

PFAS - The (Rapidly) Evolving Technical and Legal Landscape

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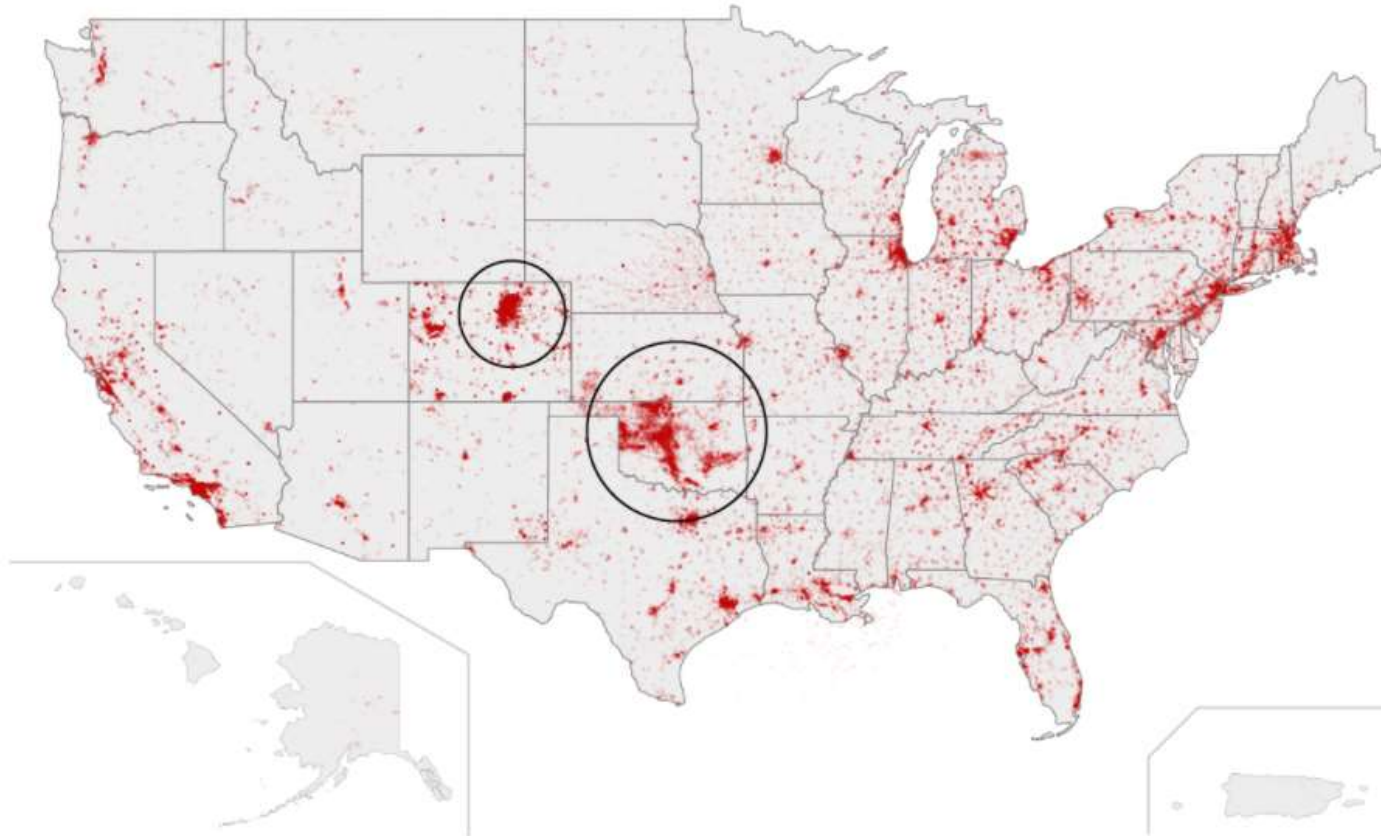
Legal Landscape

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The EPA identified more than 120,000 facilities that may expose people to PFAS

