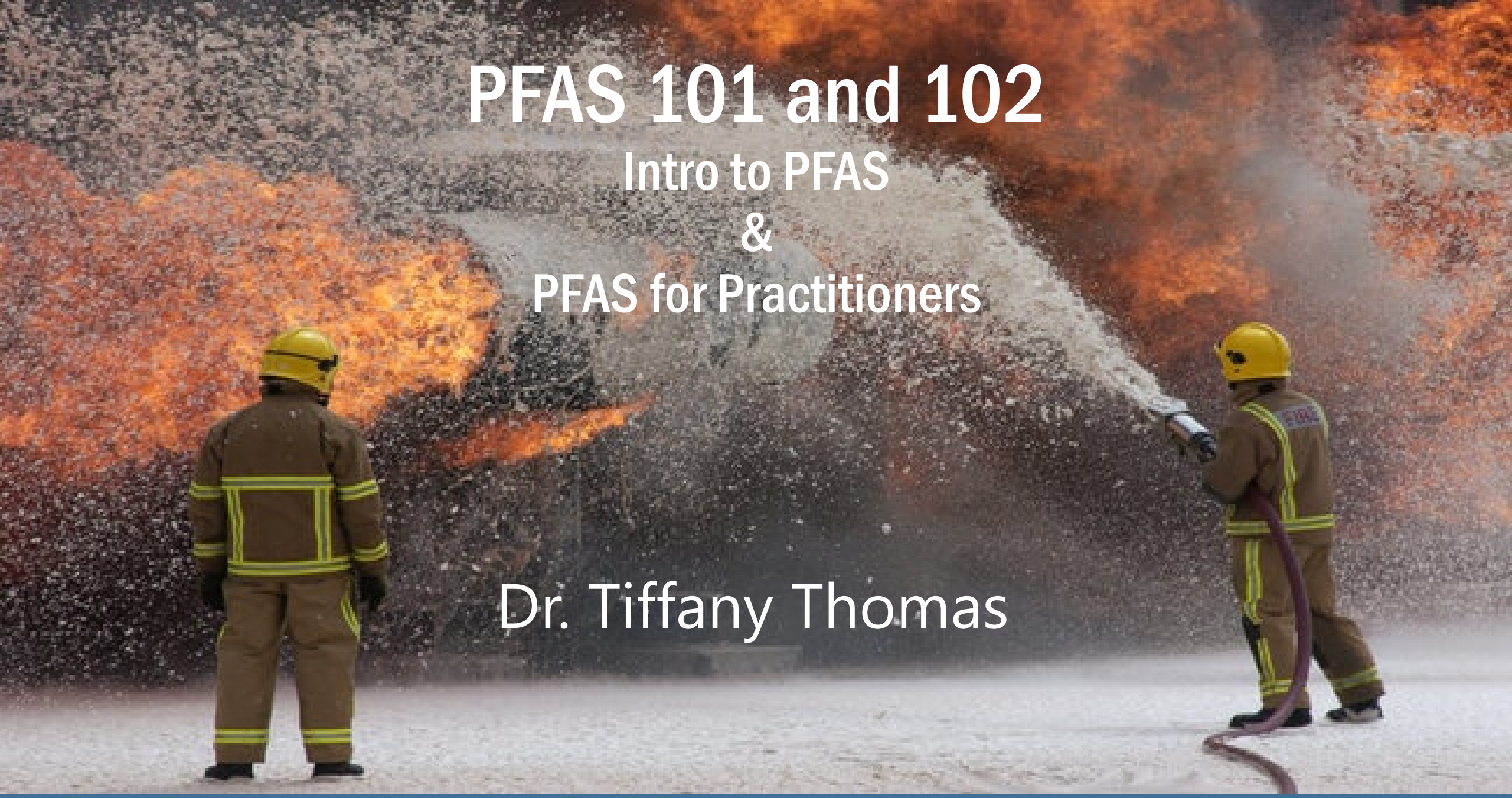
Brief Bio

- 2000 - B.S. in A.C.S. Environmental Chemistry, Northern Arizona University
  - Summa Cum Laude
  - Honors College
- 2004 – Ph.D. in Inorganic Chemistry, University of California at Davis
  - Student-Employee at Lawrence Livermore National Lab
- 2005 – Post-Doctoral Fellow
- National Academy of Science Panelist
- MENSA member



