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ENVIRONMENTAL® STANDARDS

Regulatory and Technical Strategies in Detecting and Quantifying Per- and Polyfluoroalkyl Substances

May 2020

Today's Presenters

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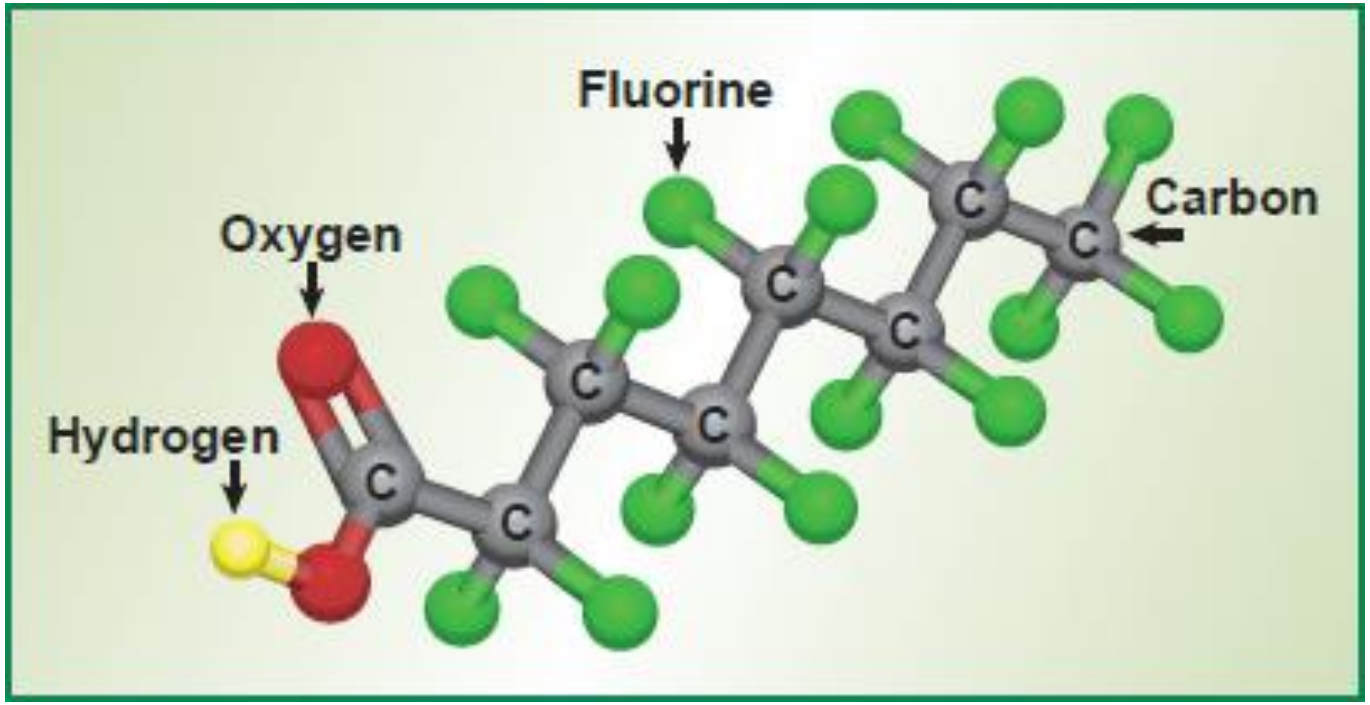
Agenda

- PFAS in Industry and the Environment
- Current and Potential Future Federal Regulation
- State Regulation and Sampling Directives
- EPA Sampling Methodologies
- Chemistry of PFAS
- Environmental Forensics
- Best Practices



PFAS Uses/Sources

Firefighting (high-temperature fires)

- Airports
- Military (DoD)
- Petroleum Refineries and Terminals

Manufacturing

- Electronics
- Metal Plating
- Aerospace/Automotive
- Fluoropolymers

Non-Industrial

- Wastewater treatment
- Biosolids Application
- Waste Disposal

Commercial and Consumer Products Containing PFAS:

- paper and packaging
- clothing and carpets
- outdoor textiles and sporting equipment
- ski and snowboard waxes
- non-stick cookware
- cleaning agents and fabric softeners
- polishes and waxes, and latex paints
- pesticides and herbicides
- hydraulic fluids
- windshield wipers
- paints, varnishes, dyes, and inks
- adhesives
- medical products
- personal care products (for example, shampoo, hair conditioners, sunscreen, cosmetics, toothpaste, dental floss)

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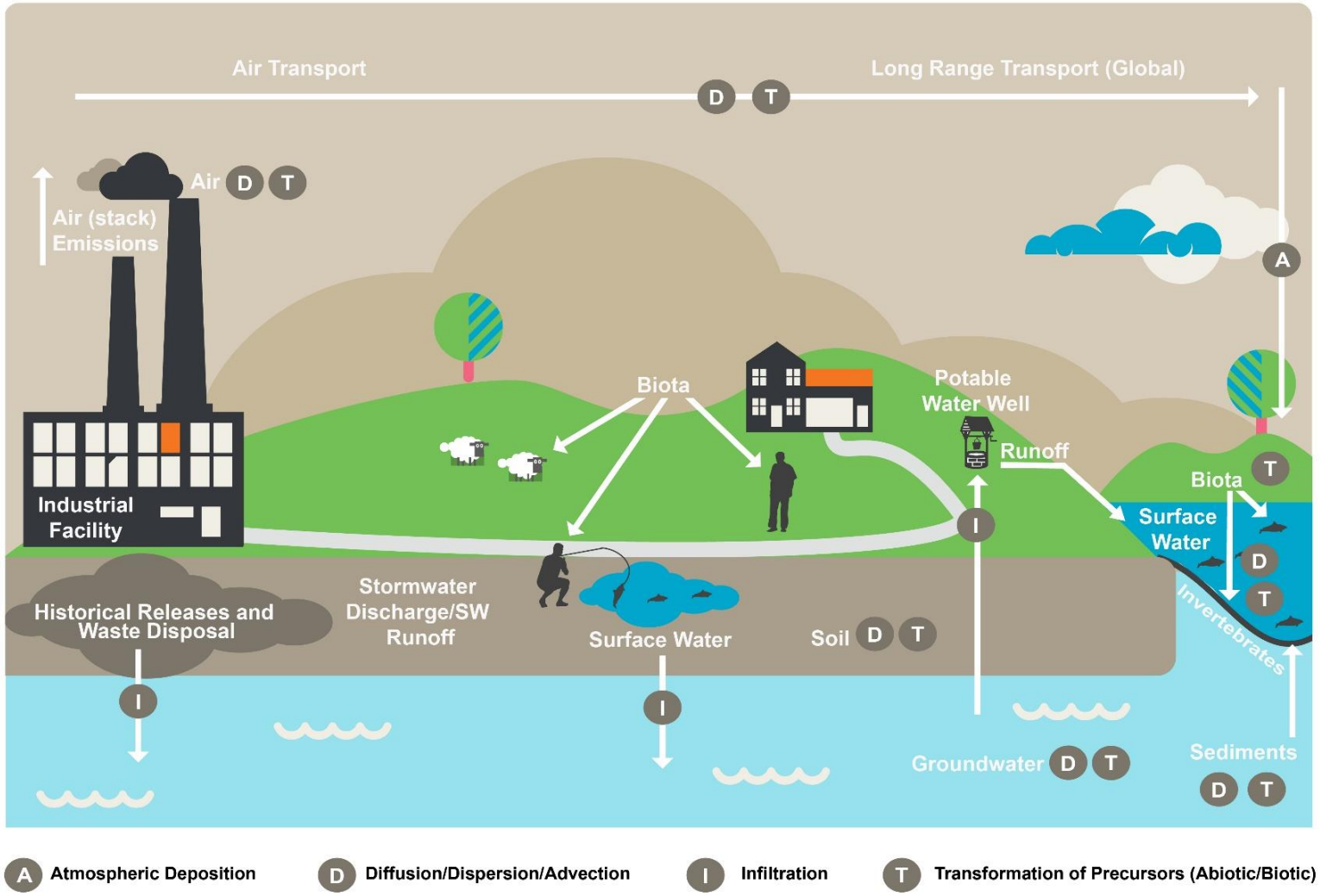
PFAS Dramatically Dubbed By the Media as "Forever Chemicals"