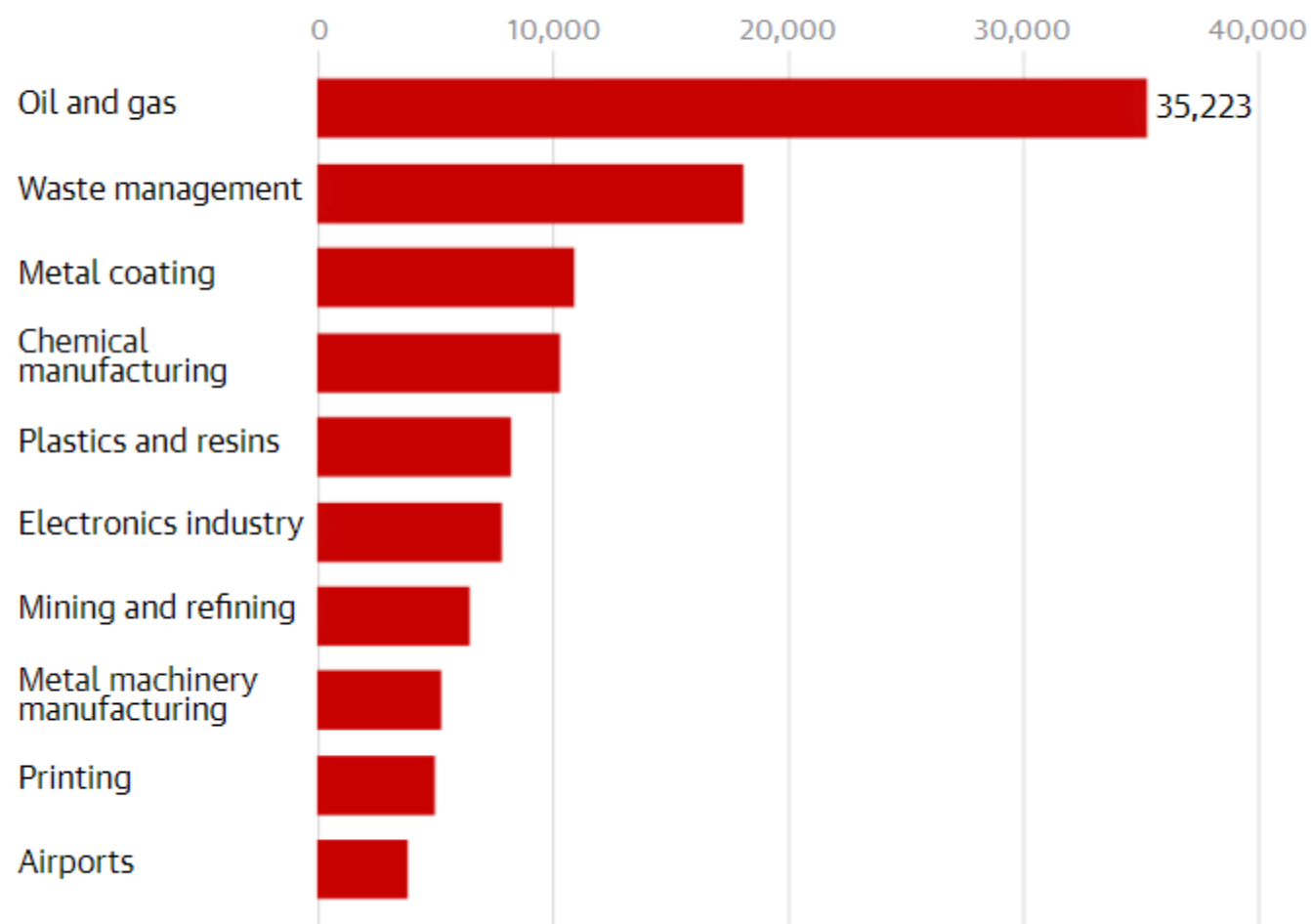
The biggest clusters of facilities are in Oklahoma and Colorado