PFAS 101 and 102

Intro to PFAS
&
PFAS for Practitioners

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PFAS 101 – Intro to PFAS

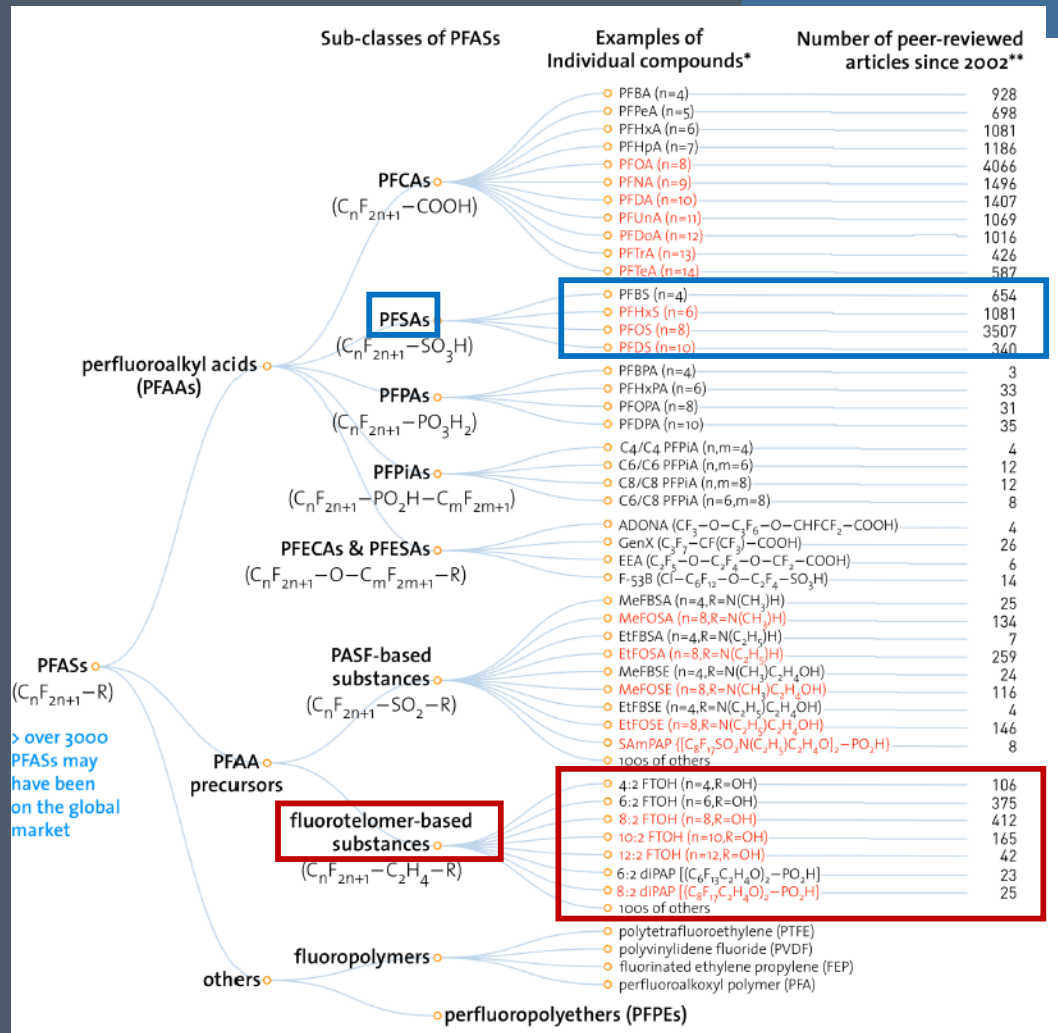
Intro to PFAS

Chemistry of AFFF product family

AFFF degradation and PFOA “precursors”

Data gaps and key takeaways

Example Case Studies



Wang, et al. *A Never-Ending Story of Per- and Polyfluoroalkyl Substances (PFASs)?* Environ. Sci. Technol. 2017, 51, 2508–2518; DOI: 10.1021/acs.est.6b04806

Intro to PFAS

- Per- and Polyfluorinated Alkyl Substances (PFAS)
- Broad class of chemistry with over 6,500 known compounds
- Historically associated with Aqueous Film-Forming Foam (AFFF)
- MANY commercial uses

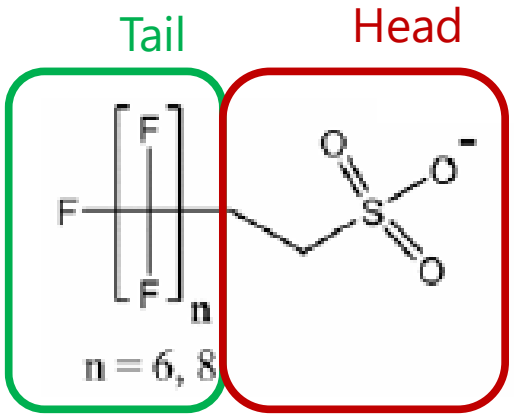
Examples of Common PFAS Applications

- Paper and packaging
- Clothing and carpets
- Outdoor textiles and sporting equipment (inc. ski/snowboard waxes)
- Non-stick cookware
- Cleaning agents and fabric softeners
- **Polishes, waxes, varnishes, dyes, inks, latex paints, and marine paints**
- **Hydraulic fluids**
- Adhesives
- Medical products
- Personal care products
  - (SkinDeep database)
- Rubber and plastics
- Fabricated metal
- **"Chemically-driven oil production"**
- **Oil-field and pipeline equipment**