- By synthesis design – repels water and oil and is remarkably thermally stable
- Forms ions in soil, which are water soluble and then becomes mobile in groundwater and surface water pathways.
  - Does not biodegrade (fluorine bond very strong), but can biotransform.
- Found at low levels in the environment – first real "part-per-trillion – OMG!"
  - For perspective - carcinogenic THMs allowable up to 200,000 ppt in drinking water.
- Little toxicity information is known about ~ 99.9% of PFAS compounds.
- Regarding the < 0.1% of the remaining PFAS compounds
  - PFOA is a Group 3 carcinogen (thyroid disease)
  - PFOS bioaccumulates in aquatic lifeforms

Pathways in the Environment – The PFAS Cycle



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Varying Degrees of Hysteria in the Media – Scientists Deal with the Challenges

- PFAS analytes have garnered a ton of media attention.
  - Be ready for the PFAS discussion – no industry is immune.
- The generation of high-quality analytical data cannot be reliably accomplished solely using the current US EPA methods.
- Laboratories are being requested to analyze for PFAS in matrices that have no approved US EPA methodology.
- Laboratories have developed their own procedures, which may or may not be reliable.
- When it comes to a sound corporate risk-management plan, thoughtful program/project planning is critical.
- Pressure by the public for legislation has driven science to “catch up” with the law, burdening the regulated community.
- The legislative and regulatory directives are growing by the day.

Key Federal Regulatory Events

Toxic Substances Control Act

- **2002**: Voluntary phase out of PFOS from 2000-2002, Significant New Use Rules (SNURs) under TSCA covering 88 related PFAS compounds
- **2006**: Launch of the 2010/2015 PFOA Stewardship Program, voluntary phase out program for a certain PFAS compounds that included PFOA
- **2015/2020**: Proposed SNUR related to 2010/2015 PFOA Stewardship Program and surface coatings on imported articles
- **Ongoing:** New Chemicals Program review of replacement PFAS compounds as they are developed

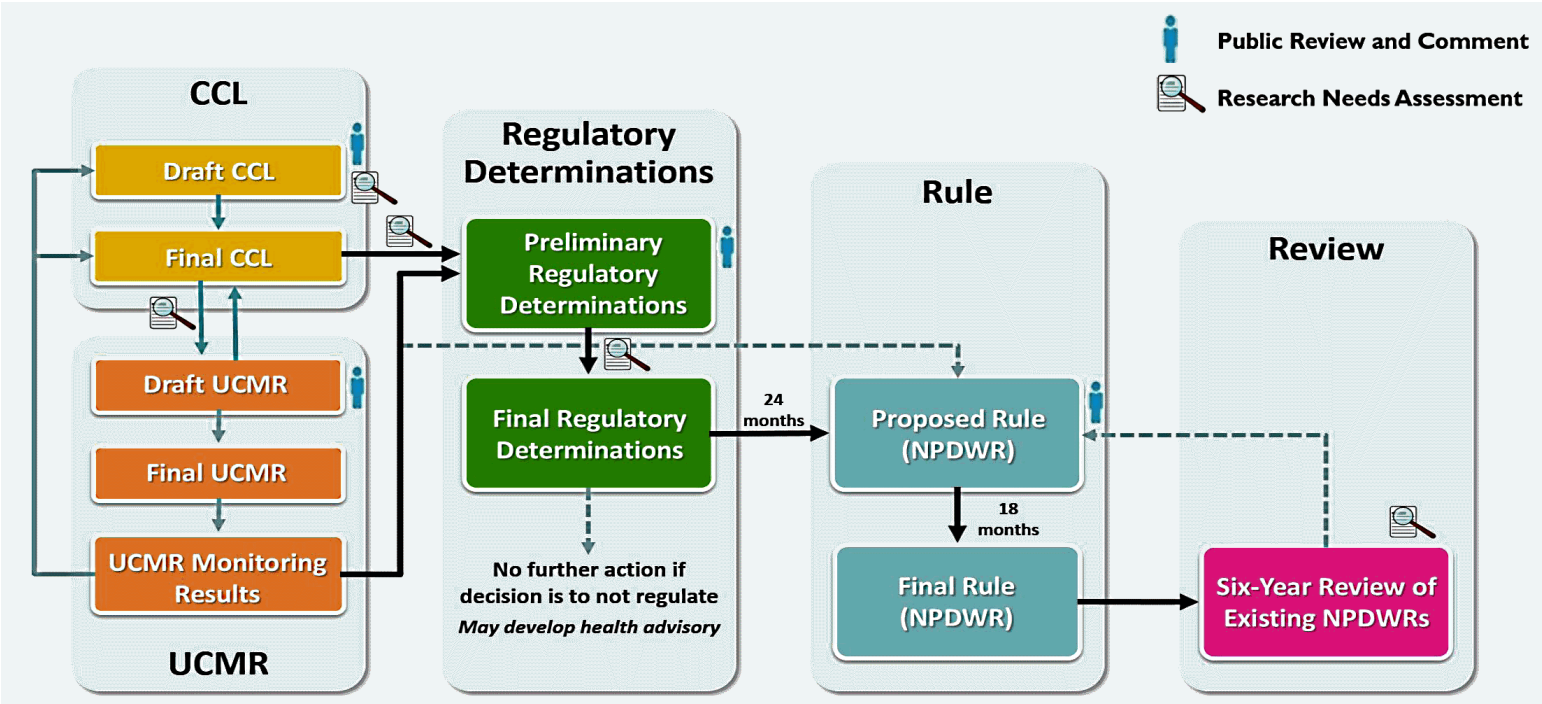
Safe Drinking Water Act

- **May 2012**: Unregulated Contaminant Monitoring Rule 3 included six PFAS, including PFOA and PFOS
- **May 2016**: Lifetime health advisory of 70 PPT under Safe Drinking Water Act for PFOA and PFOS
- **January 2017**: Final data from UCMR 3 published
- **March 2020:** EPA published its proposed Preliminary Regulatory Determinations for PFOS and PFOA in drinking water

