

Per- and Polyfluoroalkyl Substances

What

Where

How to Manage

How Many “rabbit holes” can you jump down?

Per- and Polyfluoroalkyl Substances

“Slide/house keeping notes”:
lots of acronyms, slide #'s

Questions (show of hands) ?

- How many know what PFAS is ?
- How many have been in a meeting about it ?
- Who is actively addressing it ?
- Who has programs in-place ?
- Who is exhausted hearing about it ?

Per- and Polyfluoroalkyl Substances

Acknowledgments:

- “PFAS Substances” Agency for Toxic Substances and Disease Registry (**ATSDR**)
- “PFAS Basics”, **Eurofin** Environmental Testing, 2023
- “PFAS Roadmap” **USEPA**
- “Tox Profile of Perfluoroalkyls” **ATSDR** 2021
- “PFAS Battelle Workshop”, **ITRC** 2023
- “PFAS Technical and Regulatory Guidance Document”, Interstate Technical Regulatory Council (**ITRC**)
- “PFAS Restrictions Proposal”, **European Chemical Agency**
- “PFAS in US Tap water” US Geological Survey (**USGS**)
- “PFAS Contamination in the US”, Environmental Working Group (**EWP**)
- Toxic Release Inventory (**TRI**), EPA
- “PFAS in Tap Water Supplies”, interactive map, **Northwestern University**
- “Emerging Technologies For Remedial and Disposal of PFAS”, (2022) Dept of Defense, (**DOD**)
- “Comment Letter ... PFOA and PFOS... Hazardous Substance”, 2022, **ATSWMO**
- “PFAS Analytic Tools”, EPA Enforcement and Compliance History Online (**ECHO**)
- “CompTox Chemicals Dashboard”, **USEPA**
- **SCS Internal** – Environmental Services College Resources
Multiple people addressing it in air, water, waste, and land
[Wisconsin, Oregon, California, Florida, Virginia, North Carolina, Maryland, Washington]

Per- and Polyfluoroalkyl Substances

Ever Changing World !!!

What:

- Chemical Make-Up
- Polymers (long chain), Non-Polymers (short chain)
- **Problems**
- Past Analogies, but different (Aroclors, MTBE, dioxins) – all initially beneficial

Where:

- History
- Transformation
- Degradation
- Fate/Transport
- Toxicity/Exposure
- **Panic! ??**

Per- and Polyfluoroalkyl Substances

Ever Changing World !!!

How to Manage:

- Regulatory Status(s)
- Treatment
- Company Actions to Consider – “The Plan”

Per- and Polyfluoroalkyl Substances

PFAS

What ?

PFAS – What ?

- Organofluorine compounds (carbon-fluorine), carbon chain not carbon ring (aromatic)

“... the PFAS class comprises distinct substances with very different structures and properties. high-molecular-weight polymers and high-molecular-weight nonpolymers, neutral, anionic, cationic and zwitterionic substances, solids, liquids, and gases; highly reactive and non-reactive (inert) substances; soluble and insoluble substances, and volatile and in volatile substances. In the environment, some PFAS are mobile and others immobile, and some bioaccumulate while others do not.”