- Metal finishing/plating operations – particularly in chrome plating mist suppression systems
- **Pesticides and herbicides**
- **Sulfluramid-containing insecticides and as an anti-foaming agent in pesticides**
- Specialty cleaning product storage and disposal

Fate and Transport

- Highly soluble, highly mobile – particularly shorter chain PFAS compounds
- Persistent – half-lives of daughter products >40+ years
- Typically have low vapor pressures and Henry's Law constants
- Does not generally sorb to soil (low Koc)
- Atmospheric distribution possible
- Because AFFF contained mixtures of different PFAS, groundwater transport characteristics will vary with each chemical's properties

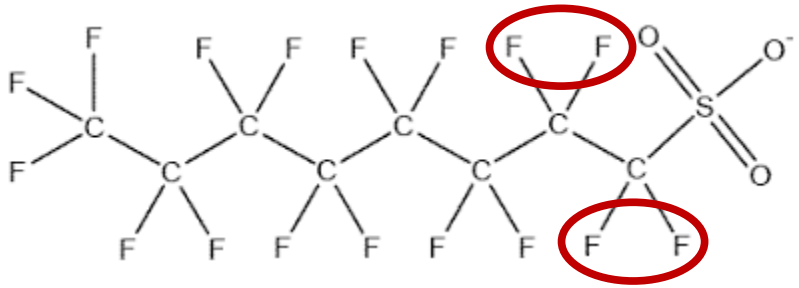


FT Sulfonate

3M vs Other AFFF

Electrochemical Fluorination (ECF)
3M

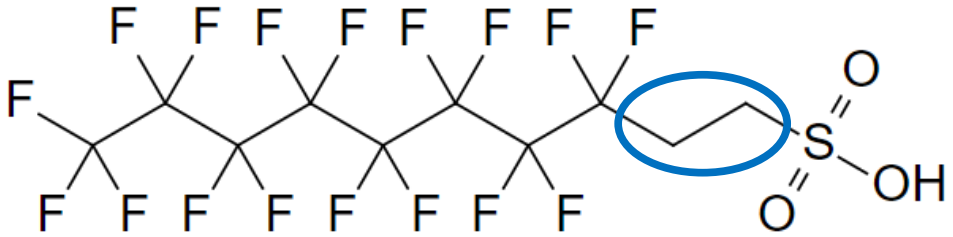
- Branched and linear structures
- Fully fluorinated carbon “tails”
- Sulfonate “heads”



PFOS – Perfluorooctanoic sulfonate

Fluorotelomerization (FT)
All other AFFF

- Linear structures only
- Partially fluorinated carbon “tails”
  - Even-numbered lengths only
- Variable “head” group chemistry



8:2 Fluorotelomer sulfonate

The Concept of "Precursors"