Guardian graphic. Source: US Environmental Protection Agency

Facilities potentially handling PFAS - top 10 industries

Facilities may be counted twice if they belong to multiple industries



Guardian graphic. Source: US Environmental Protection Agency

Even More Data on the Way

- ▶ Expanded TRI Reporting
- ▶ TSCA Section 8 Reporting
- ▶ Nationwide Drinking Water Monitoring
- ▶ Multi-laboratory Validated Analytical Method for 40 PFAS
- ▶ Update PFAS Analytical Methods for Drinking Water
- ▶ Monitor Fish Tissue for PFAS

Effluent Guidelines and Risk Assessments

- ▶ Primary Drinking Water Regulation for PFOS and PFOA
- ▶ Effluent Limitation Guidelines for PFAS Discharge
- ▶ NPDES Permit Limits
- ▶ Water Quality Standards
- ▶ GenX, PFBS and other toxicity assessment and health advisories
- ▶ Risk Assessment for PFOA and PFOS in Biosolids

CERCLA Listing and Remediation

- ▶ Certain PFAS as CERCLA Hazardous Substances
- ▶ Consideration of Precursors as Hazardous Substances
- ▶ Guidance on Destruction and Disposal



Identification

Focus on Expanding Analytical Capabilities

▶ Target Methods

- EPA Method 531.1 – 18 PFAS in Drinking Water
- EPA Method 533 – 29 PFAS in Drinking Water
- Modified Methods – 75 PFAS
- Draft EPA Method 1633 – 40 PFAS in Waste Water, Surface Water, Groundwater, Soil, Biosolids, Sediment, Landfill Leachate, and Fish Tissue

▶ Total oxidizable precursor (TOP) assay [ppt]

- Oxidation of precursors to detectable byproducts
- Commercially Available

▶ Estimates as high as 8,000 PFAS

▶ 241 commercially relevant PFAS (Buck et al., 2021, IEMA)