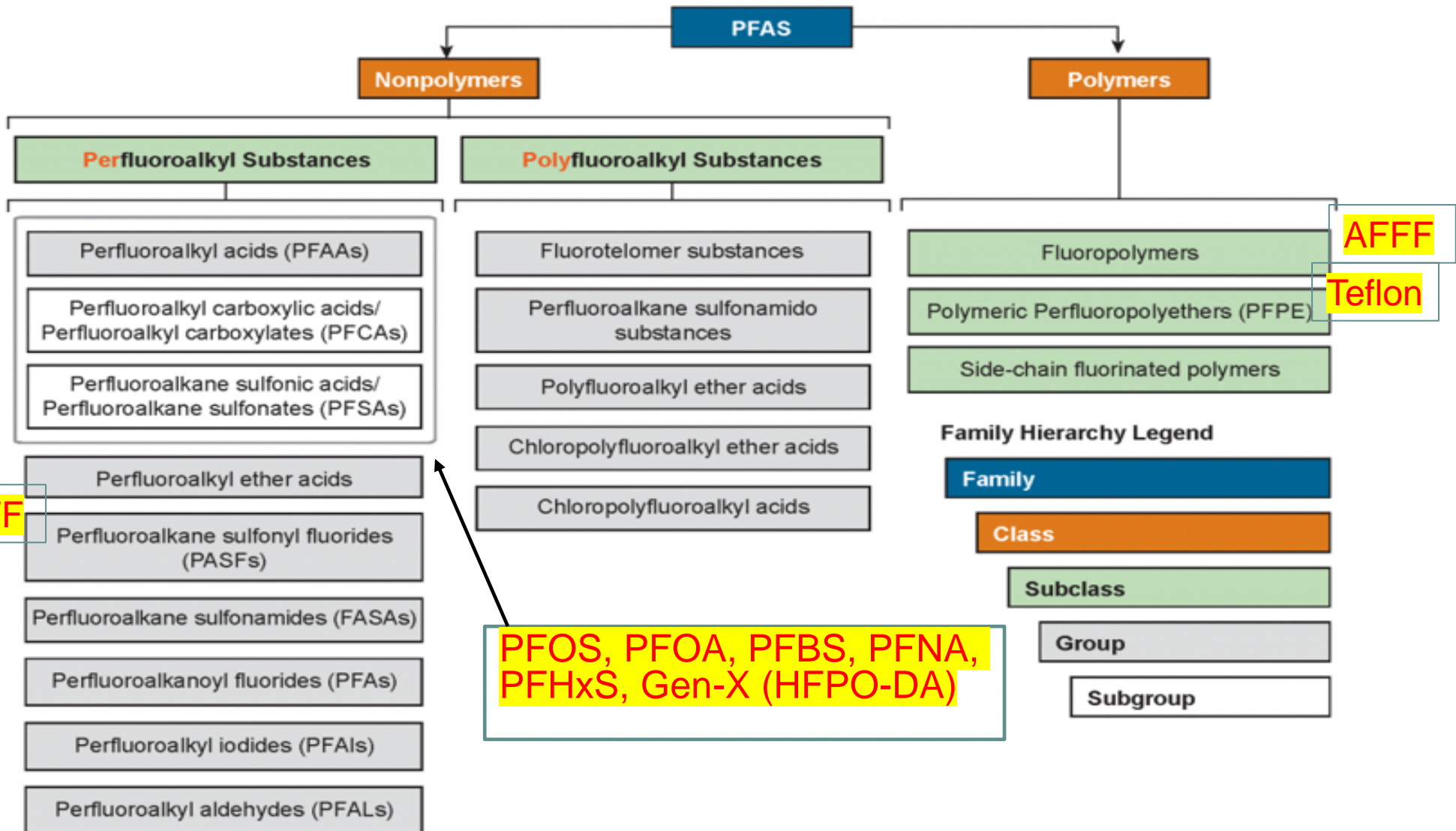
- Unique properties of interest – water and oil-resistant, flame and stain-resistant, low-friction coatings, surfactants, solvents, paints

PFAS – What ?

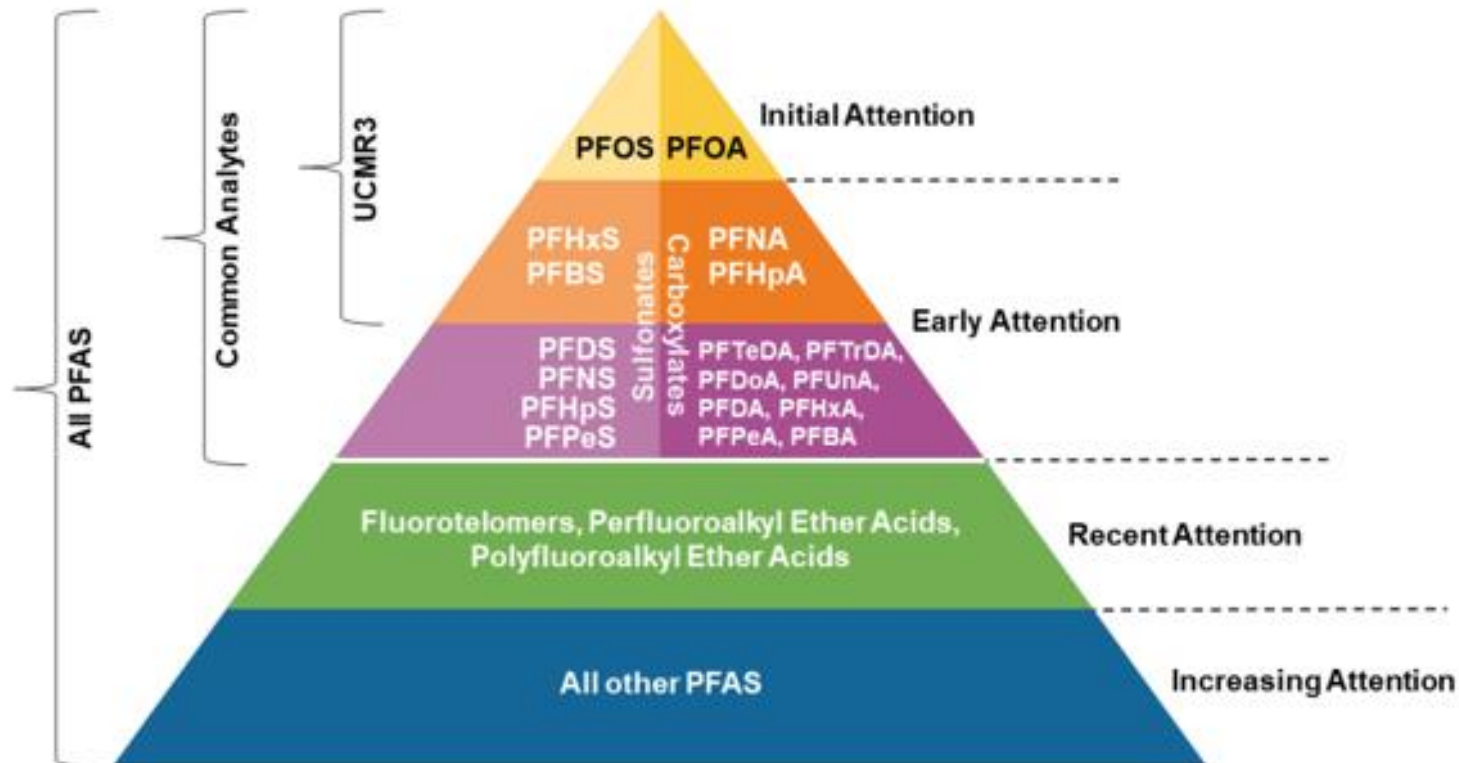
No universally accepted definition **(Problem #1)**