- 1981 – Hagen et al noted biotransformation of 8:2 FTOH to PFOA

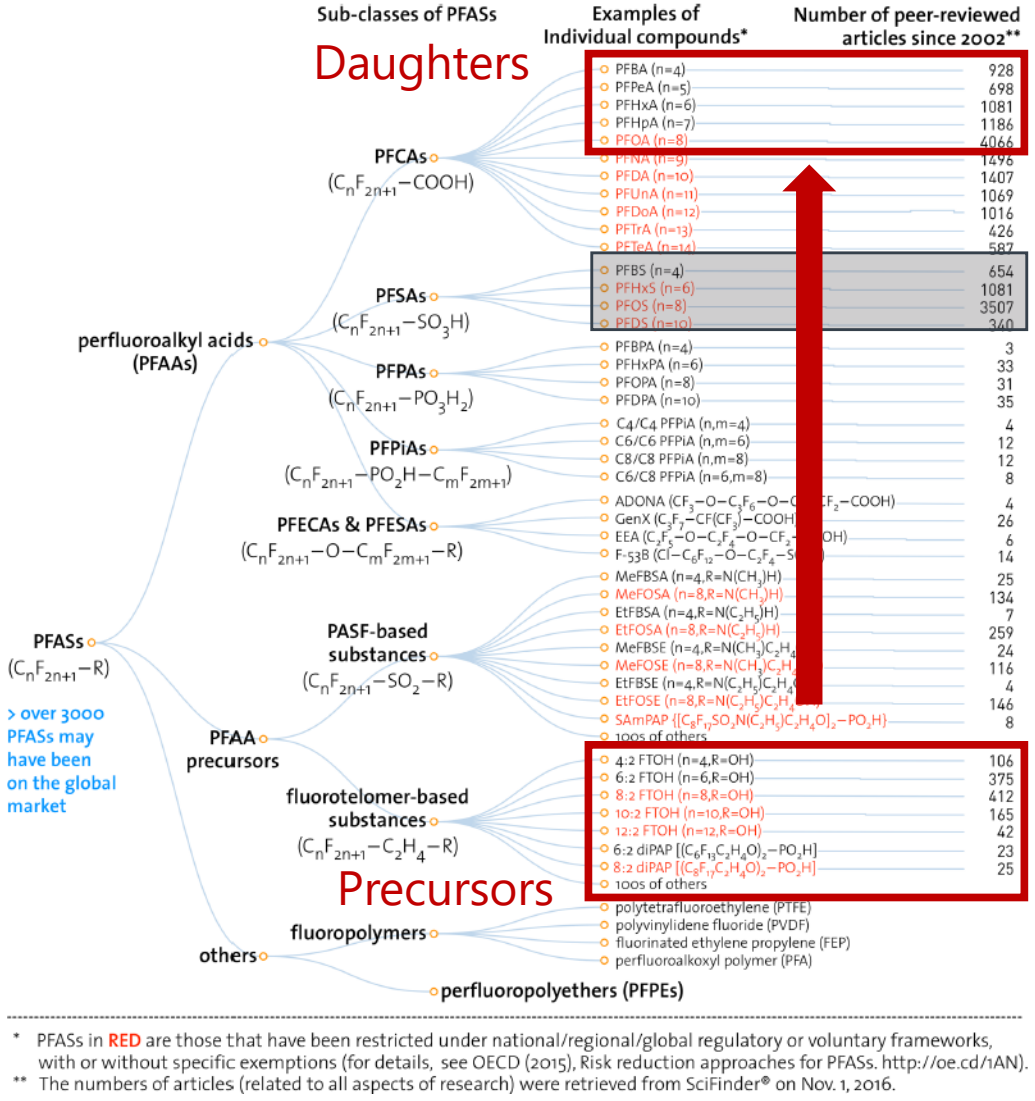
No mention of degradation in the literature for 30+ years…

- 2002 – 3M study of FTOH degradation (request pending)
- 2003 – Ellis et al notes FTOH in atmosphere degrades, suggests products are responsible for PFAS detections in remote areas
- 2004 – Dinglasan et al, Martin et al, Ellis et al, and Mabury et al publish first focused studies on FTOH degradation

- 2013 – First papers on AFFF degradation published

Degradation of AFFF and "Precursors"

- 8:2 AFFF and other FTs= PFOA precursors
- PFOA and PFCAs = daughter products
- PFOS and other PFSAs are NOT FT AFFF daughter products
- Precursors do not mineralize/degrade completely to innocuous end products



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General Degradation "Rules"

- FTs degrade through a series of chemical intermediates
- Rate of degradation is highly dependent upon the geochemical regime
- Reactions may "stall" at intermediate steps
- 100% yield is not observed

FT AFFF → PFOA – "Known Unknowns"

1. Lack of analytical standards for majority of PFAS family

2. Limited set of analytes are certified (24) and commercially available

   AFFF starting products are NOT certified analytes and FTS is not historically reported.

3. Starting material and intermediate sorption and mobility differences may invalidate assumption of parallel degradation pathways

4. Lack of degradation studies

Additional research required to address these issues.

AFFF in the Environment – "Known Knowns"

