BURGESS & NIPLE
Engineers ■ Architects ■ Planners

A PFAS Primer: Terminology, Sources, Regulations and Treatment

Brian Yates, PE

Monday, June 3, 2019

What you're in for…

- Per- and polyfluoroalkyl Substances (PFAS)
  - What are they?
  - Where are they found?
  - Why are they bad?
  - What are the USEPA and States doing?
  - How do I treat for them?
  - What should I be doing?

Delaware News Journal

U.S. DoD Elsworth AFB

The Intercept

Per and Polyfluoroalkyl Substances (PFAS) - Terminology

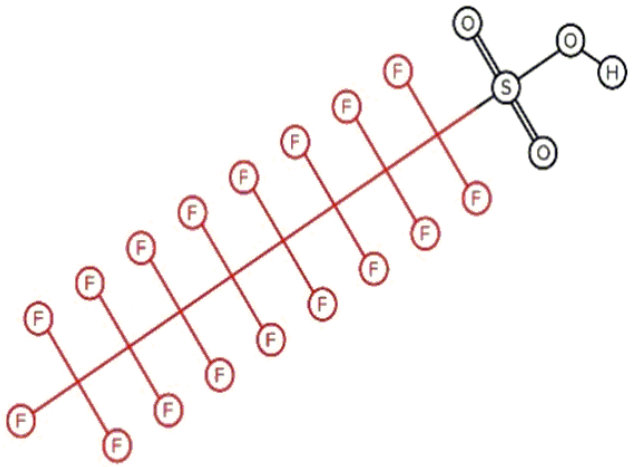
- Overview of PFAS
  - Over 5,000 exclusively anthropogenic compounds (only a handful can be analyzed commercially)
  - Similar to PCBs in that they are a class of compounds with different structural configuration, halogen substitution positions, and often found as mixtures of many different compounds (cf. PCB Aroclors)
- Terminology
  - PFAS is plural; “PFASs” is incorrect.
  - S = Substances; “PFAS Compounds”, “PFAS Substances”, etc. is redundant
  - The acronym PFC refers to PerFluorinated Compounds; it is not inclusive of all PFAS and refers to compounds that are not PFAS.
  - PFAS ≠ PFOS ≠ PFOA

We will use the term “moiety”