Federal Regulation - Safe Drinking Water Act

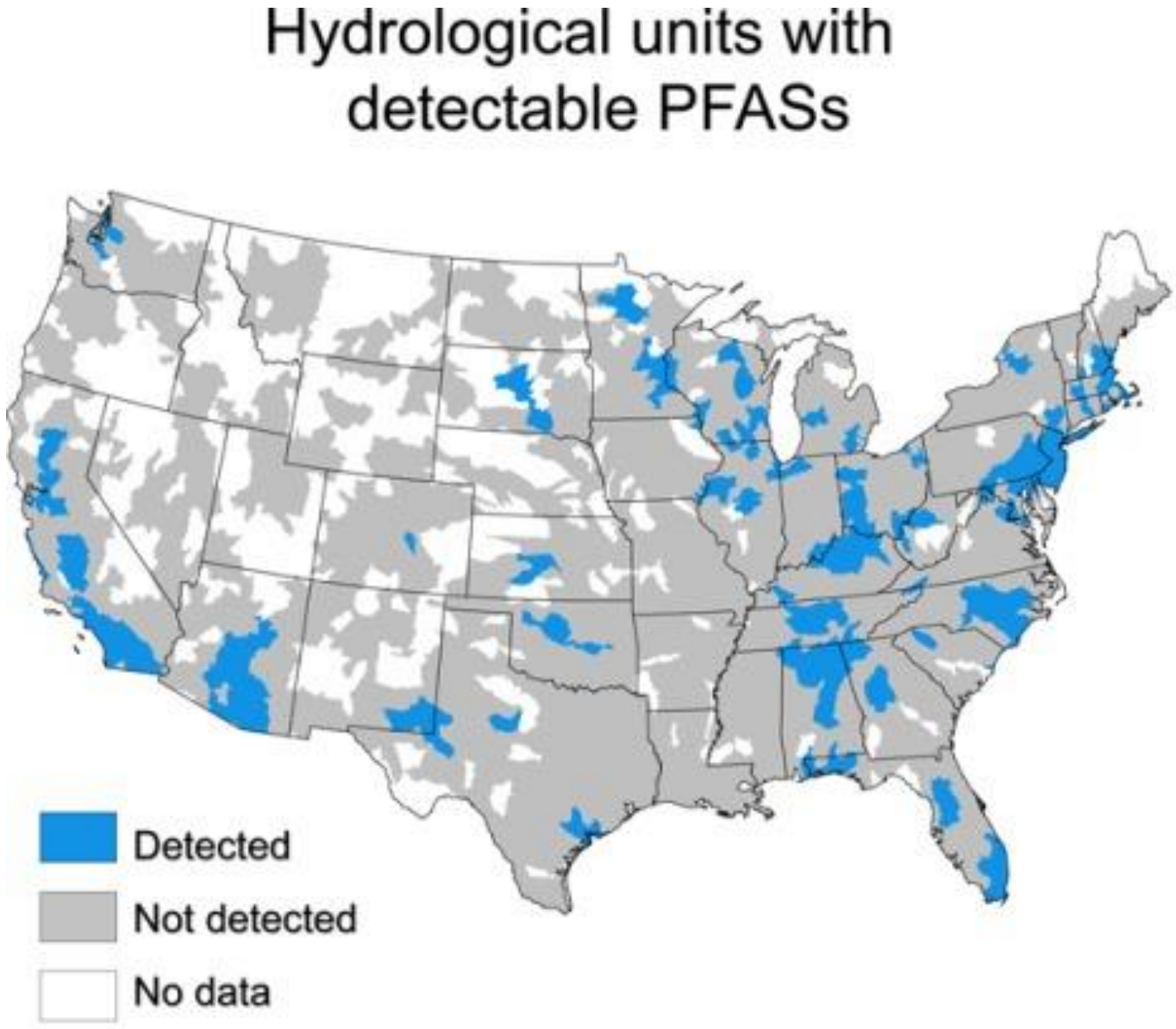
- Contaminant Candidate List (CCL) and Unregulated Contaminant Monitoring Rule (UCMR)
  - Contaminants without drinking water standards
- Large public water systems (PWS) serving more than 10,000 people and a limited number of smaller systems
- 4,920 PWS tested nationwide
- Included PFOA, PFOS, PFNA, PFHxS, PFHpA, PFBS

Regulatory Process under SDWA



Findings in UCMR 3

- PFAS found in 194 public water systems
  - PFOS: .9% of systems > 70 ppt
  - PFOA: .3% systems > 70 ppt
- 75% of detections in 13 states California, New Jersey, North Carolina, Alabama, Florida, Pennsylvania, Ohio, New York, Georgia, Minnesota, Arizona, Massachusetts, and Illinois



Federal Regulation - SDWA

- Drinking Water Health Advisory – 70 parts per trillion
  - Non-enforceable, non-regulatory
  - Only applies to drinking water, not to ingestion of food containing PFAS
- Emergency Authority (4 PFAS sites since 2002, 3 DOD sites)
- March 10, 2020: EPA issued proposed Preliminary Regulatory Determinations for PFOS and PFOA in drinking water
  - Determined that PFOA and PFOS require primary drinking water standards
  - Comment period extended to June 10, 2020

Federal Regulation - CERCLA

CURRENT

- PFAS are not currently regulated under CERCLA as hazardous substances
  - EPA can require cleanup of PFAS if imminent and substantial danger
  - EPA can require cleanup of PFAS if designated a secondary contaminant
- EPA CERLCA clean up recommendations

FUTURE

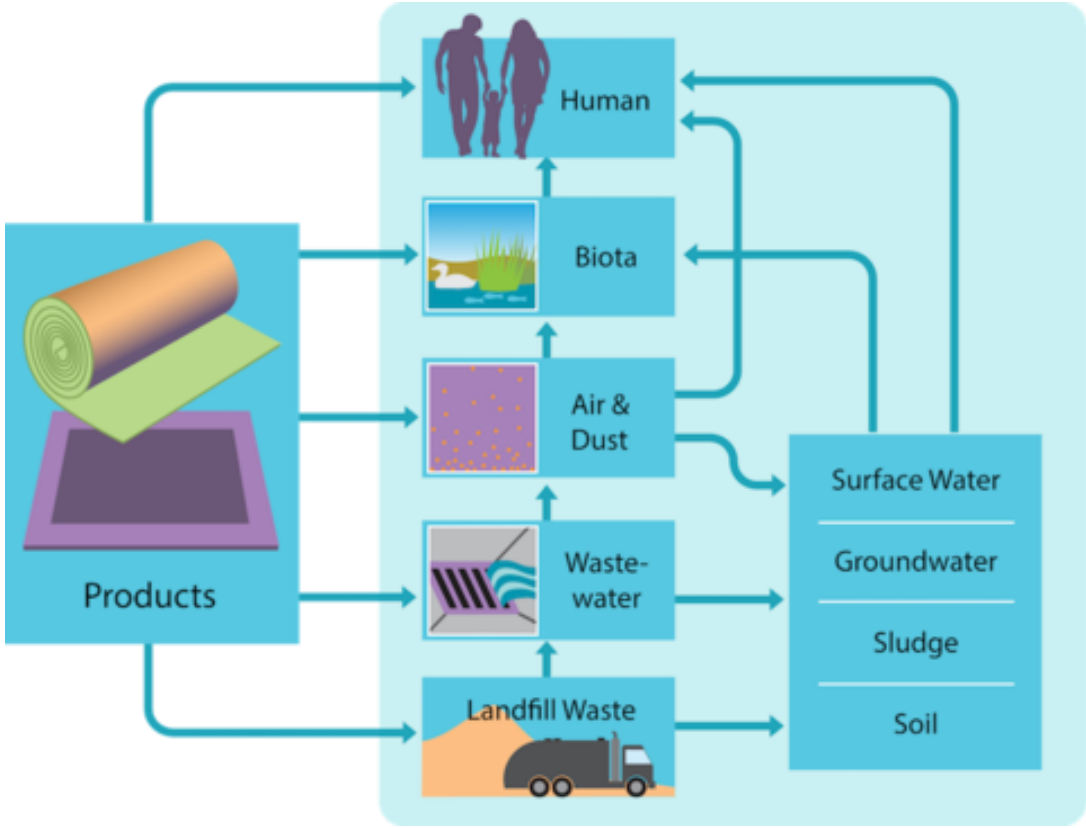
- EPA Action Plan: EPA considering listing PFOA and PFOS as hazardous substances
- Pending legislation to require EPA to designate all PFAS as hazardous substances under CERCLA
  - Potentially large price tag for government

Federal Regulation – Cleanup Recommendations

- EPA published interim cleanup guidance on December 19, 2019
- 40 ppt screening level for PFOA and PFOS individually
- 70 ppt preliminary remediation goal for PFOA, PFOS individually or combined (unless more stringent state standard applies)
  - Applies to groundwater that is a “current or potential” source of drinking water

Screening for PFAS

- What is the industry?
  - Plating operations (mist suppressant and in plating baths); Airports (firefighting foams); Landfills (site that have accepted PFAS containing products)
- What is the historical property use?
  - Is there a history of fires at the site? Was it used for land application? Industrial history?
- Water supply testing data?
  - States have only recently required testing
- Phase I Environmental Site Assessments
  - PFAS are not generally classified as a “Hazardous Substance”