- 1) Complete and incomplete fluoridation || per-, poly-
 - 2) Organic polymers (linear – repeated chemically bonded subunits, macromolecules) and organic non-polymers (everything else) – held together by ionic bonds, intermolecular forces - || cellulose, lignin, rubber, ethylene, polyethylene vs. everything else
- Summary: long chain, short chain, completely fluorinated, incomplete fluorinated

PFAS – What?



PFAS - What ?



Thematic and not proportional. Bottom of triangle indicates additional number of compounds; not a greater quantity by mass, concentration, or frequency of detection.

UCMR3 –
Unregulated
Contaminant
Monitoring Rule
(2012)

UCMR5 (2021
- 2026)

More later

PFAS – What?

So, how many PFAS's are there:

Total: 3000+ - 9000+ **(Problem #2)**

Why are we concerned ?

“Forever chemicals” **(Problem #3)**

bioaccumulate, mobile, biomagnification

PFAS – What?

Regulated / Of Interest (US):

- Air (Occupational / Emissions) - **3** {2001} / 0
- SDWA - UCMR3 - **6** {May 2012} [2013 – 2015]
- TRI - **172** substances {Jan. 2020}
- SDWA - UCMR5 - **29** substances {Dec. 2021}
- NPDES (ELG's / biosolids / water quality / pre-treatment)
- **0 / 0 / 6** / BMPs Dec.2022
- SDWA – Primary Drinking Water (MCLs,MCLGs)
- **6** {proposed March 2023}
- CERCLA (haz. substances (wastes),...)
- **9+**, PFOS and PFOA
precursors {April 2023}

Chronological order – next up? SDWA – NPDW

PFAS – What?

What About **Teflon** (PTFE - polytetrafluoroethylene) [polymer, completely fluoridated] – since 1930's PFOA part removed by 2013. During old manufacturing, air released most of the PFOA during the process via heat.

Per- and Polyfluoroalkyl Substances

PFAS

Where ?

PFAS – Where?

Maybe a little about “When” first:

PFAS Emergence Timeline

	1930s	1940s	1950s	1960s	1970s	1980s	1990s	2000s	2010s	2020s
Production	Synthesis / Development									
			Manufacturing and Commercial Production							
									Phase-outs / Reductions / Alternatives	
Health & Environment					Health Concerns					
									Environmental Detection & Analytical Improvements	

1966 US Navy USS Oriskany aircraft carrier, killed 34

1967 US Navy USS Forrestal aircraft fire, killed 134

=> AFFF

2006 EPA “PFOA Stewardship Program” (voluntary changes in production)

- ATSDR- studied/studying US communities

PFAS – Where?

Aqueous Film Forming Foam (AFFF)

- Military installations & civil airport
- Petroleum refineries & chemical facilities
- Firefighting training areas and responses

Industrial (primary production and secondary manufacturing)

- Surfactants, resins, molds, plastics
- Plating and etching (esp., chrome)
- Coating (textiles, leather, paper, carpet, etc.)