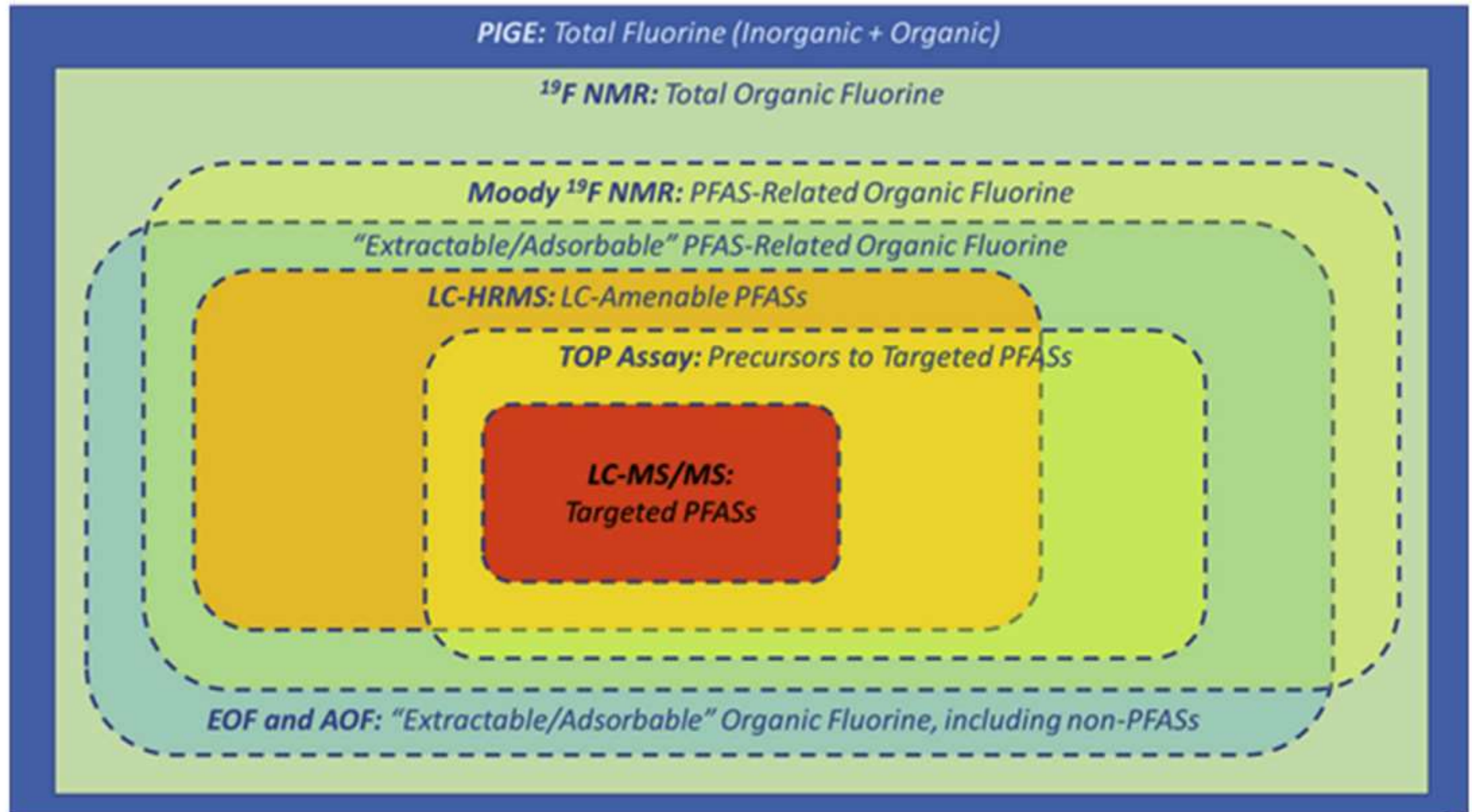
▶ Clear gap in analytical capabilities

▶ EPA commitment to update analytical methods (Fall 2024)

▶ Calls to manage PFAS as a class of chemicals

Total PFAS via Organofluorine Measurement

- ▶ Extractable organic fluorine (EOF) / adsorbable organic fluorine (AOF) [ppt/ppb]
 - Sample prepared to isolate organofluorine
 - combustion ion chromatography (CIC) to mineralize and measure organic fluorine
 - CIC does not differentiate between organic fluorine and fluoride, nor does it offer any structural details about the detected compounds.
 - Commercially Available
- ▶ Particle-induced gamma ray emission (PIGE) [ppb]
 - Generally Nondestructive
 - Surface analysis technique for quantification of elemental fluorine
 - Beam of protons excites ^{19}F nuclei, emits Gamma rays
 - Best suited for solid-phase samples.
 - Currently in R&D stage (SERDP/ESTCPER19-1142)
- ▶ Fluorine-19 nuclear magnetic resonance spectroscopy [ppb]



McDonough, Guelfo, Higgins, 2019

Current Opinion in Environmental Science & Health

Applications of TOF methods

- ▶ Screening Methods
 - Presence or Absence of PFAS in products, wastes, etc.
- ▶ Remediation / Treatability
 - Closing mass balance
 - Performance monitoring
 - Influent / effluent mass balance
- ▶ Risk Management
 - Are there PFAS in this waste, soil, biosolids?
- ▶ Consumer Product Verification
 - Demonstration of “PFAS Free”

Non-Target Analysis - LC/MS-qTOF (quadrupole time of flight mass spectrometry)

- ▶ Higher Cost
- ▶ Comparison of peaks to library
- ▶ Quantitative results for hundreds of non-target PFAS
- ▶ Qualitatively identify many more PFAS
- ▶ More comprehensive understanding of sample than target-methods. But, some limitations in interpretation.
- ▶ When to use?
 - Forensic evaluations – Is this my PFAS?
 - Due diligence – Document conditions at the time of sale/purchase
 - Mass balance assessments



Investigation

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PFAS Characterization Challenges