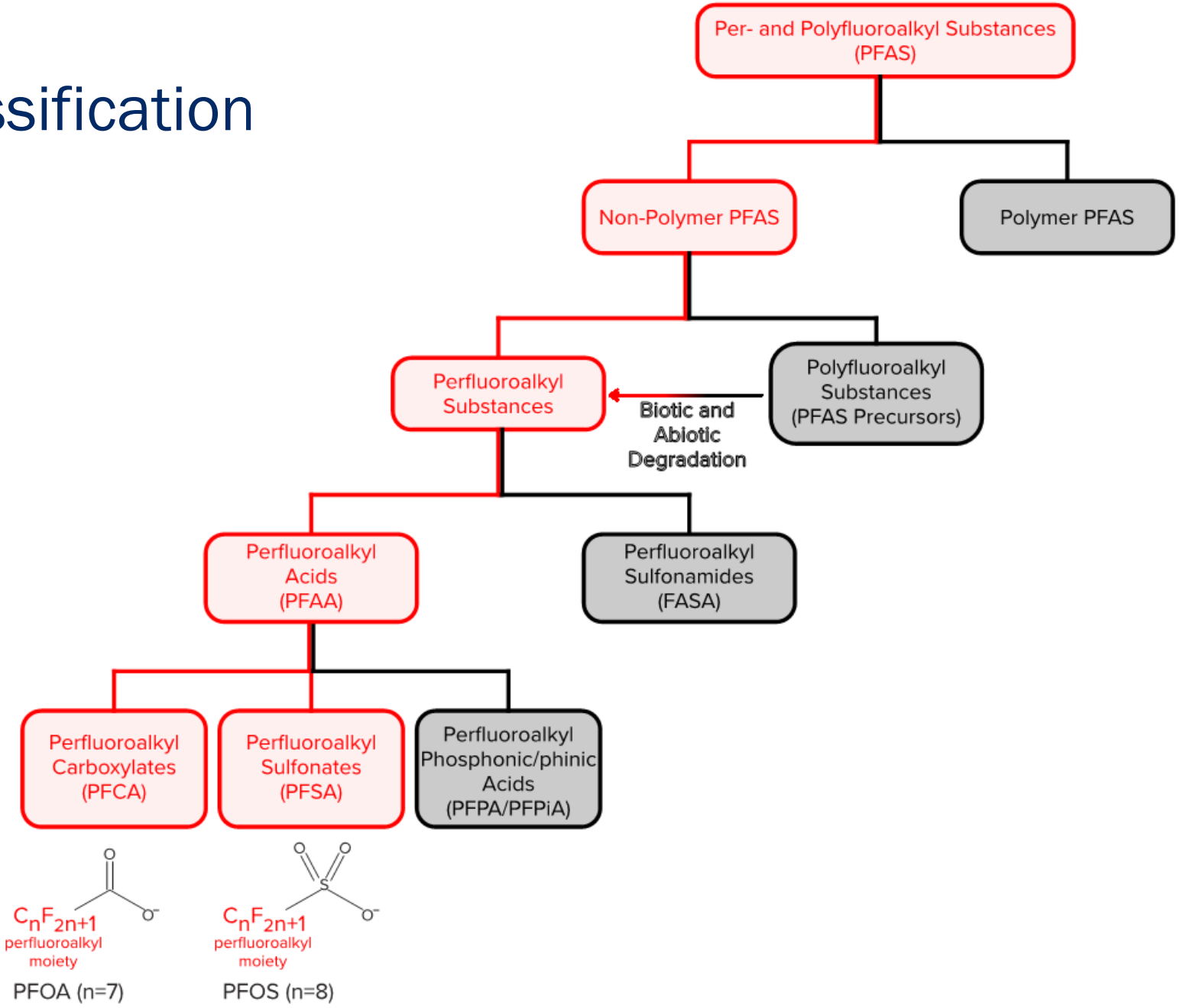
- Each of two (or more) parts into which a thing can be divided

Perfluoroalkyl Moiety

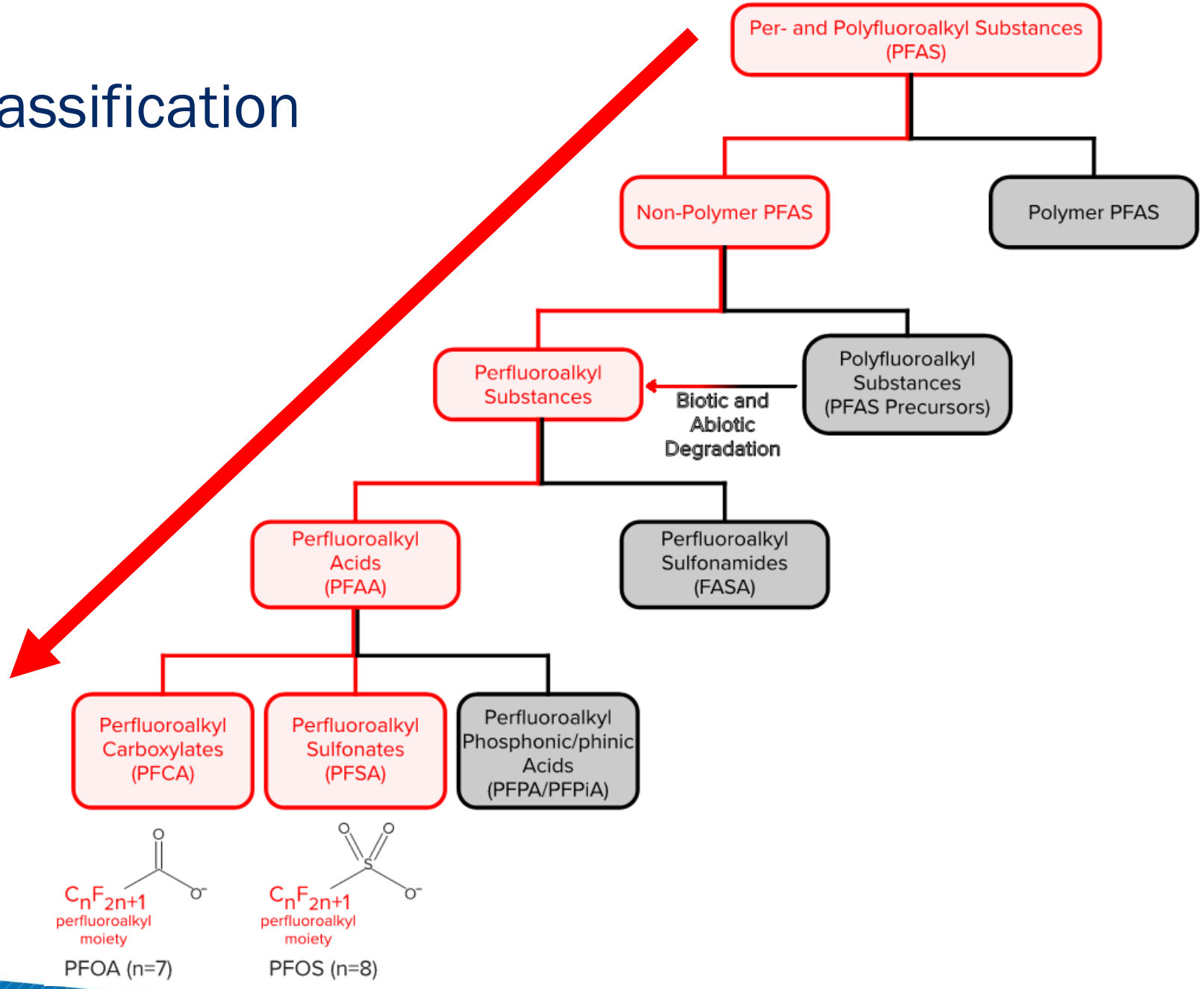
- The chemical part of a specific PFAS that is fully fluorinated
- This is the “forever part” of PFAS
- This is the Epoxy-coated rebar