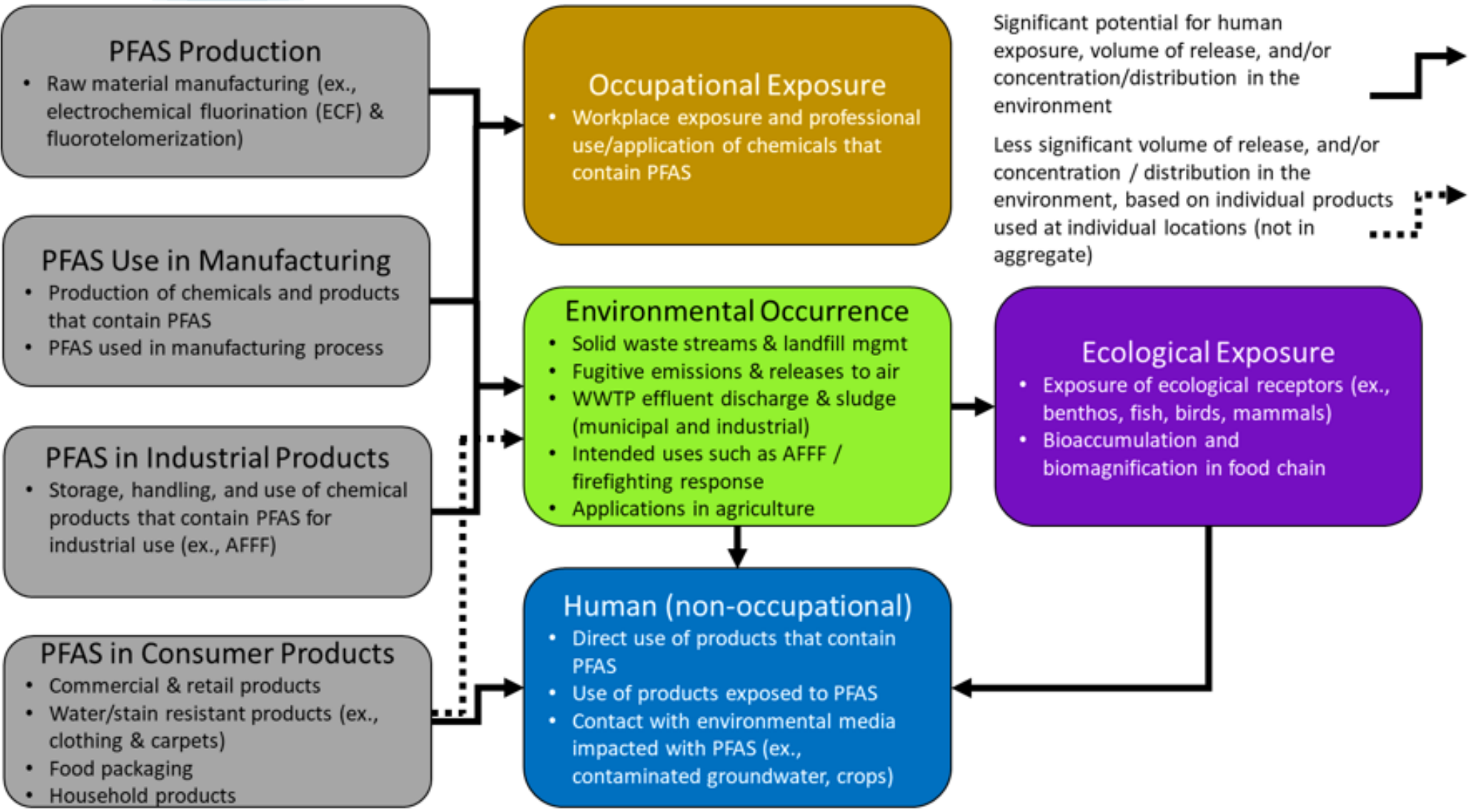
Landfills

- Consumer products, industrial waste, demolition debris
- Biosolids from WWTP

Wastewater Treatment Plants

- PFAS in influent from industrial & and domestic sources – may not be treated and end up in effluent
- Biosolids created in the treatment process

PFAS – Where?



PFAS – Where?

We've heard:

AFFF, textile treatment (stain and fire), food wrappers

Other where's? – In This? Really?

Microwave popcorn bags

Snow ski wax

Firefighter clothing

Sunscreen

Dental floss

Climbing ropes

Ammunition

Guitar strings

Artificial turf

PFAS – Where?

Just keep in mind:

PFASs can be divided into two categories – long and short-chain. The most widely known are long-chain perfluorinated chemicals or **C9+ fluorocarbons**.

Two PFAS compounds, **perfluorooctane acid (PFOA)** and **perfluorooctanesulfonic acid (PFOS)**, **C8, short chain**, present in firefighting aqueous film forming foam (AFFF) solutions, maybe Teflon, etc... and PFOS used to make Scotchgard.

PFAS is in firefighters clothing (forest fire fighters, city, county rural firefighters) – so, PFAS protects our (firefighters).