Complex Interactions/Transport Behavior

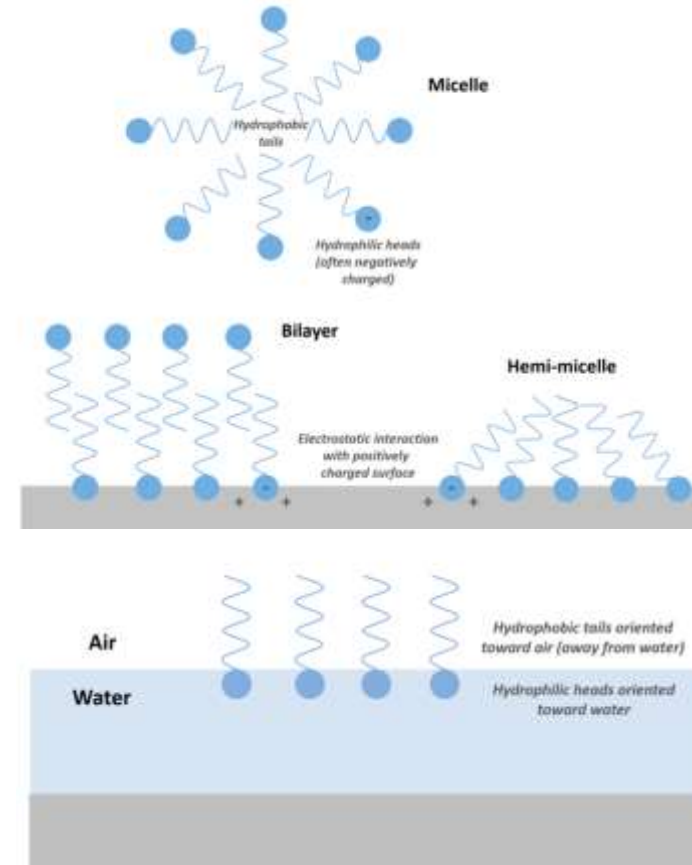