2020 National Defense Authorization Act

- October 2019 – Dems send letter saying they would not support the NDAA if it did not "significantly address" PFAS. No CERCLA designation, BUT
- Prohibits the use of AFFF containing PFAS after 2024 (except on ships), and immediately in training exercises
- Broad incineration standards for incineration of PFAS for DOD
- Additional PFAS to UCMR 5
- Deadline to finalize 2015 SNUR by June 22, 2020 for articles
  - Proposal in Feb 2020 requiring notification of imported long-chain perfluoroalkyl carboxylate ("LCPFAC") substances on surface coatings
- **Immediate addition of PFAS** to the Toxics Release Inventory (TRI) starting January 1, 2020
  - Facilities that use or manufacture 100 lbs/ year
  - Reporting due to EPA by July 1, 2021
  - NDAA specifically required listing of 14 types of PFAS, list now includes **172** PFAS compounds based on NDAA criteria

EPA Guidance & Challenges to TRI Reporting

Guidance	Challenge
In determining threshold requirements, look to Safety Data Sheets (SDS)	• But don't expect to see "PFAS" on the label • Any terminology indicating a fluorinated compound • Ex: "perfluoro," "fluoro," or "fluorosurfactant" • May be listed as "proprietary" • Consider requesting additional information from manufacturer or independent sampling
The *de minimis* concentration for PFOA is 0.1%. All other PFAS have a *de minimis* level of 1%	• Listed PFAS can be created through manufacturing process • Document your threshold determination calculation
100-pound threshold applies to each PFAS, and not to the class of PFAS chemicals as a whole	• Even *de minimis* quantities can add up! • EPA is required to revaluate whether 100 lb threshold is appropriate within 5 years- and many commenters say its too high
Preliminary determination that aqueous film forming foams (AFFF) containing PFAS, would not require TRI reporting until system is used in training or emergency action	• How to dispose of AFFF stockpiles?

Federal Regulation – Clean Water Act

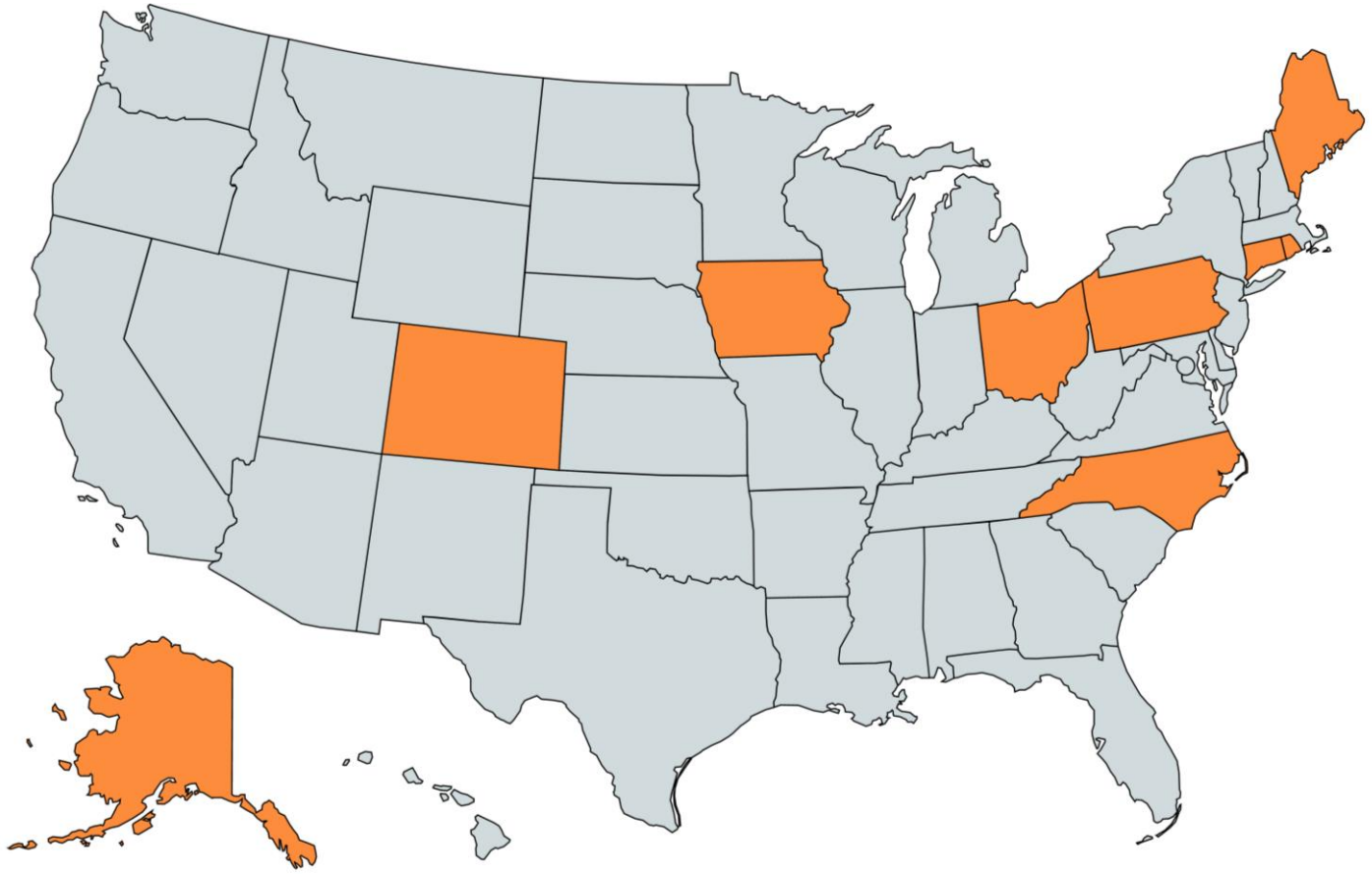
- Clean Water Act – could create effluent limitations and WQS
  - February 26, 2020 update to PFAS Action Plan
    - Risk assessment for land-applied biosolids
    - EPA study of industrial sources and discharges of PFAS to develop effluent guidelines
    - Evaluating development of water quality criteria for PFAS

Proposed Federal Regulation – H.R. 535, the PFAS Action Act

- Requires EPA to add PFOA and PFOS to the Superfund list of hazardous substances within one year and to assess all other PFAS within five years
- Sets air emission limits, prohibiting unsafe incineration of PFAS, and limiting the introduction of new PFAS chemicals into commerce
- Requires monitoring for drinking water, authorizing grants for local water systems, pausing approval of new commercial uses and permitting a "PFAS-free" label for nonstick cookware

States with standards or guidance at EPA's 70 ppt health advisory level

Alaska:	Action Level
Colorado:	Site GW Quality Standard
Connecticut:	Drinking Water Standard
Delaware:	Reporting Level
Iowa:	State GW Standard
Maine:	Remedial Action Guidelines Maximum Exposure Guidelines
New Hampshire:	GW Quality Standard
North Carolina:	Recommended GW Standard
Ohio:	Proposed Drinking Water Standard
Pennsylvania:	Medium Specific Concentration
Rhode Island:	Health Advisory