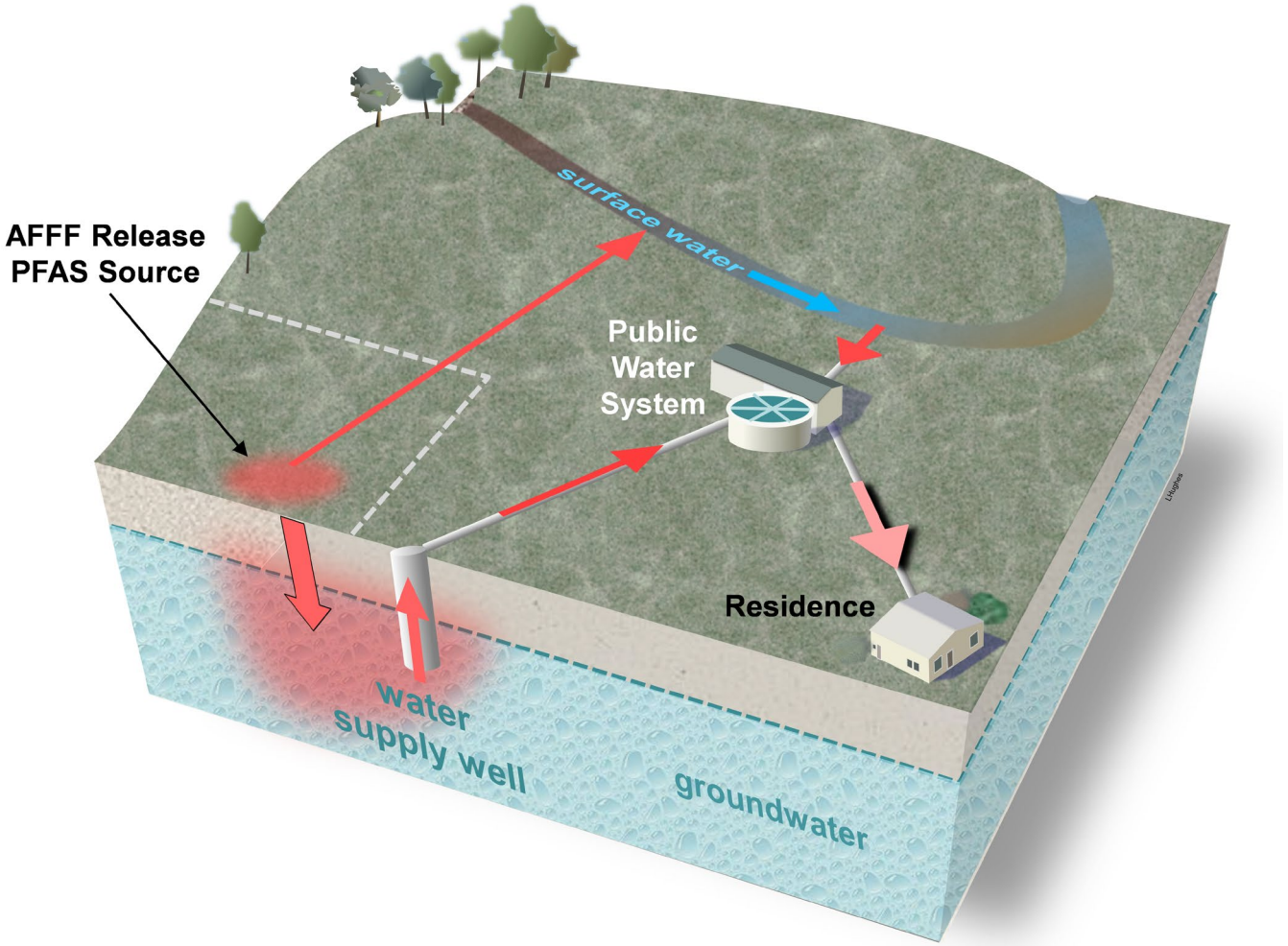
1. FT AFFF does not contain or degrade to PFOS*.
2. 8:2 (or longer) FT can degrade to PFOA through several steps.
3. Aerobic (oxygen-rich) conditions required for degradation to PFOA.
4. Not all 8:2 FT becomes PFOA (not 100% conversion).

*3M patent #3562156

AFFF related PFAS releases

- Fire stations and fire-fighting training areas
- Airports and Marine Ports
  - Runways, taxiways, maintenance ramps, and aprons (and associated drainage features)
  - Plane or drone crash sites
  - Crash debris storage areas
  - Aircraft fuel purge stations
  - Refueler truck ramp and parking areas
  - Bulk fuel storage areas with “foam lines”
  - Hangar fire-suppression systems
- Engine testing/manufacturing
- Tank farms and oil refineries