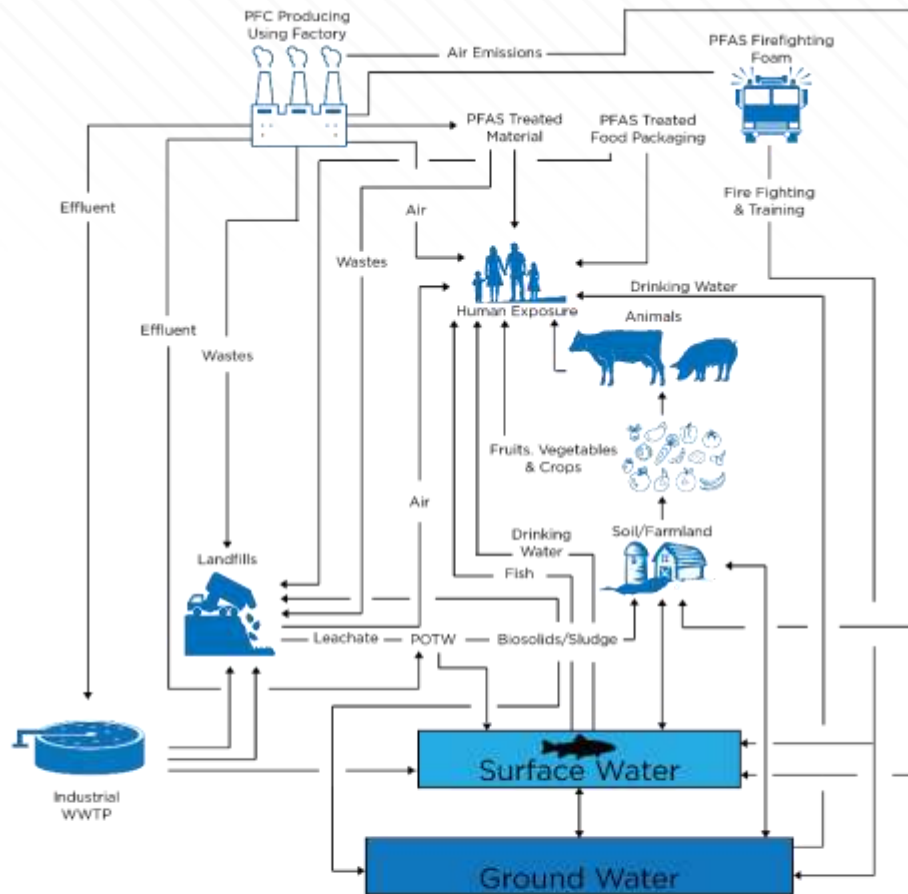
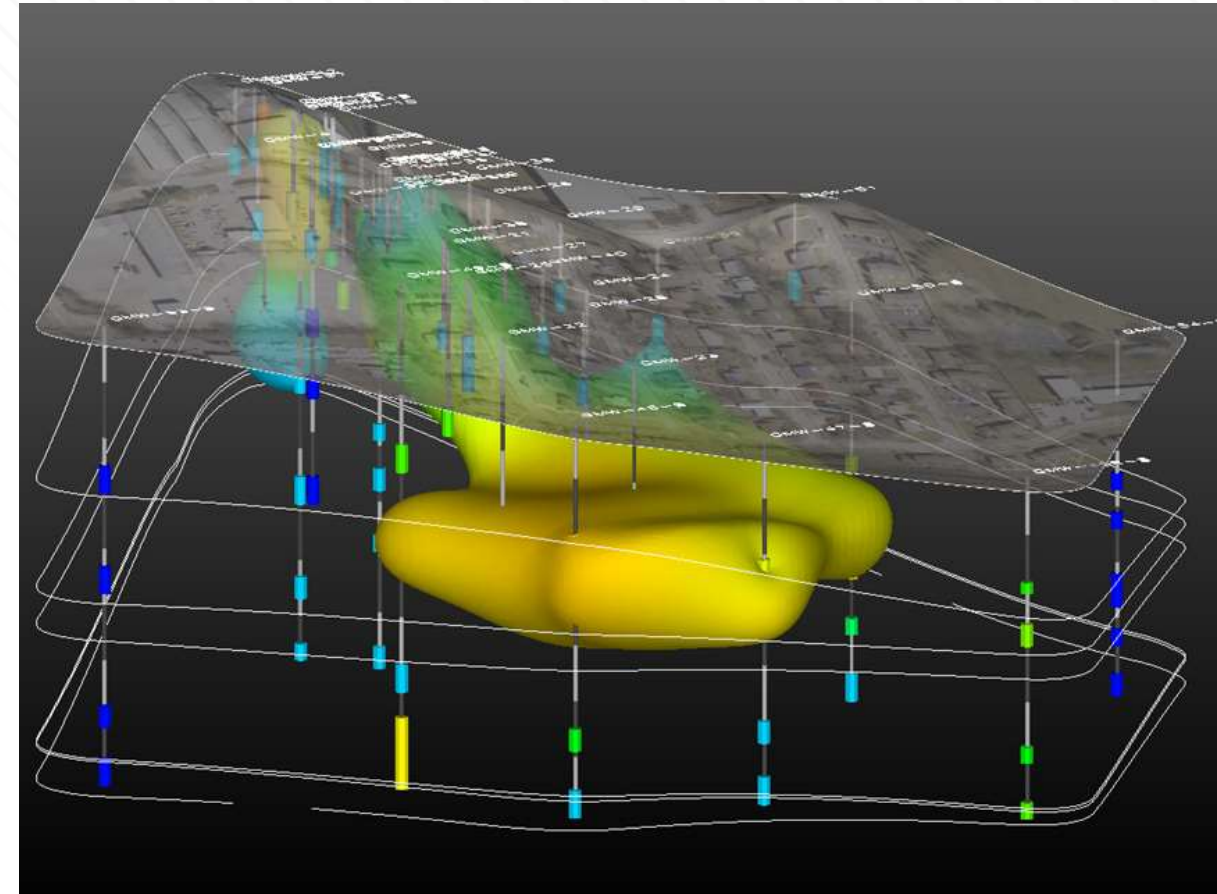