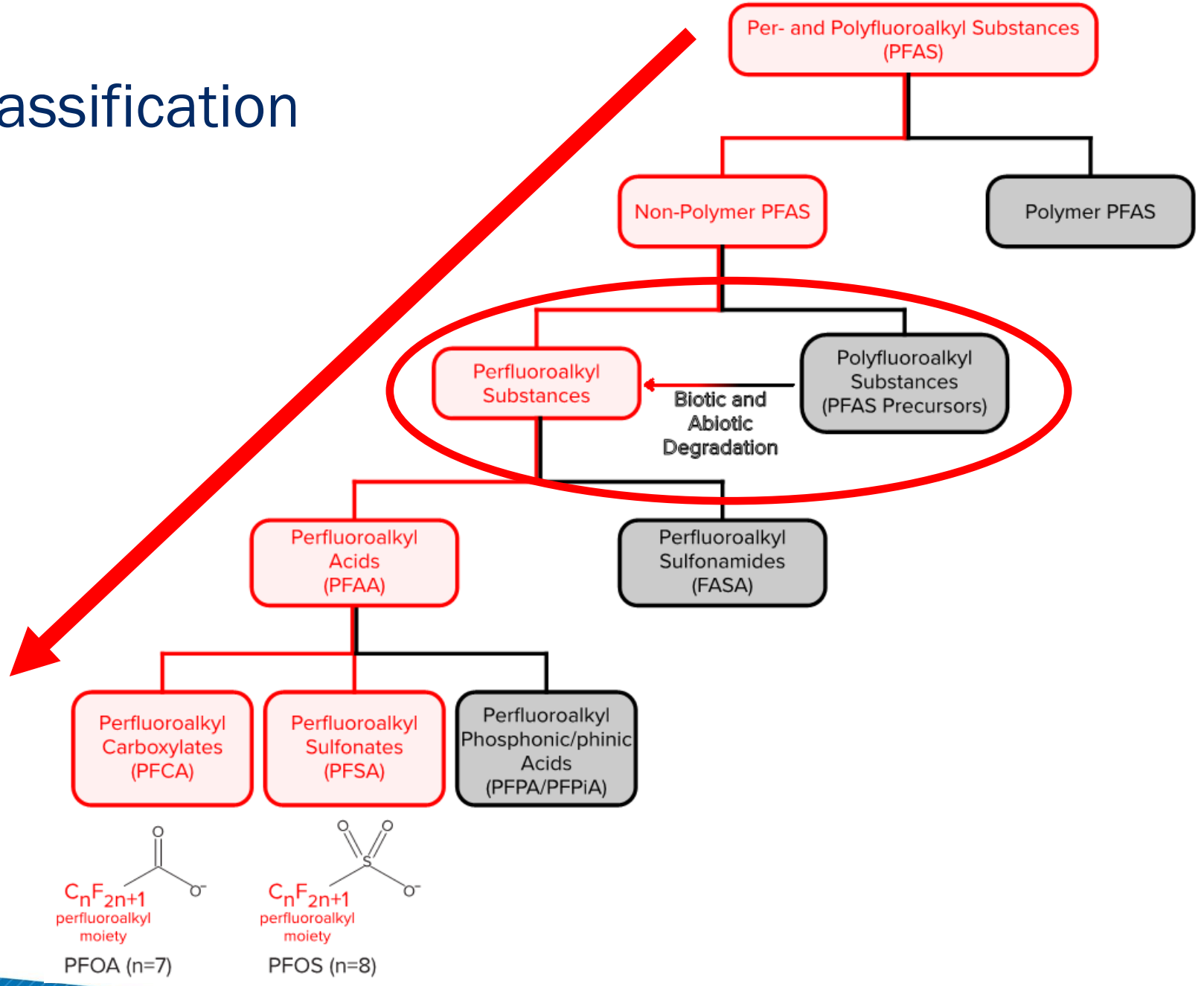
PFAS Classification

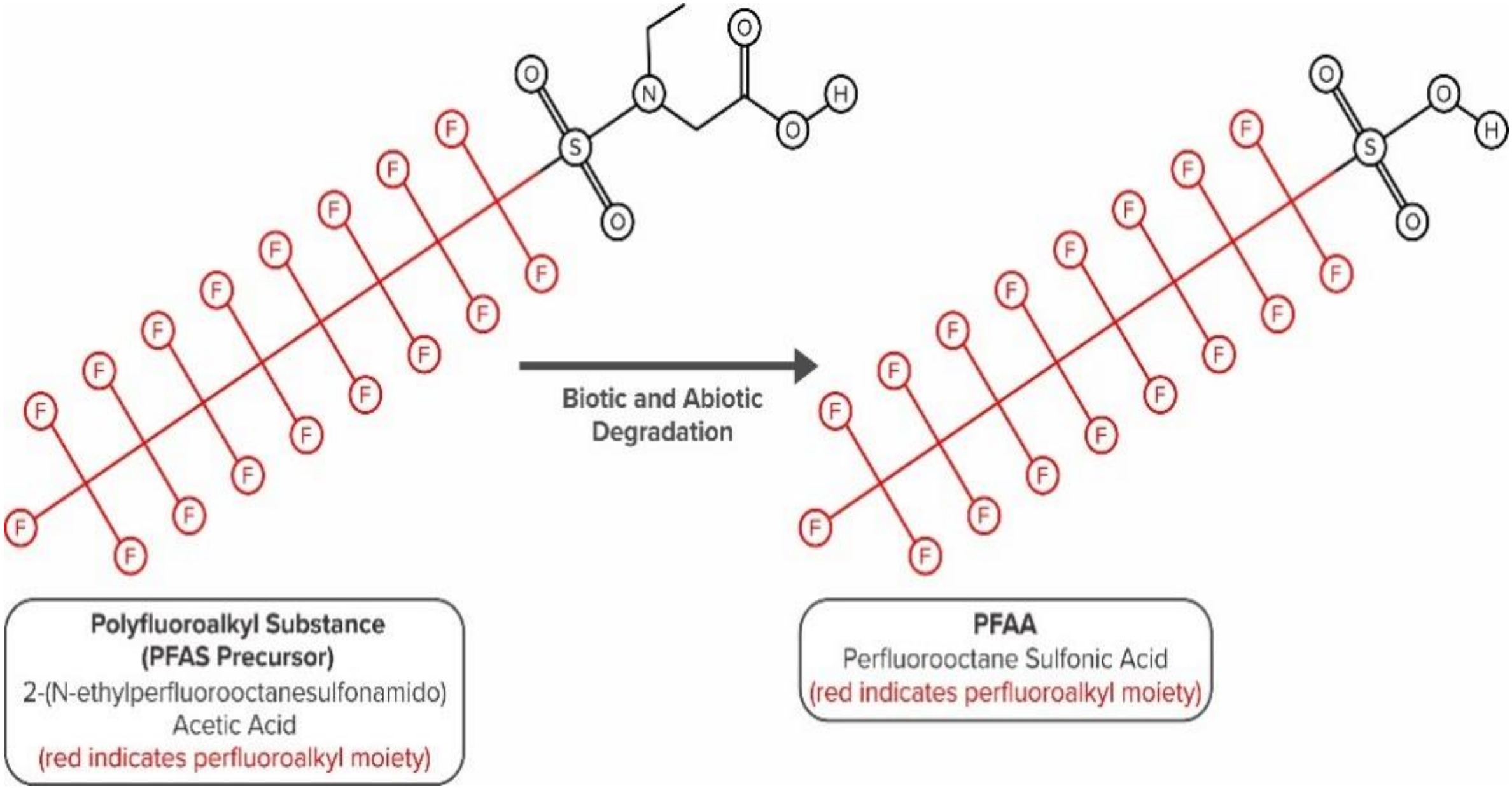


PFAS Classification



PFAS Classification



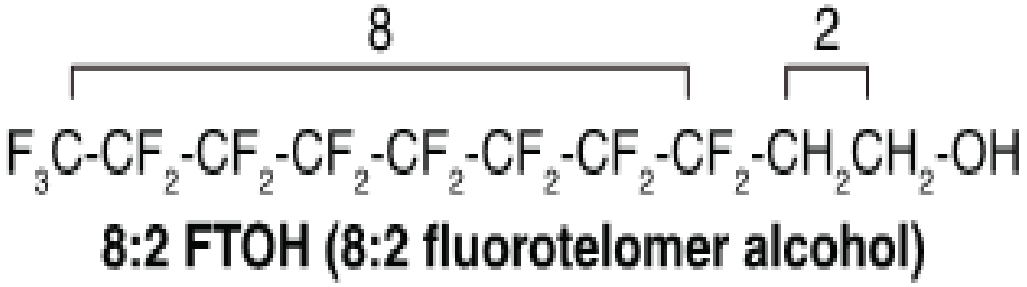


Polyfluoroalkyl Substance (PFAS Precursor)
2-(N-ethylperfluorooctanesulfonamido) Acetic Acid