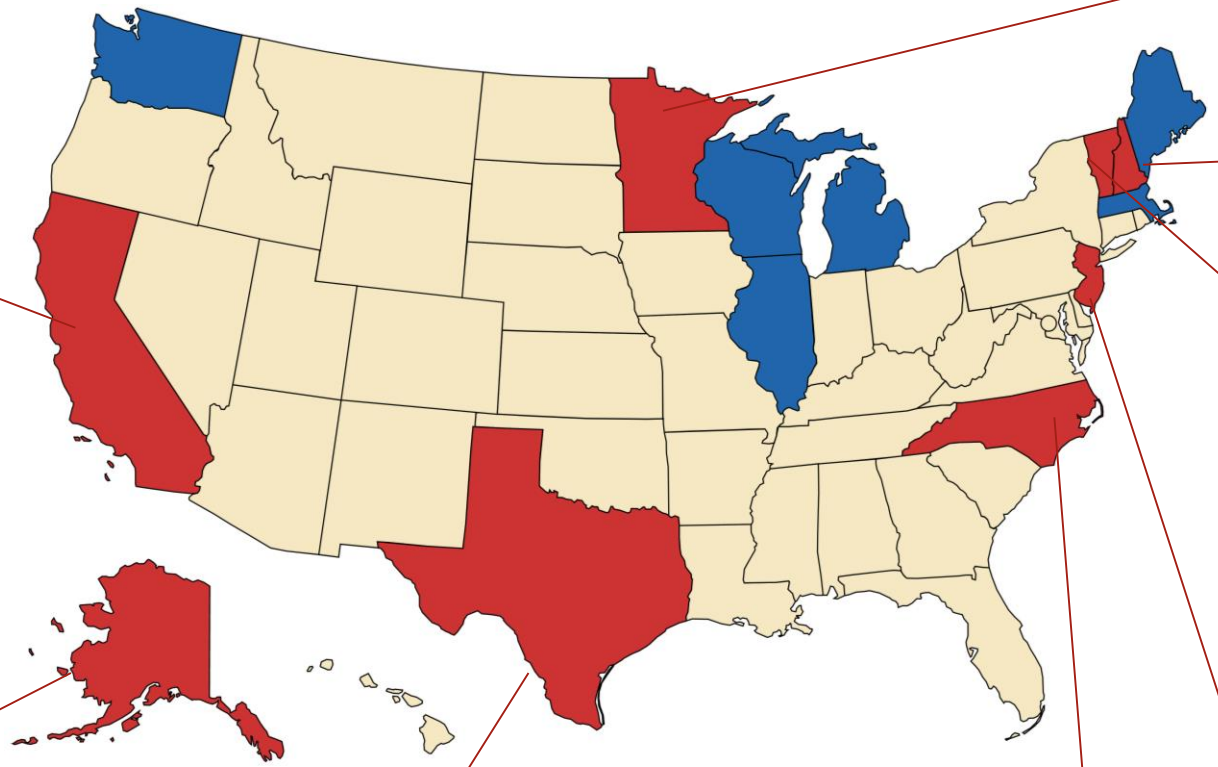


States with more stringent numeric criteria

California (drinking water notification and (response level))
5.1 (10) ppt for PFOA
6.5 (40) ppt for PFOS

Proposed Standard

Enacted Standard



Alaska (Cleanup Standard)
400 ppt for PFOA and PFOS

Texas Tier I Protective Concentration Level for 14 different PFAS, in addition to PFOA and PFOS

North Carolina GenX: (health goal) 140 ppt

Minnesota (health based standard)
35 ppt for PFOA
15 ppt for PFOS

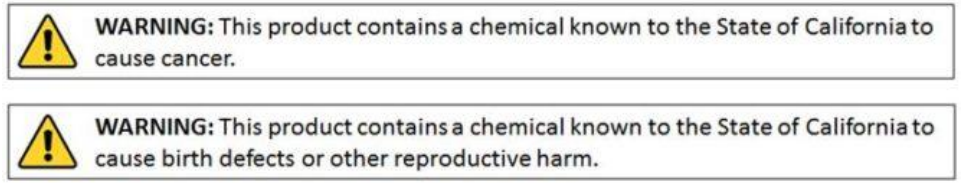
New Hampshire (DW standard (stayed per court order))
12 ppt for PFOA
15 ppt for PFOS
18 ppt for PFHxS
11 ppt for PFNA

Vermont (GW enforcement standard)
20 ppt for PFOA and PFOS, HAL for sum of 5

New Jersey (MCL)
14 ppt for PFOA
13 ppt for PFOS
Interim Class II GW
10 ppt for PFOA and PFOS

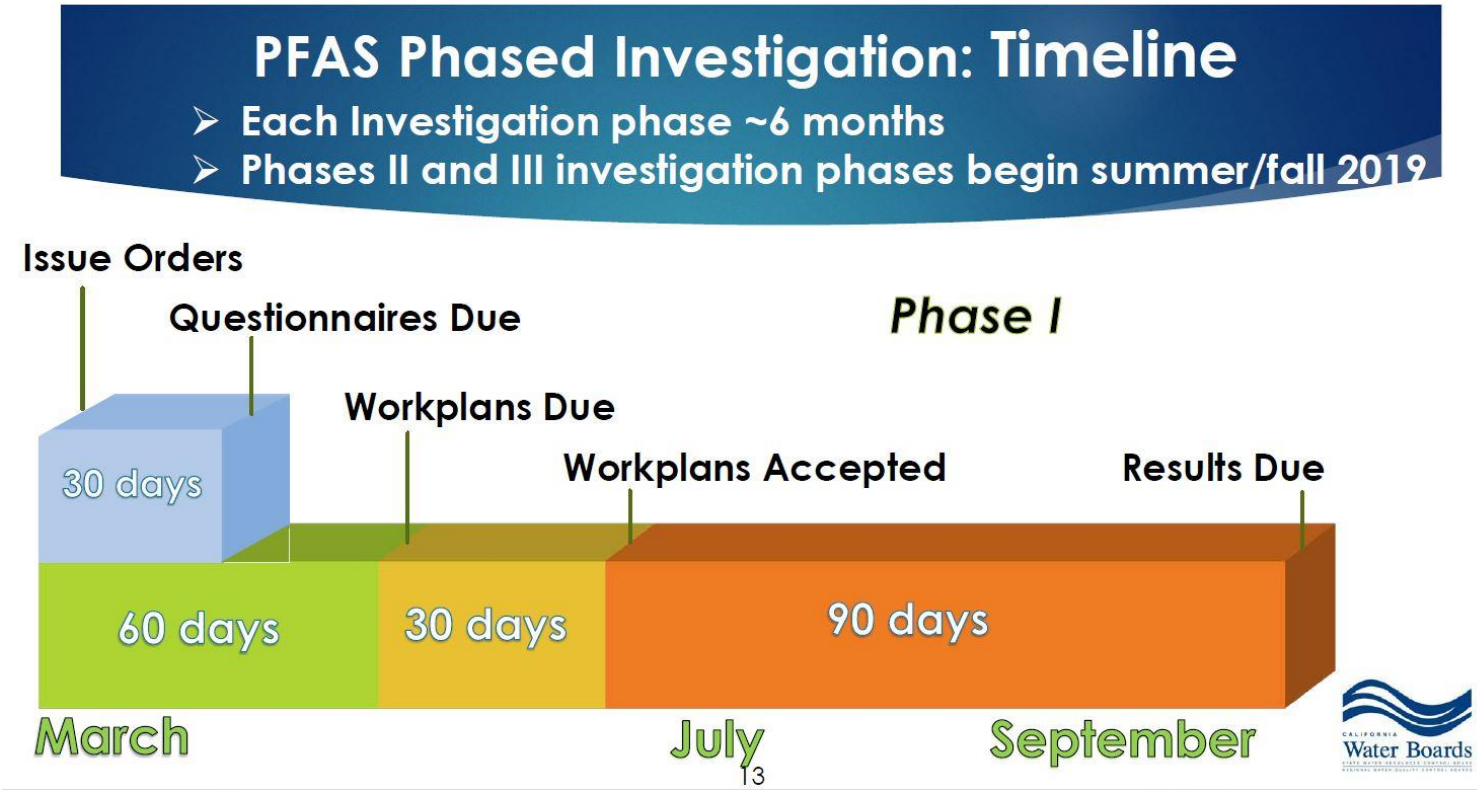
Consumer Products Laws

- November 2017 – California lists PFOA and PFOS as Developmental Toxicant under California's Prop 65
  - Warning requirement became effective on November 10, 2018 for PFOA and PFOS for "knowing and intentional exposures"
  - "Clear and reasonable warning" - labeling requirements for manufactures, distributors, and retailers
  - Discharge prohibition into sources of drinking water effective on July 10, 2019
  - No maximum allowable dose levels (MADLs) that identify levels of PFOA and PFOS exposure that are too low to require a warning