Image from ITRC, 2020

PFAS Characterization Challenges

Long Plumes

- ▶ Generally low but also variable (depending on the PFAS chain length and class) adsorption affinity
- ▶ High solubility
- ▶ High recalcitrance (terminal PFAS are not biodegradable)
- ▶ Surfactant behavior (attracted to air-water interface)
- ▶ Susceptibility to electrostatic forces (due to ionic form in solution)



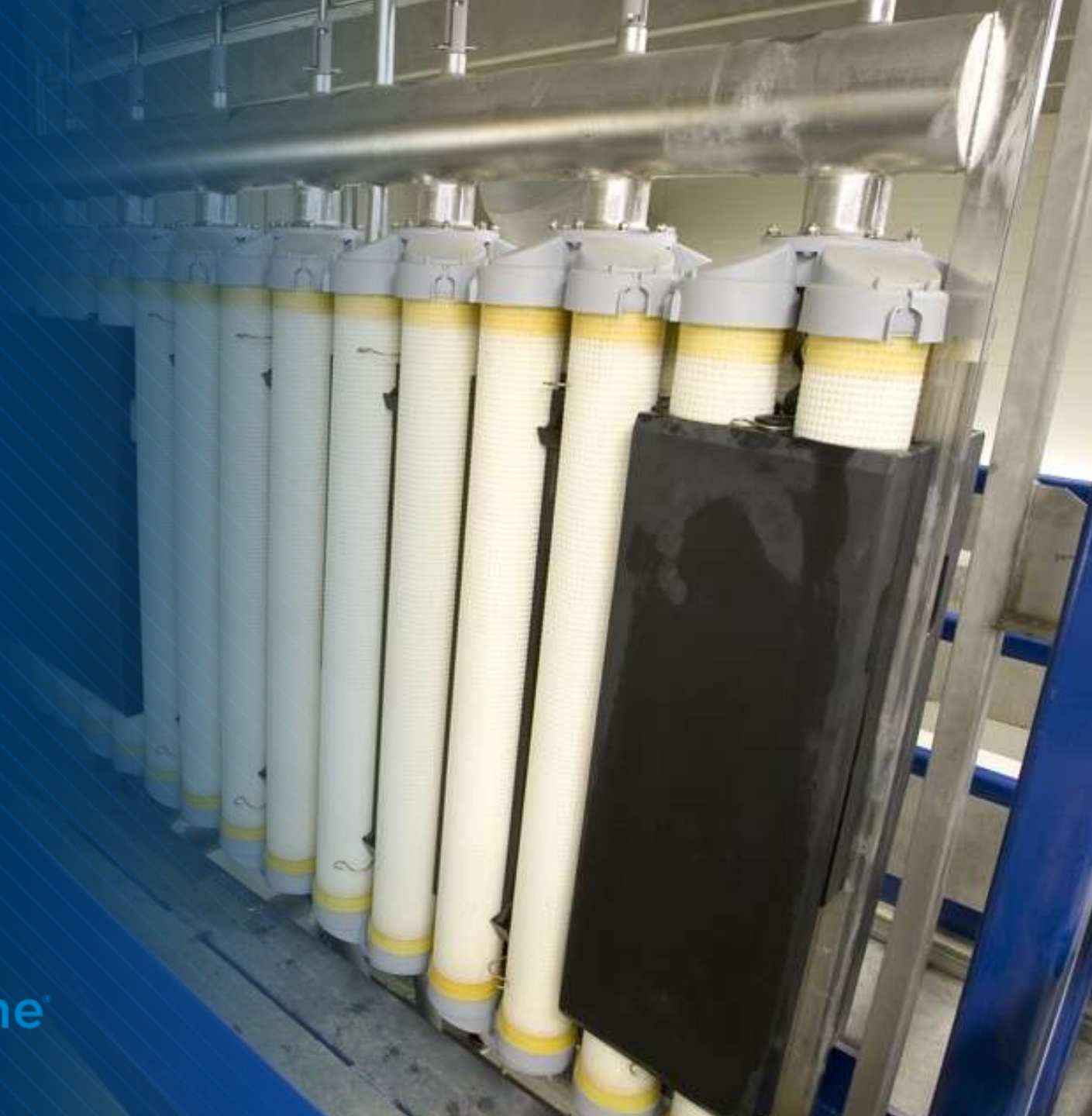


Treatment

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Adsorption Based Technologies