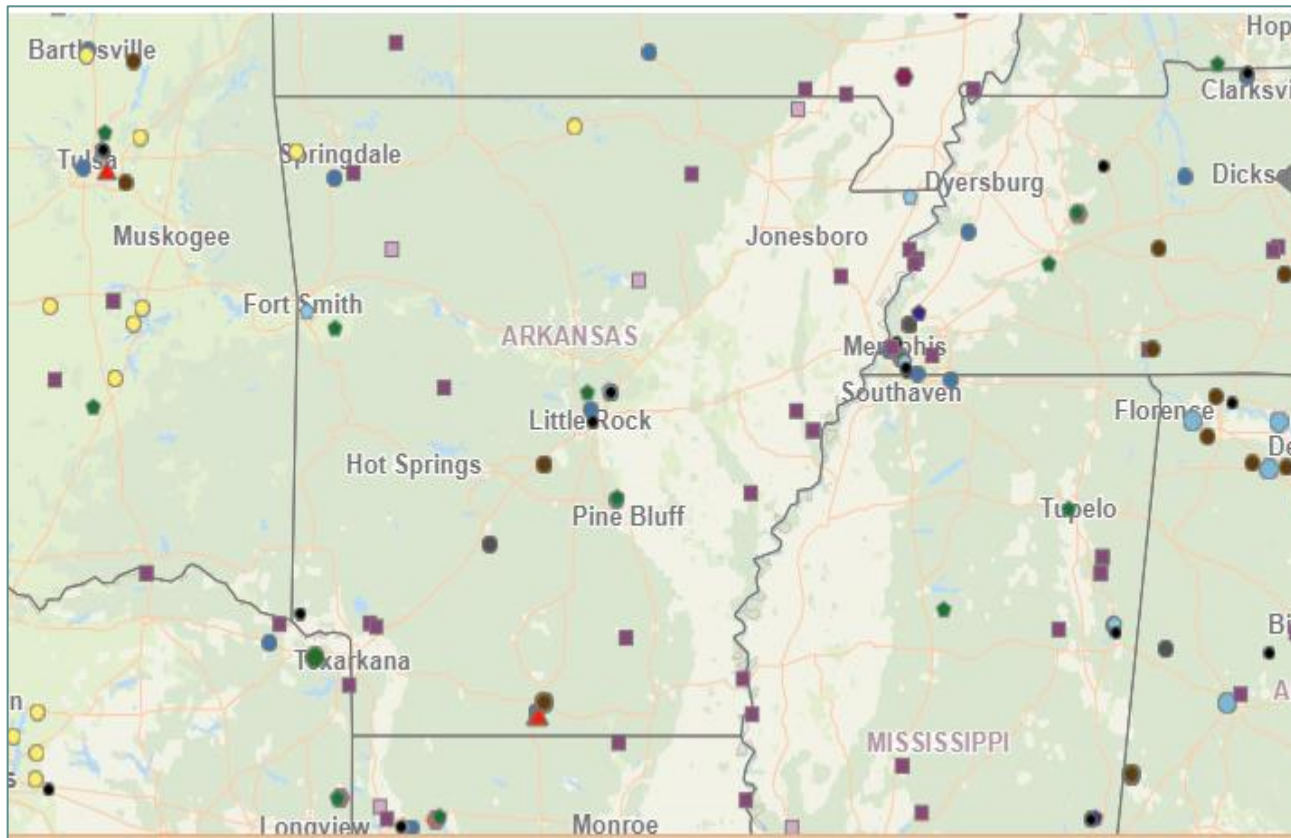
PFAS (PFOA, PFOS) – Where?

Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS)

- Found in air, surface water, groundwater, soil, and food.
- Found in fish, amphibians, reptiles, birds, and mammals.
- Found in the world's oceans and in the Arctic => long-range transport
- In/With Water: Base anions dissociated with Ph 5-9 water, undissociated acids
- Sediment/Soil to Water: mobile, not absorbed on sediment
- Air to Atmosphere: some absorbed to particulates, some transport of PFAS acids (wind and rain)

PFAS (PFOA, PFOS) – Where?

ECHO – PFAS Analytics Tool



Data Available from Water Quality Portal:

	Above Median	Below Median
<input checked="" type="checkbox"/> Water	●	●
<input checked="" type="checkbox"/> Tissue	■	■
<input checked="" type="checkbox"/> Air	▲	▲
<input checked="" type="checkbox"/> Soil	⬠	⬠
<input checked="" type="checkbox"/> Sediment	⬢	⬢
<input checked="" type="checkbox"/> Other	■	■

Drinking Water - UCMR and State Data:

- UCMR PWSs with:
 - Result(s) Above Health Advisory
 - Result(s) At or Above UCMR MRL
 - No Results At or Above UCMR MRL
- State-Reported County-Level Data (ng/L)
The counties only display once a State is selected.
 - Detection Above Health Advisory
 - Detection of at least one PFAS
 - No current record of PFAS Detection
 - No current record of samples collected

PFAS (PFOA, PFOS) – Where?