California Investigative Orders

- **133 UCMR 3 detections in California**
- **March 20, 2019:** California State Water Resources Control Board (SWRCB) Order
  - 30 airports and 196 landfills in March 2019, and 271 chrome platers in Oct 2019
    - Over 500 wells near airports and over 300 near landfills
  - PFOA, PFOS and other PFAS chemicals have been detected in roughly 50 percent of wells sampled

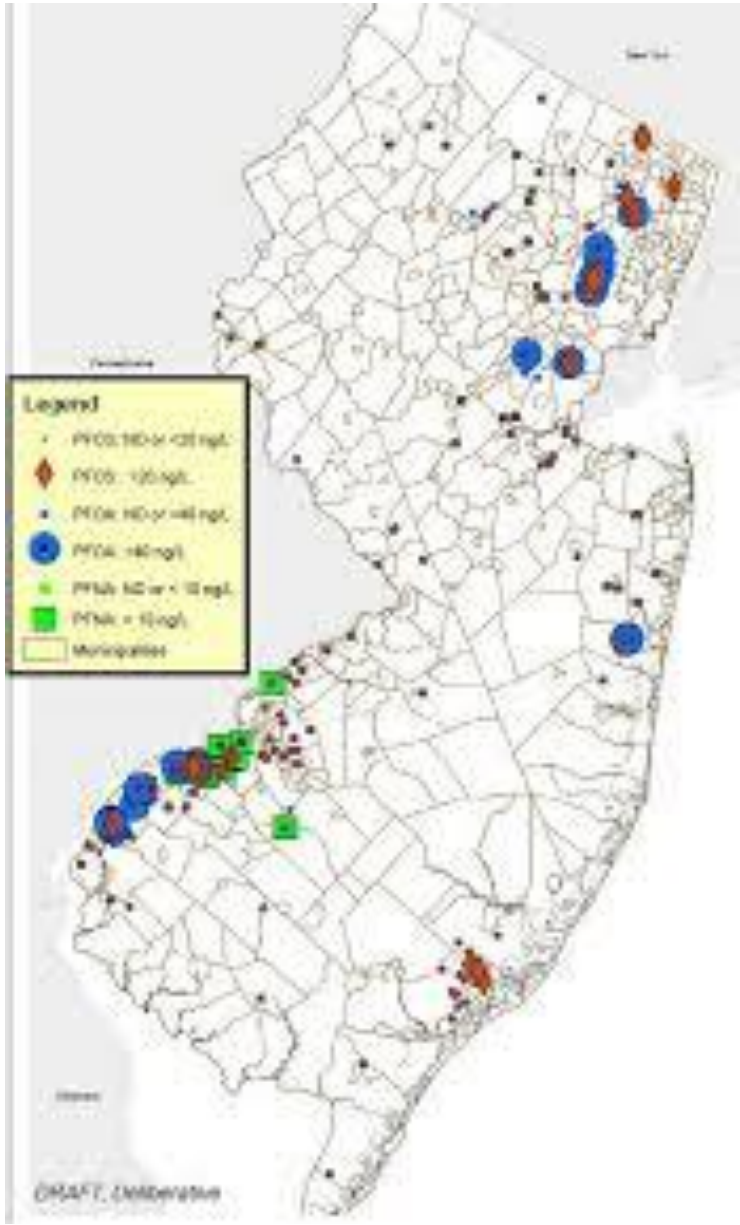


Why Chrome Plating?

- Used as mist suppressant to limit air pollution
- PFAS mixtures are used in the plating baths
- 2003 California Air Resources Board survey
- 2007 Minnesota state investigation
- 2009 USEPA Region 5 study
  - chromium electroplaters discharge PFAS to WWTPs in concentrations higher than background levels
- Fumetrol 140®

New Jersey Directive

- March 2019 – DEP issues directive to Solvay, DuPont, Dow DuPont, Chemours and 3M
  - Requires detailed accounting of PFAS use and discharge through wastewater treatment plants, air emissions, and sales of products
  - Seeks information on current development, manufacture, use and release of newer PFAS products
  - Seek to hold financially accountable for remediation and treatment



Notable PFAS Litigation

- ***Michigan v. 3M et al.***
  - On January 14, 2020, Michigan sued 3M, DuPont and 15 other chemical companies for damages, including sites that may not have been operated by the chemical manufacturers
  - State alleges that the companies "withheld scientific evidence" and "deliberately" concealed the dangers of PFAS, allowing PFAS to contaminate the state's drinking water
  - Claims include state-based cause of action under NREPA (such as transporting hazardous chemicals) and common law claims
- ***Hardwick v. 3M***
  - Hardwick is a firefighter and allegedly used foams containing PFAS
  - His suit alleges that because of the wide use of PFAS, the chemicals are in the blood of almost everybody, and requests a panel should examine the impacts

Notable PFAS Litigation

- ***In re: 3M Co. Securities Litigation***
  - Investors allege the company and its executives neglected to inform investors about the company's mounting risk of liability for its production of the PFAS chemicals
- ***In re: Aqueous Film-Forming Foams Products Liability***
  - Seventy-five cases around the U.S. against 3M and others involving contamination from the firefighting foam AFFF have been consolidated and transferred to the District of South Carolina
  - The cases are spread across eight districts, but more than half originated in Colorado

The Big Picture – Just *Go* Sample!

- The media hypes the public who demand politicians to act, who demand regulatory agencies to ACT NOW.
  - The Regulated Community is directed/pressured by Regulatory Agencies to JUST *GO* SAMPLE!!
- Industries are being *directed* to sample/analyze PFAS in environmental media (SW, soils/sediments/biomass) without US EPA methodologies.
  - US EPA has been slow to develop methods for anything but DW.
    - The only reason we have US EPA DW methods in UCMR3
- The lack of US EPA methods is a problem for the Regulated Community
  - Significant differences in procedures – forget about comparable splits.
  - Laboratory accreditation/oversight by the States is severely lacking.
  - ***Most laboratory Analysts' experience with PFAS is < 2 years***