(red indicates perfluoroalkyl moiety)

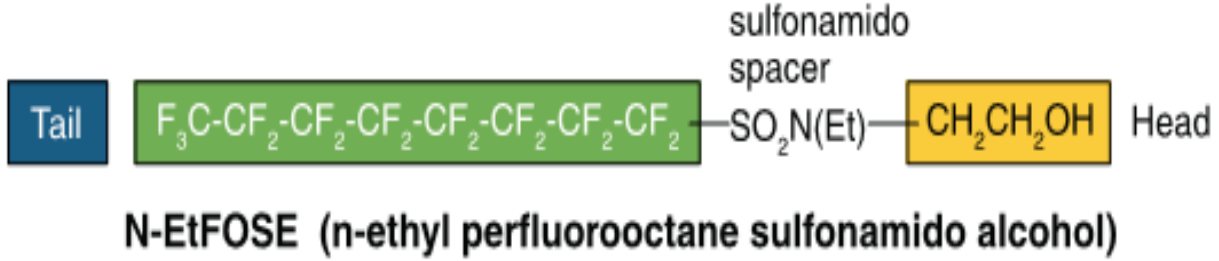
PFAA
Perfluorooctane Sulfonic Acid
(red indicates perfluoroalkyl moiety)

Per and Polyfluoroalkyl Substances (PFAS)

Polyfluoroalkyl Compounds (C_nF_{2n+1}-R + Spacers)