So, It's All About Exposure, But First: **Fate and Transport**

Transport:

(air, water (surface and ground), soil/sediment)
(single phase and multiphase)

Natural - wind, erosion, rain, human

Mechanisms: dissolution, diffusion, advection, and
more

PFAS (PFOA, PFOS) – Where?

So, What Happens to PFOA, PFOS: **Transformation and Degradation**

Environmental degradation –

Environmental half-life = 41 - 92 years {ATSDR}

Some degradation with ammonium reduction autotrophs (iron reducer with hydrogen electron donor). **Natural** – maybe?

Anaerobic defluorination. **Natural** – maybe but limited

PFAS (PFOA, PFOS) – Where?

So, What Happens to PFOA, PFOS: **Transformation and Degradation**

Degradation or lack thereof –

- strong carbon-fluorine bonds
- low volatility and mobile
- resist biodegradation, photooxidation, direct photo and hydrolysis
- human half-life = years

PFAS (PFOA, PFOS) – Where?

Exposure – 10.5.23 Article



“Don’t Panic !!!!”

“Avoid:

- Food packaging
- Cleaning products
- Cosmetics
- Outdoor or exercise gear
- Uniforms
- Nonstick cookware
- Plastics containers”

PFAS (PFOA, PFOS) – Where?

Exposure –

Pathways include mostly ingestion and inhalation: food and water ingestion, dust inhalation, and hand-to-mouth transfer, even from carpets, even inhalation from treated clothing

Per- and Polyfluoroalkyl Substances

PFAS (PFOA, PFOS)

How To Manage?

Where We Are and Where We're Going

PFAS (PFOA, PFOS) – How To Manage?

How Many States and Countries Already?

WATER (2022)

- 30 States (standards and guidelines)
- 11 countries

Health advisories, groundwater quality, health based drinking water, aquatic

New Jersey, Maine, Hawaii, Connecticut, California, Alaska

- MCL's adopted/interim, action levels
- Minnesota- water quality standards

PFAS (PFOA, PFOS) – How To Manage?

How Many States and Countries Already?

WATER (con't)

Pending standards: Delaware, Illinois, Pennsylvania, N. Carolina, Wisconsin, New York, Virginia, Washington

PFAS (PFOA, PFOS) – How To Manage?

How Many States and Countries Already?

SOIL (2022)

- 20 States (screening levels for gw and human health)
- 7 countries

PFAS (PFOA, PFOS) – How To Manage?

EPA's Strategic Roadmap (2021 – 2024) Research, Restrict, Remediate

- Approach:
 - PFAS lifecycle: (new products; to existing products/contamination; to old contamination) **[expand research]**
 - Accountability: **[prevent releases]**
 - Prioritize disadvantaged communities: **[resources and assistance]**
- Timeline: “accelerate remediation and mitigation”
“do not create new pollution problems”

PFAS (PFOA, PFOS) – How To Manage?

EPA Standards and Guides **WATER** and **SOIL**

WATER: (Office of Water) 0.000004 and 0.00002 ug/L
(Regions – screening levels) 0.060 and 0.040 ug/L
(Office of Land and Emergency Management)
0.040 and 0.040 ug/L

SOIL: 0.915 and 0.038 ug/kg (gw protection)
190 and 130 ug/kg (human health)

PFAS (PFOA, PFOS) – How To Manage?

EPA Updates WATER and SOIL

WATER: Mar 2023 - Proposed **NPDW**
PFOA and PFOS (MCLG = 0, MCL = 4 ng/L)
4 other PFASs included: cumulative HI ≤ 1

Anticipated promulgation Dec. 2023
Anticipated effective date: Dec. 2026

WASTEWATER:

Effluent Guidelines Program Plan 15 (January, 2023)
Multiple industries – plastics, leather, paint, and **landfills**
“revisions to **ELG’s** for **landfills** are warranted”

SOIL: May 2023 – PFAS’s PFBA, PFHxA, and PFOS (**Cal EPA**)
(toxicity numbers)

PFAS (PFOA, PFOS) – How To Manage?

EPA Updates

CERCLA – Hazardous Substance (PFOA and PFOS)

September 6, 2022 – **proposed rule**
Report releases > 1 lb.

Office of Enforcement and Compliance Assurance – responses to outreach listening sessions

- Q: responses actions A: already pollutant and contaminant

Significant impacts “removal” or remedial” actions

Comment period ended Dec 2022 with 64,000+ comments.

Still no Final Rule

PFAS (PFOA, PFOS) – How To Manage?

EPA Updates

CERCLA – Hazardous Substance (PFOA and PFOS)

April 13, 2023 – advanced notice of proposed rule-making

Request for input and information on HFPO-DA (GenX)

- Comment period extended but ended August 11, 2023
- 37,000 comments

PFAS (PFOA, PFOS) – How To Manage?