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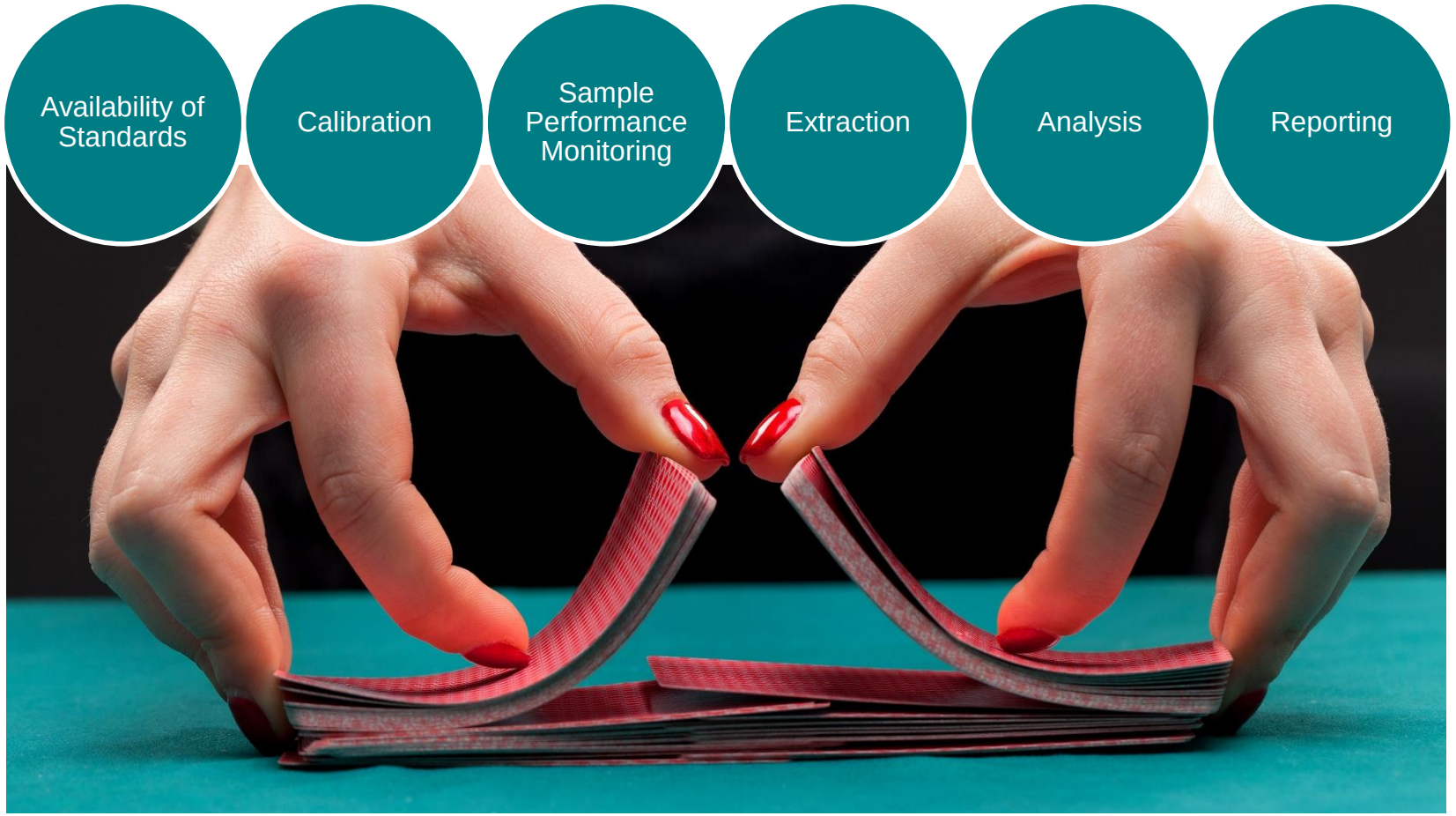
Current US EPA PFAS Methods

- US EPA Method 537.0 – Drinking Water - First Published in 2009
- US EPA Method 537.1 – In 2018 - *Same* as 537.0 but added four PFAS
- US EPA Method 533 – Drinking Water - December 2019
  - Added 11 PFAS (shorter chains) – Finally, isotope dilution quantitation
- US EPA SW-846 Method 8327 – Non-DW Aqueous
  - June 2019 - Direct injection, screening only *and not usable*
  - Environmental Standards draft method comments can be found at *https://www.regulations.gov/document?D=EPA-HQ-OLEM-2018-0846-0103*
- Solids: No published/validated US EPA methods yet
- Ambient Air: No published/validated US EPA methods yet
- Commercial laboratories are “making up” analytical methods for PFAS analysis in non-DW matrices due to lack of approved US EPA methodologies.

Laboratories “Making Up” Their Own Analytical Methods for Non-Drinking Water Matrices

Variations impact data comparability and increase *chaos*



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Reference Materials and Standards

- US EPA Method 537, 533 and DoD QSM indicate that standards should include linear and branched isomers unless unavailable.
- Standards are not available for all branched and linear PFAS target compounds.
- There are a limited number of isotope-labeled compounds available, and the list of PFAS analytes being requested is growing quickly.

Calibration Model Variability

- External standard *or* Internal standard *or* Isotope dilution
- Calibration models:
  - Average RF or RRF, Linear equation with/without weighting
  - Quadratic equation with or without weighting
- Forcing the calibration curve through the origin (or not)

Sample-specific Performance Monitoring

- External standard technique or internal standard technique
  - Surrogate compounds added prior to extraction monitors extraction performance
  - Internal standard added immediately prior to instrument analysis monitors instrument
- Isotope dilution technique – this is the *gold* standard
  - FINALLY in Method 533, but was not in Method 537 or 537.1
  - Labeled compounds added prior to extraction for isotope dilution compensates for extraction efficiency
  - Labeled compounds used to calculate target results
  - Internal standard added prior to analysis to quantitate labeled compounds (well, not all laboratories)

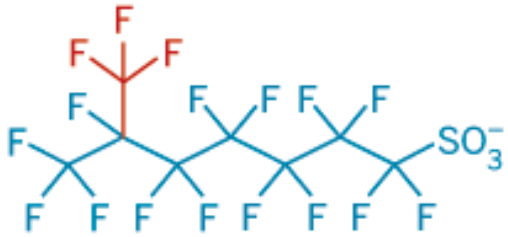
Solid Matrix Extraction Techniques

- ASTM Method D7979-16 and D7979-17 – methanol shake/vortex (aqueous and sludge)
- ASTM Method D7968-17 – methanol and vortex
- DoD QSM 5.3 - not specified for solids/sediments
- Laboratory-specific modified methods - ***anything*** goes
- Solid (Soils/Sediments/Biomass) extractions may include:
  - Shake/Vortex Sonicate, automated extraction or microwave
- Extraction solvents (reagent water, methanol, acetonitrile)
- Extract cleanups – important in complex solids (biomass)
- Extract blowdowns:
  - Concentrated to dryness then transferred into final solvent
  - Concentrated, but not to dryness or … or not at all

Down in the PFAS Isomer Weeds

- Integration of PFAS Chromatographic Peaks
  - There are many PFAS analytes – some have lots of isomers.
  - We have branched and linear isomers.
  - Integration of the isomer peak(s) *is not straight forward*
- Synthesis by Electrochemical Fluorination (historic)
  - Mix of branched and linear isomers
  - Odd & even number carbon chain lengths
  - Manufacturer- 3M
- Synthesis by Telomerization
  - Results in an “Isomerically pure” product
  - Maintains the geometry of starting telogen
  - Major product C8 or C9
  - Manufacturer- DuPont

PFOS linear isomer



PFOS branched isomer

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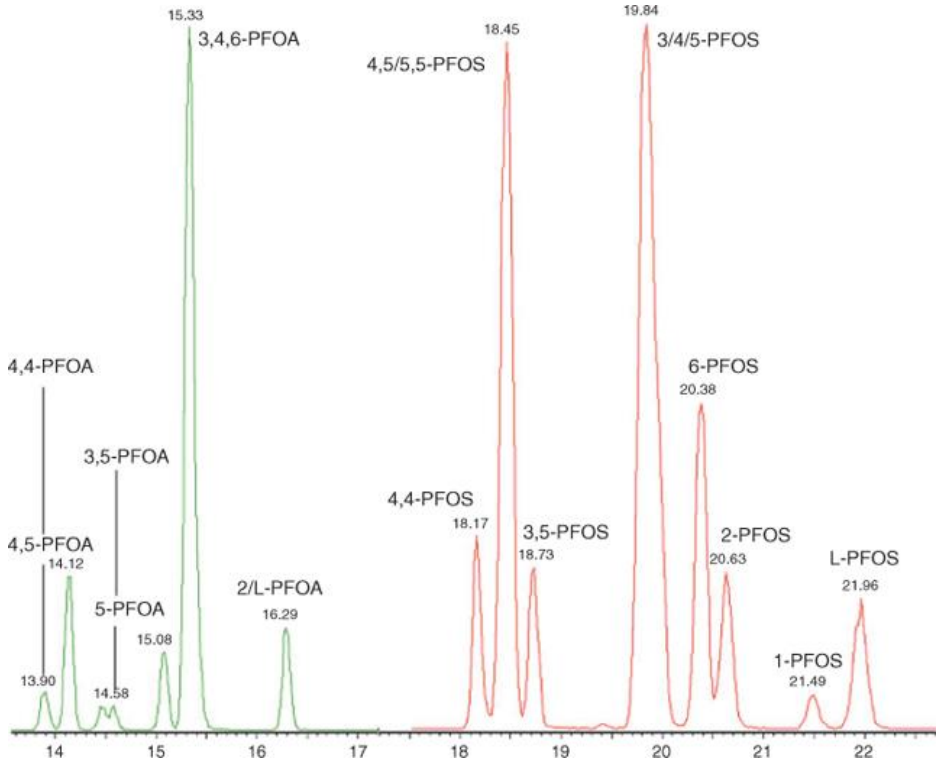
Branched/Linear Configurations