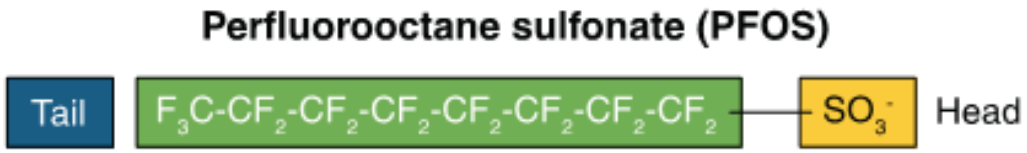


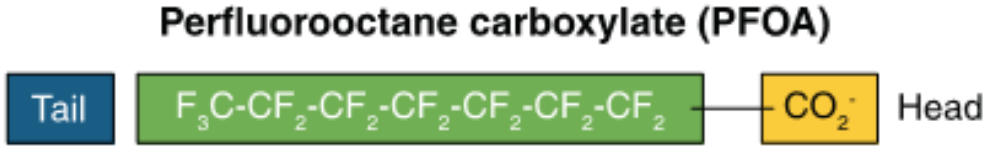
ITRC, 2019



ITRC, 2019

Perfluoroalkyl Compounds (C_nF_{2n+1}-R - No Spacers)





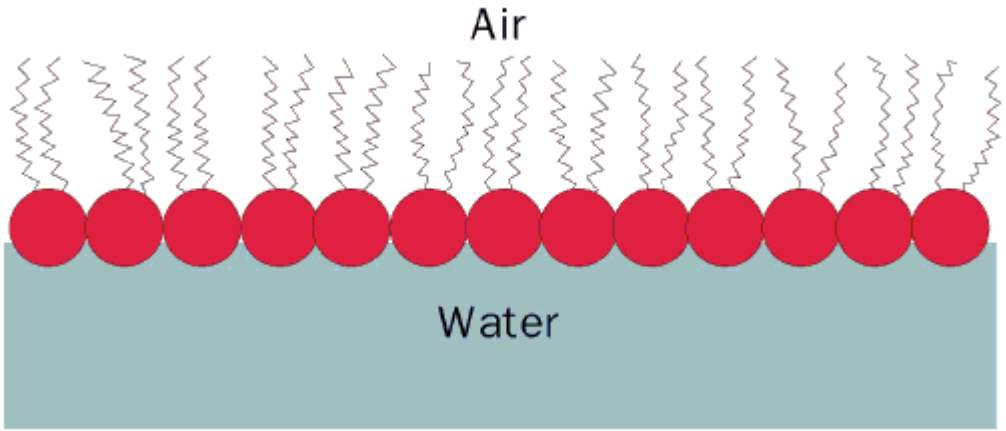
ITRC, 2019

Perfluoroalkyl Compounds (C_nF_{2n+1}-R)

Hydrophobic/Lipophobic Hydrophilic

Perfluorooctane sulfonate (PFOS)