So, What Do You Do? Maybe Five (5) Alternatives

1. Wait and see?
2. Actively evaluate?
3. Review current and past operations?
4. Actively change/reduce materials?
5. Treatment?
6. ?

PFAS (PFOA, PFOS) – How To Manage?

So, What Do You Do? Alternative #1 - Wait and See

Some can, but others cannot (i.e., water treatment plants)

PFOA and PFOS are no longer produced in US – will issue go away?

Constantly changing – more toxicity info, etc...

- Although some actions have been taken since the early 2000's, the environmental community (industry, government, activists, watchdogs, everyone) is just starting to get a handle on the “big picture”.
- There are some definites for all media: PFOA and PFOS

PFAS (PFOA, PFOS) – How To Manage?

So, What Do You Do? Alternative #2 - Actively Evaluate

Commercial, manufacturing, industrial, public utilities, construction, transportation, mining, and agricultural - none are immune.

So, look at products, bi-products, processes, and wastes.

Will eventually effect real estate, rental, and leasing businesses – just like other contaminants have. (Phase I – ESA).

PFAS (PFOA, PFOS) – How To Manage?

So, What Do You Do? Alternative #3 - Review Operations

- Current and Past Operations
 - Both are essential because of potential liabilities
 - Incoming, outgoing materials, even internal products, by-products, and derivatives that are produced.

PFAS (PFOA, PFOS) – How To Manage?

So, What Do You Do? Alternative #3 - Review Operations (con't)

Actual questionnaire:

	YES	NO
1. Do you produce any products, byproducts, wastes, or other materials that you know to contain or reasonably suspect to contain any PFAS chemical?	<input type="checkbox"/>	<input checked="" type="checkbox"/>
2. Do you purchase, otherwise obtain, or use any raw material(s), commercial products, or other substances that contain, or that you would reasonably suspect to contain, any PFAS chemical?	<input type="checkbox"/>	<input checked="" type="checkbox"/>
3. Do you have or have access to, or are you aware of, any information or data on the occurrence, concentration, or amount, of any PFAS chemical or constituent in water, air, solid waste or other discharges, emissions, or waste stream from or associated with your facility?	<input type="checkbox"/>	<input checked="" type="checkbox"/>
4. Is PFAS, PFOS, PFOA, GenX, or any other fluorinated chemical (typically “fluoro” in the SDS chemical listing or product name) located at your facility?	<input type="checkbox"/>	<input checked="" type="checkbox"/>

If the answer to any of the above is “Yes”, fully identify the product, byproduct, wastes, raw materials, commercial products, or other materials. Attach additional sheets to this information request to fully document as needed. Provide any SDS/MSDS chemical listing or product name.

PFAS (PFOA, PFOS) – How To Manage?

So, What Do You Do? Alternative #3 - Review Operations (con't)

Questionnaire:

Please provide any other information, sampling, and analysis and other data that you believe would be helpful in the understanding any use, storage, or production of any PFAS chemicals by your organization.

Identify the nature, source, and location of any data of which you are aware, but which is not in your possession or under your control, relating to the occurrence, concentration or amount of any PFAS chemical(s) or constituents identified as being present at your facility.

Effluent data may not be treated as confidential.

This is the current reality

PFAS (PFOA, PFOS) – How To Manage?

So, What Do You Do? Alternative #4 - Change/Reduce

First, find out exactly which compounds you might have !
Use CAS numbers

- Challenges-

Laboratory Capabilities

Analytical Method Limitations (media driven)

Second, if it's a product/raw materials

1. Look for substitutions/replacements
2. Look at process changes – efficiency vs. benefits

PFAS (PFOA, PFOS) – How To Manage?

So, What Do You Do? Alternative #4 - Change/Reduce (con't)

Third, if it's a “waste”:

1. Determine if it has to be a “waste”, can it be a product, intermediate, transitional material
2. Determine potential for reuse, blending (if acceptable)
3. Determine potential for reduction – more efficiency, process effectiveness