- *High concentration, short duration releases (acute)*



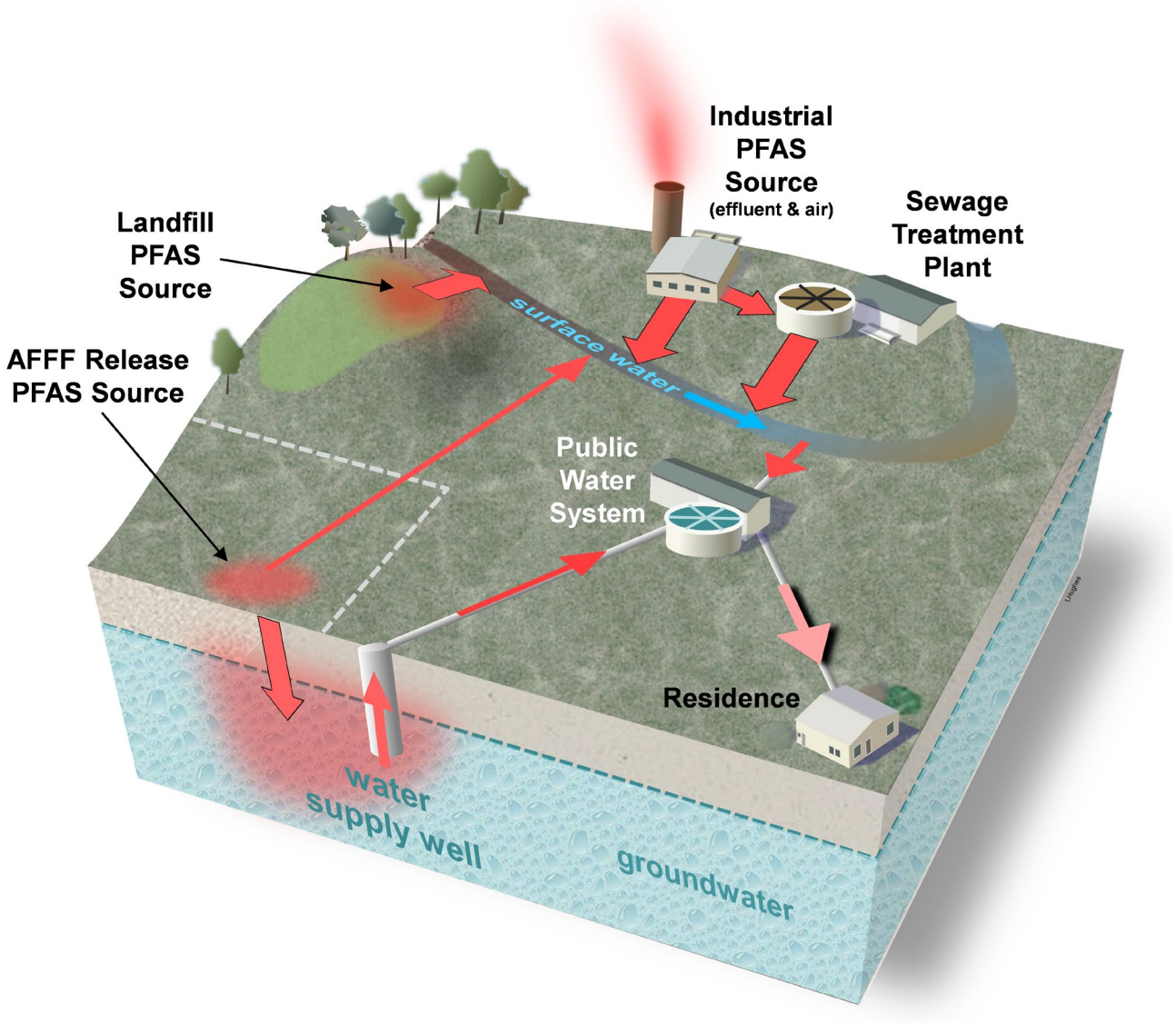
Simple Case Study

Single Source

Non-AFFF related Secondary "Sources"

- Private industrial sites – ex: West Virginia, Ohio
  - Landfills with off-spec products, wastes, sludges, etc.
  - Lagoons
  - Onsite wastewater treatment systems
- Industrial waste landfills – industrial wastes from PFAS-producers
- Municipal landfills – received "ordinary" commercial products (couches, carpets, clothing, cardboard/paper, etc.)
- Wastewater treatment plants and associated infrastructure, including drying beds, spray fields, and sludge lagoons
- Agricultural application of treated sludge leads to distribution of PFAS over a wider footprint, into a larger groundwater basin, and into food chain

- *Could be low or high concentration, but are long duration releases (chronic)*



Complex Case Study

Multiple Sources

PFAS 102 – PFAS for Practitioners

Execution of a Successful Sampling Program

- Method Selection and Expectations
- Pre-Field Planning
- Sampling Considerations
- Analyte Reporting
- Data Interpretation
- IDW Management
- Regulatory Updates

