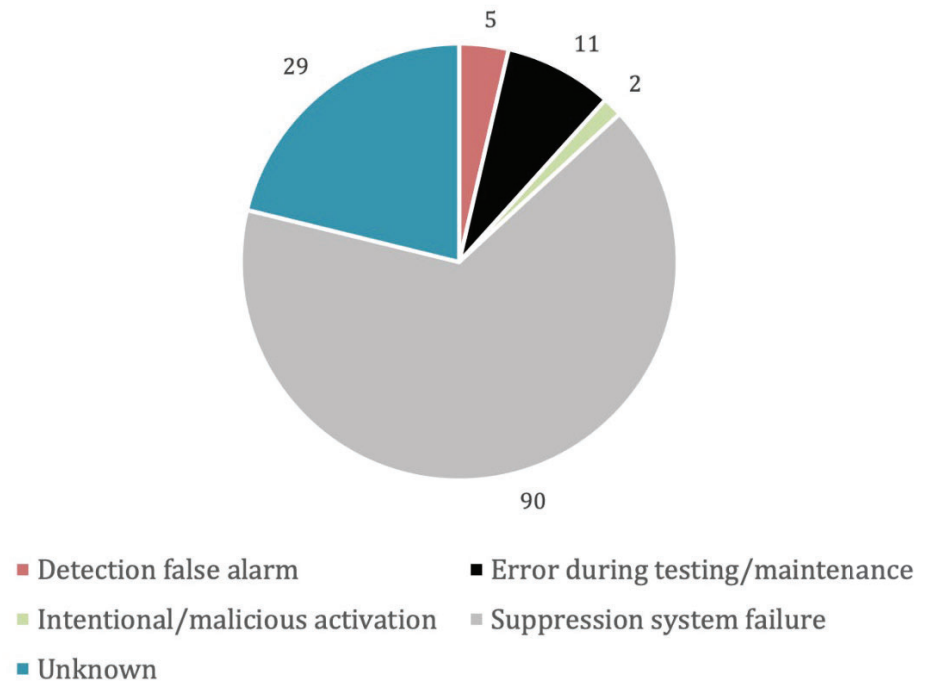


Figure 7. Cause of Accidental Foam Discharge

- Evaluation of alternatives
- Transition to different chains
- Retrofitting and upgrading systems
- Future compliance planning and management through operations and physical controls



# Texas Mitigation and Management - Applied Approach

Fire Suppression  
Conceptual  
Model

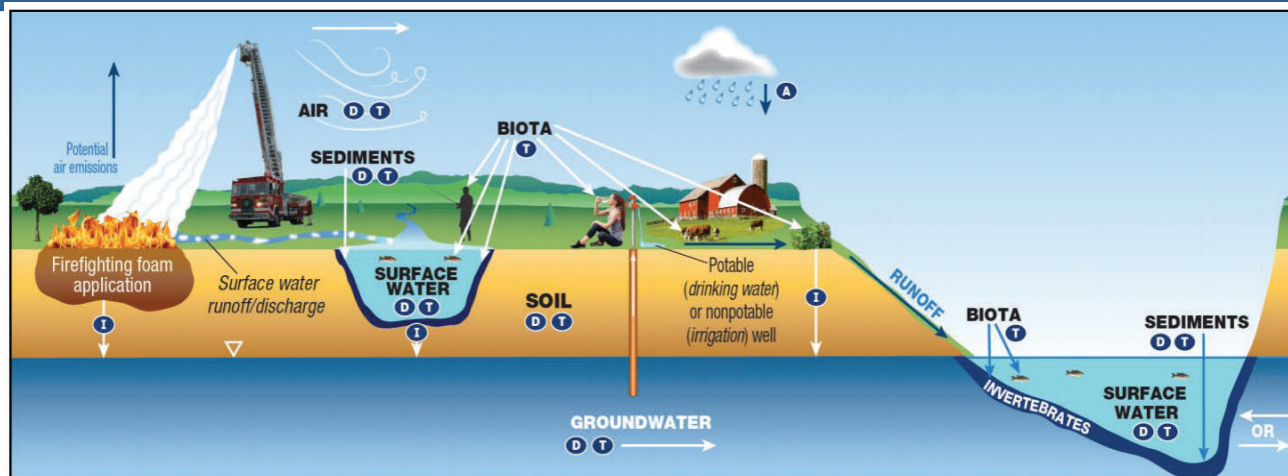
Inventory of  
Equipment and  
Storage

Worst Case  
Scenario and  
Receptor Impact  
Assessment

Mitigation  
Operating  
Procedure  
Development



# Conceptual Model Development



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

## • Sources of PFAS:

- Terminals, Refining and Chemical Processing Facilities
- Manufacturing: raw materials, electronics, plastics, textiles
- Coatings applications
- Mist suppression systems for chrome plating
- Performance chemicals (hydraulic fluid, fuel)
- Fire Suppression Systems

## • Pathways to the Environment:

- Air (Stack) Emissions (long range and short-range transport possible)
- Discharges to WWTPs
- Stormwater & discharges to surface water
- Historic releases and on-site disposal
- Maintenance and cleaning of equipment
- Leaking storage tanks



# Inventory of Equipment, Storage and Chemicals

- Tank capacities
- Fire suppression chemical SDSs
- Operational procedures
- Locations of critical infrastructure (facility details)
- Containment Details
- Environmental and health impacts of the components in AFFF
- Federal permitting, reporting and remediation requirements
- Additional state or local requirements



# System Management Options

- Containment systems
- Foam system hardening
  - Cross-zoned detection
  - Closed-Head sprinkler system
  - Abort stations
  - Manual shut down of systems
- Alternative Foams
  - C6 Foams
  - Fluorine-Free Foams (FFF)
- Water-only suppression systems
- Standard Practices
  - Time and volume released until Fire Marshal arrives



- Through modeling, mapping of critical infrastructure and understanding of operating procedures for fire suppression, will determine potential impacts to sensitive receptors:
  - Public water supply sources
  - Marine food sources
  - Contact recreation areas
- Increase risk liabilities to long-term environmental and human health impacts



- Segregation of stormwater laden with differing pollutants
- Notifications to local, state and federal agencies
- Agreements with contractors for best practices managing PFAS waters
- Incorporate PFAS containment and documentation procedures into fire pre-plans





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