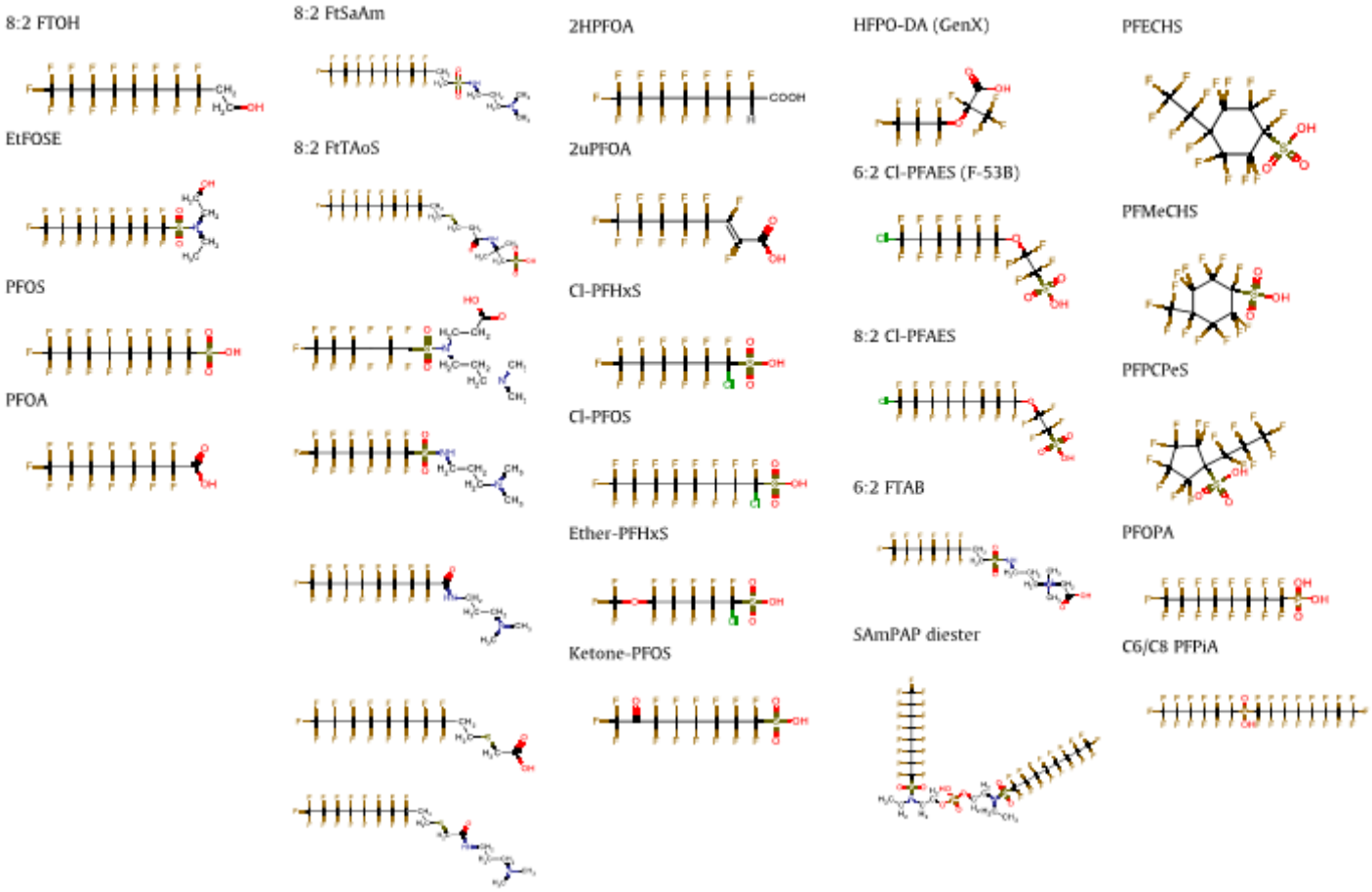
ITRC, 2019



University of Notre Dame

Per and Polyfluoroalkyl Substances (PFAS) - Terminology

- Other distinctions
  - Long Chain vs. Short Chain
    - 8 or more carbons for perfluoroalkyl carboxylates
    - 7 or more carbons for perfluoroalkane sulfonates
  - Acid vs. Anion
    - Example: Perfluorooctanoate (anion form) and perflurooctanoic acid (acid form) – **Both use the same acronym!**
  - Linear vs. Branched
    - Linear compounds have a straight carbon backbone (only one isomer)
    - Branched compounds have at least one carbon bonded to more than two carbons within the backbone (many isomers)



Xiao, 2017

Per and Polyfluoroalkyl Substances (PFAS) - Physical and Chemical Properties

Property	Unit	PFOS	PFOA	TCE
CAS Number	-	1763-23-1	335-67-1	79-01-6
Molecular Formula	-	$C_8HF_{17}O_3S$	$C_8HF_{15}O_2$	C_2HCl_3
Molecular weight	g/mol	500	414	131
Water Solubility	mg/L at 25°C	680	9,500	1.1×10^3
Boiling Point	°C	260	192	87
Vapor Pressure	mm Hg at 25°C	0.002	0.525	9.2×10^3
Log Organic Carbon Partitioning Coefficient (K_{OC})	-	2.57	2.06	1.93