- ▶ Activated Carbon (Granular, Powder, Colloidal)
- ▶ Ion Exchange Resin
- ▶ Others
 - Fluorosorb
 - RemBind
 - PQ-Osorb
 - Puraffinity
 - Biochar
 - Graphene
 - Zeolite
 - Pryolyzed Cellulose
 - Flocculation (PerfluorAd)

Relative effectiveness is based upon influent chemistry / presence of co-contaminants

Competition for receptor sites

Selectivity of adsorption media
(e.g. – PFAS selective ions)

Compatibility of treatment media / technology with application
(e.g. – certain resins are not compatible with DW)

Treatment Objectives – Which PFAS are targeted?

Potential to Regenerate

Vessel Size

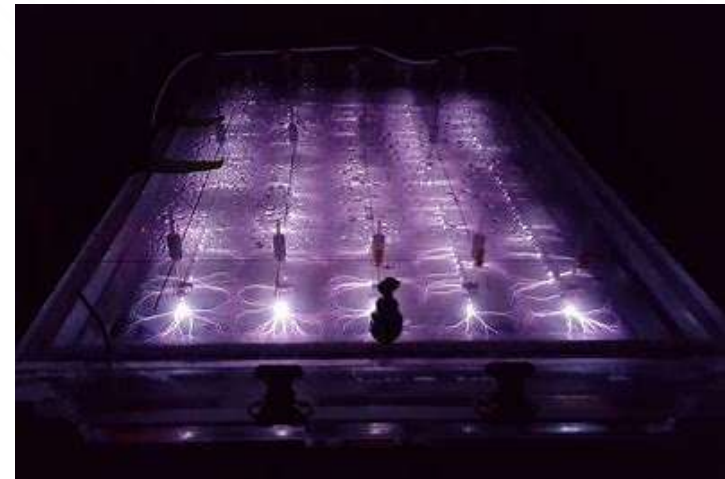
Separation

- ▶ Reverse Osmosis
 - ▶ Engineered Membranes
 - ▶ Foam Fractionation
-
- ▶ Pros
 - Effective at removing wide range of PFAS.
 - ▶ Cons
 - Management of rejects / concentrates
 - Maintenance



Destruction

- ▶ Incineration
- ▶ Sonolysis
- ▶ Smoldering
- ▶ Electrochemical Oxidation
- ▶ Non-Thermal Plasma
- ▶ Super Critical Water Oxidation
- ▶ UV Radiation of Sulfite
- ▶ Chemical Oxidation
- ▶ Thermal Oxidation
- ▶ Chemical Reduction
- ▶ Photolysis
- ▶ Electron Beam
- ▶ Biological Enzymatic Defluorination



Sequestration

► Landfills

- Subtitle D
- Subtitle C
- Leachate Management



► Class I disposal wells

- Considered suitable for PFAS-containing wastes
- Reduces risk of exposure to wastes
- Little potential for air emissions



Goals in Managing / Disposing of PFAS-Containing Soil

► Inherent risks associated with waste management

- Shorter Term Risks
 - Preventing spread of contamination
 - Dust / Runoff-control
 - Account for worker exposures
 - Transportation risks
 - Regulatory compliance
- Long Term Risks
 - Future Releases
 - Leachate to SW
 - Leachate to GW
 - Air Emissions
 - Transport to receptor

Future of PFAS Treatment

- ▶ Strategies for concentration and destruction
 - Sorption / Separation (e.g. - Regenerable IX / Fractionation) → Destruction (e.g. - incineration / non-thermal plasma)
- ▶ Need to overcome in-situ treatment challenges
 - Current technologies limited to colloidal carbon
 - Sorption / “PFAS Sink”
 - Current focus / advancements – in situ application of other proven ex situ technologies
 - Need to destroy PFAS in situ
- ▶ Need to demonstrate complete destruction – limited by analytical capabilities