PFOS anion ($C_8F_{17}O_3S$) for Example

- There are 89 structural isomers
- There are 11 isomers in most current reference standards
- Technical-grade standard
  - 68.3% linear
  - 30.1% methyl isomers
  - 1.6% dimethyl isomers
- Quantitation-grade standard
  - 78.8% linear
  - 20.4% methyl isomers
  - 0.7% dimethyl isomers



Kärrman, et al., *Environmental Chemistry* 8(4) 372-380 2011
http://dx.doi.org/10.1071/EN10145

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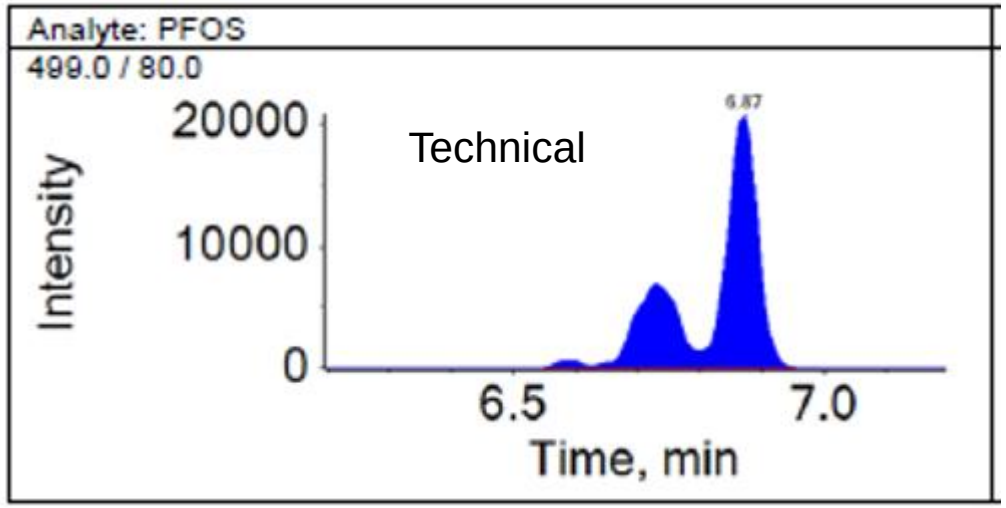
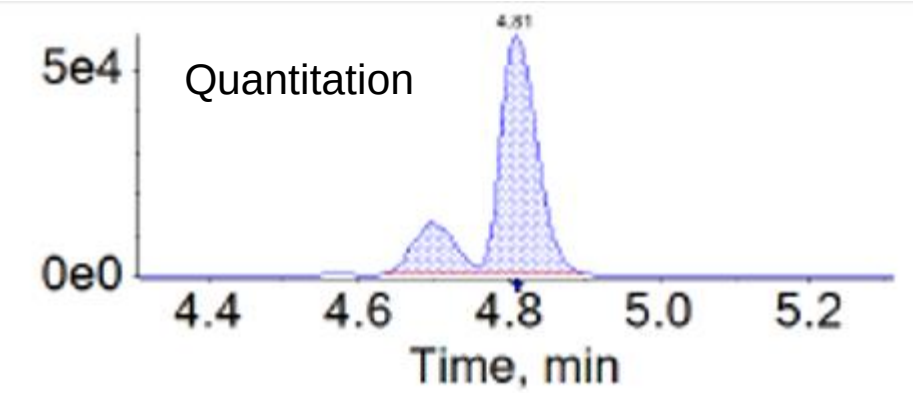
Branched/Linear Configurations (Cont.)

PFOS anion ($C_8F_{17}O_3S$)

- Technical-grade standard
  - 68.3% linear
  - 30.1% methyl isomers
  - 1.6% dimethyl isomers
- Quantitation-grade standard
  - 78.8% linear
  - 20.4% methyl isomers
  - 0.7% dimethyl isomers
- Dimethyl isomers often not included for quantitation





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Sampling Is Not a Trivial Undertaking

- PFAS are everywhere and traditionally actually in materials used in environmental investigations (field and laboratory !!)
  - Sampling bailers and laboratory instrument fittings made from Teflon®
  - Samplers don Tyvek® and clothes treated with PFAS
- Samplers must take extraordinary precautions to minimize contamination beyond “clean hands-dirty hands” techniques
  - Quality control samples are extremely important to track adulterants
  - Blanks of all kinds – bottle, field, rinsate/equipment
  - Field duplicates/replicates and *even* blind performance samples

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Targeted and Non-Targeted PFAS

- Literature sources suggest that there are 3000 to 6000 PFAS compounds
- PFAS target compounds listed in Methods 537, 533 and 8327 – < 0.1% of total
- Currently, there are certified reference standards for about 50 PFAS compounds
- Linear *vs.* Branched isomer resolution/separation – *complicating* wild card
- Recent US EPA TRI rule requires information on 172 compounds
- TOPs (total oxidizable precursors) Assay
  - "Cook" (digest) samples under strong alkaline oxidizing conditions to convert the telomers to shorter-chain PFAS
  - TOPs Assay theoretically simulates the potential PFAS that may, given time, *weather* to target PFAS substances of concern – NOT proven to be a reliable predictor of abiotic and biotic breakdown in natural environments
  - Worse-case assumptions and a regulatory reporting nightmare – RUN AWAY !!

PFAS – Environmental Forensics

- Target compounds are only about 50 compounds (~ 1%)
- For forensic applications develop project-specific fingerprinting strategies to assess/identify/rule out sources
- Fingerprinting by Non-Targeted Analysis (NTA)
  - Known unknowns (Suspect Screening Analysis) (~ 5 to 10%)
  - Unknown unknowns (Non-Targeted Analysis) (90-95%)
  - ENTACT (US EPA's Non-Targeted Analysis Collaborative Trial)

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Additional Forensics/Fingerprinting Tools

- Use standard and research-grade high-resolution methods.
  - Finer separation of isomers utilizing multiple runs on different elution columns.
  - LC/MS/MS TOF to further fingerprint other non-target PFAS.
- Evaluate data-dependent and data-independent acquisitions.
- Evaluate chromatographic pattern recognition in totality.
- Explore spectral deconvolutions and apply peak-matching algorithms across multiple files to identify potentially relevant signatures.
- Determine precursors and degradation products from suspected sources.
- Use exact mass results to pull structures and physicochemical properties from PFAS databases.
  - US EPA's DSSTox database ~ 875,000 mass spectrally ready structures.
  - US EPA CompTox database includes NIST mass spectral library database.

Additional Forensics/Statistical Tools

- Cluster analysis for scoring profile similarities
- Multivariate analysis for identifying source profiles
- Linear mixing models or dimension reducing analyses to find best fit for allocations

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Best Practice Risk Management Actions

- Understand your drinking water and process water sources.
- Understand the PFAS Action Plan in States where you have assets.
- Prepare a company-wide PFAS risk-management plan.
  - Conduct a thoughtful and realistic PFAS inventory.
  - Identify and contract with qualified sampling and laboratory vendors.
  - Prepare technical specifications for contracting sampling consultants and analytical laboratories.
- Engage with State legislators and manufacturing associations and get a seat at relevant discussion tables.

Proactively Direct, Audit and Manage PFAS Liability – Best Practices

- Critically review consultants' sampling procedures.
- Contractually *Mandate* laboratory analytical requirements.
- Actively *audit* your sampling and analytical vendors.
- Contract a qualified third-party PFAS chemistry consultant to assess *field* and laboratory data quality as data are being generated and reported.
  - Immediately troubleshoot/correct suspicious data.
- Centralize your sampling and analytical PFAS data using enterprise data management platforms - larger scale programs.

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Questions? Thank you!