Method Selection

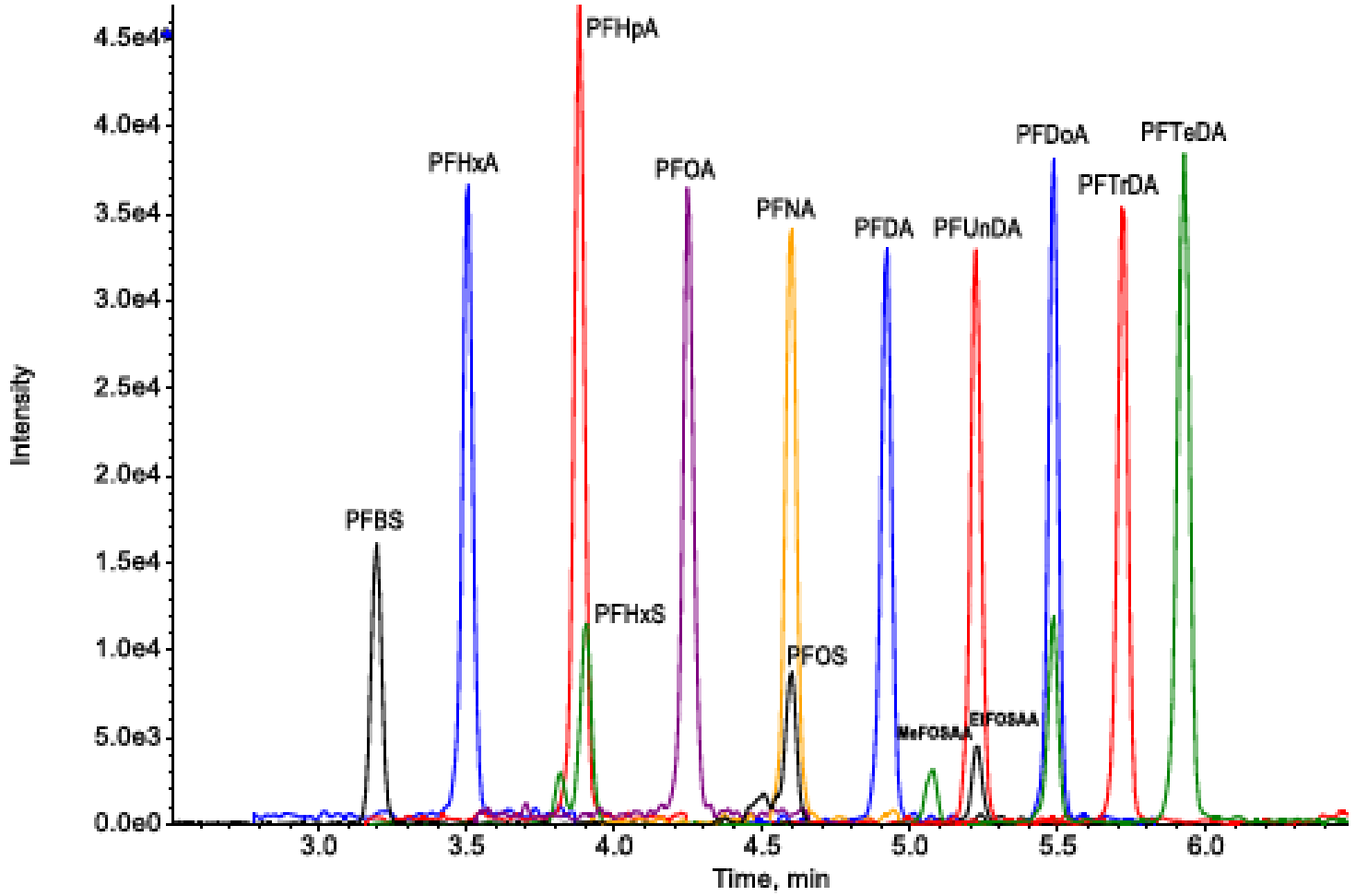
- EPA Method 533 – Drinking Water ONLY (25 analytes)
- EPA Method 537/537.1 – Drinking water ONLY (18 analytes)
- EPA Method 537 Modified – All other matrices

- Methods currently in development:
  - EPA Method 8327 – Non-potable water
  - EPA Method 3512 – Non-potable water
  - Others pending

- Total Oxidizable Precursor (TOP) Assay
- QTOF – Quantitative Time-of-Flight mass spectroscopy

Data Packages and Validation

- Branched vs linear isomers makes quantitation somewhat subjective and labor intensive
- Importance of Level IV data packages
  - Request for full data set
  - Validate minimum 10% of data
- Consider additional budget and time required



Pre-Field Planning

- Cross-contamination is a MAJOR concern
  - Careful selection of field supplies
  - Issues with personal care products, including sunscreen and bug spray
  - Food wrappers – the silent threat
  - Teflon Teflon everywhere – Discrepancies in guidance docs
  - Decon and PFAS-free water
- Field QC Samples are ESSENTIAL
  - Field, Equipment, and Trip Blanks
  - Remember extra volume of water required
  - Again – this requires additional budget!