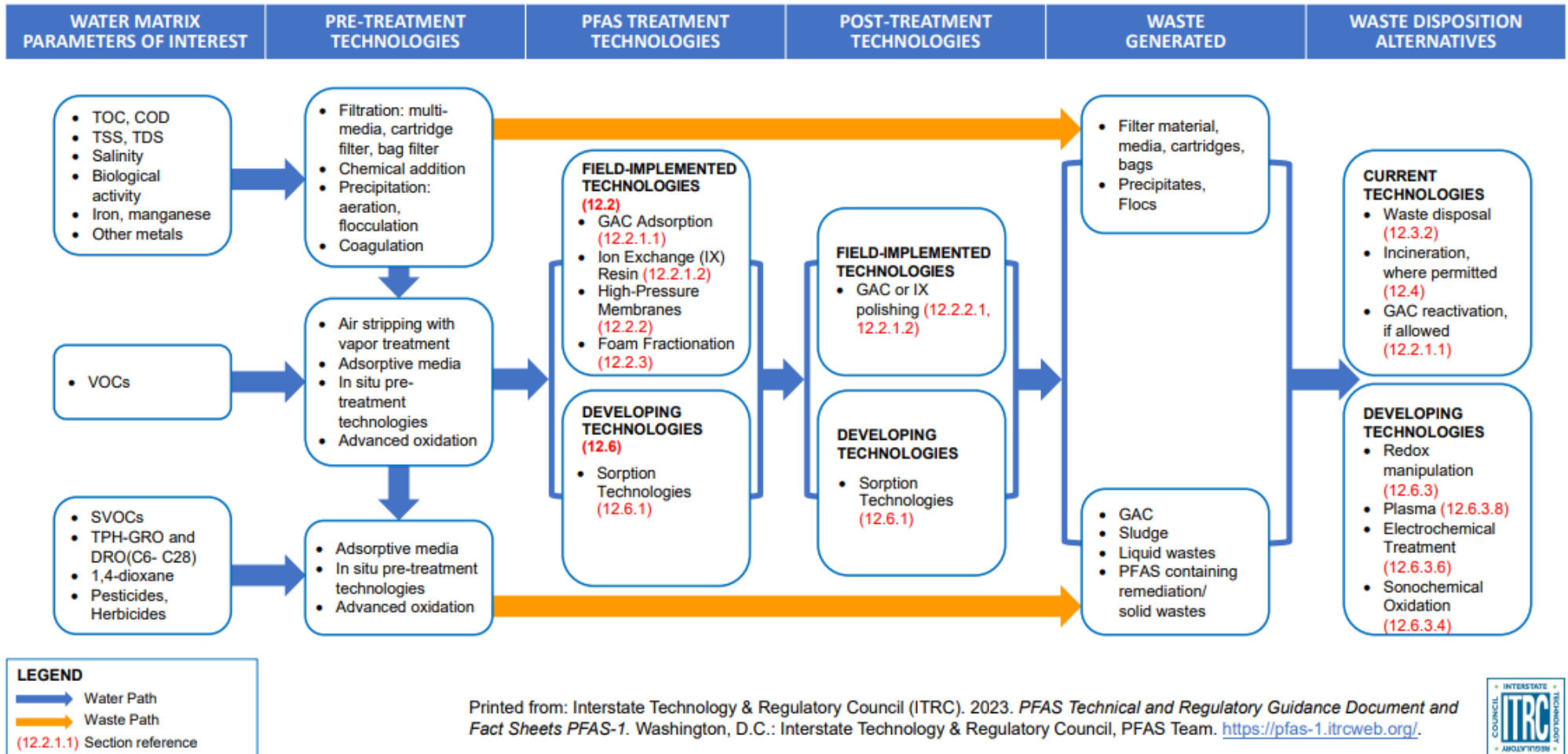
PFAS (PFOA, PFOS) – How To Manage?

So, What Do You Do? Alternative #5 - Treatment?

- Onsite or Offsite
 - **traditional treatments** (e.g., volatilization, chemical oxidation, thermal don't work great) – strong carbon-fluorine bonding
 - wide variety of effectiveness in the information
 - traditional adsorption, ion exchange, reverse osmosis, and nanofiltration are effective but require **pre-treatment**.
- More technologies (some “emerging”) -
 - Ozone + peroxide (free radicals)
 - Catalyzed Hydrogen Peroxide
 - Activated persulfate
 - Sonochemical Oxidation/Ultrasound
 - Photolysis/Photochemical
 - Electrochemical
 - Solvated Electrons (reductive degradation)
 - Plasma
 - Alkaline Metals – Hydrothermal

PFAS (PFOA, PFOS) – How To Manage?

So, What Do You Do? Alternative #5 - Treatment? (con't)



PFAS (PFOA, PFOS) – How To Manage?

So, What Do You Do? Alternative #5 - Treatment? (con't)

- Some are traditional treatments used in different ways or at different parts of the process.
- Traditional is always the first place to evaluate because of commonality and availability.
- But traditional is not going to work this time around. Limited effectiveness and expensive.
- New and innovative treatments are here now.
- What will happen? No one really knows, BUT new and innovative ideas are being researched and applied constantly.

PFAS (PFOA, PFOS) – How To Manage?

So, What Do You Do? Alternative # 6

ALL OF THE ABOVE !

Analyze, evaluate, prepare, change

Per- and Polyfluoroalkyl Substances

Questions (again) ?

- Should you be exhausted hearing about it ?
- Should you know what it is ?
- Should you have meetings about it ?
- Should you be actively addressing it ?
- Should you have a program in-place ?

- Input ? Comments ? Requests ? Points of Issue ?

Per- and Polyfluoroalkyl Substances

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