Analyte Reporting

- Only PFOA and PFOS are consistently required from state-to-state
- Check local regulatory requirements
  - CA Water Board requires specific list of 39 analytes*
  - TX PCL screening values for 16 analytes
- Value of precursors and the full analyte list*
- Critical to establish data quality objectives and understand how the data will be used and where it will be reported

TRRP Tier 1 Listed PFAS	Acronym
Perfluorooctanoic sulfonic acid	PFOS
Perfluoroundecanoic acid	PFUnA
Perfluoropentanoic acid	PFPeA
Perfluorohexanoic acid	PFHxA
Perfluorododecanoic acid	PFDoA
Perfluorooctanoic acid	PFOA
Perfluorodecanoic acid	PFDA
Perfluorodecane sulfonic acid	PFDS
Perfluorohexane sulfonic acid	PFHxS
Perfluorobutyric acid	PFBA
Perfluorobutane sulfonic acid	PFBS
Perfluoroheptanoic acid	PFHpA
Perfluorononanoic acid	PFNA
Perfluorotetradecanoic acid	PFTeDA
Perfluorotridecanoic acid	PFTrDA
Perfluorooctane sulfonamide	PFOSA

Data Interpretation – Background and Context

- Thorough review of
  - Site history
  - Infrastructure
  - Operations/Processes – Purchasing records, SDSs, etc.
  - Emergency response action
- Desktop review is a critical time and money saving exercise
  - Focuses sampling program design
  - Provides temporal framework
- Assume PFAS is there until proven otherwise!!!

MSDS Excerpt

2. COMPOSITION / INFORMATION ON INGREDIENTS

CAS NO.	Common Name
7732-18-5	water
57018-52-7	propylene glycol t-butyl ether
7487-88-9	magnesium sulfate
proprietary mixture	proprietary hydrocarbon surfactant
proprietary mixture	proprietary fluorosurfactant

IDW Management

- Ambiguity without CERCLA designation
  - See state-specific regulations
  - EPA Interim Disposal Guidance at OMB for review
- Selection of disposal is up to property owner – risk management decision
- Characterization still necessary
  - Remember ancillary materials such as PPE
- Disposal options:
  - Sewer or landfill discharge – still retain liability
  - Destruction – Incineration, fuel blending
  - Deep-well injection
  - Filtration and disposal – on loaded GAC or resin
- Many practical considerations – case-by-case basis

Extra Credit – Regulatory Landscape

Emerging Awareness

- First came PFOA and PFOS
- Expanded to the 6 UCMR 3 compounds
- State-level regulations expanded list to 18 analytes (PFCAs and PFSAs)
- Fluorotelomers garnering increasing attention – Precursors!
- BUT over **6,500** PFAS compounds have been created
- WHAT'S NEXT???

U.S. EPA's List of 6 PFAS Compounds
Perfluorooctane sulfonate (PFOS)
Perfluorooctanoic acid (PFOA)
Perfluorohexane sulfonic acid
Perfluorobutane sulfonic acid (PFBS)
Perfluoroheptanoic acid
Perfluorononanoic acid

U.S. EPA Action Plan

- Moving forward with the process for generating MCLs for PFOA and PFOS.
- List both PFOA and PFOS as CERCLA hazardous substances and develop interim groundwater cleanup levels?
  - PFOA and PFOS are currently listed as CERCLA pollutants or contaminants
  - Advanced Notice for Proposed Rule out for comment
- 172 PFAS included in the Toxic Release Inventory and addressed under the Toxic Substances Control Act new chemicals program (or SNUR).

EPA Action Plan (cont.)

- UCMR 5 list to OMB for review – 29 PFAS Analytes (533/537.1)
- Health Advisory Levels of 70 ppt for PFOS and/or PFOA are being functionally applied under enforcement actions for drinking water clean-up.
- In states with lower promulgated standards, EPA is honoring those limits and is providing technical assistance to those states.
- Additional method development, risk assessments, remedial technology research, etc. is currently underway and will continue.

Example: California Regional Water Board Orders

- Already issued 4 orders targeting:
  - FAA-Part 139 Airports (AFFF users)
  - Landfills
  - Chrome-plating facilities
  - Wastewater Treatment Plants
- **Planned 2020** order will target refineries and bulk terminals**
  - Previous orders required soil and groundwater characterization
  - **60 days to submit Work Plans**
  - **90 days to execute and report after Work Plan approval**
  - Must report results to the state – 39 PFAS analytes
  - Results are not actionable at present *UNLESS* drinking water supplies are impacted.

Points to Ponder

- Potential sources
- Liabilities
  - Current operations
  - Historical operations
  - Industries adjacent to water supplies
- Regulatory variability
- Public perception

If You Need Support

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