Per and Polyfluoroalkyl Substances (PFAS) - Physical and Chemical Properties

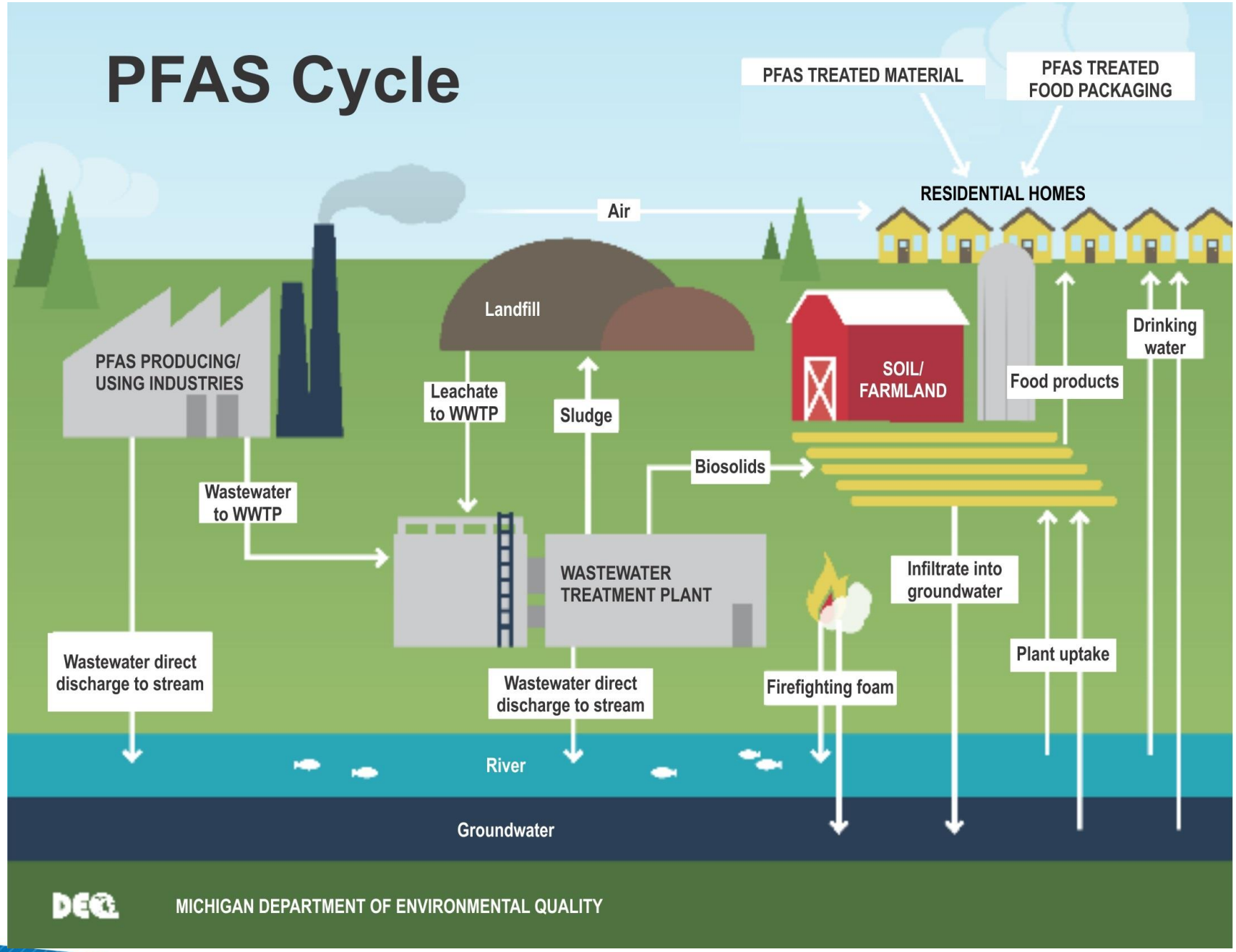
Fluorine – most electronegative element in the periodic table

C-F bond – strongest covalent bond in organic chemistry

- Resulting Chemical/Biological Properties:
  - High thermal stability (400°C – 1,000°C)
  - High chemical stability (low reactivity even with highly reactive free radicals)
  - Strong acidity (pK_a 1.0 – 3.0)
  - Zwitterionic, amphoteric, lipophobic/proteinphilic, surfactant properties, **hydrophobicity depends on chain length and head groups**.
  - Long half-lives in the human body (5-8 years)

Per and Polyfluoroalkyl Substances (PFAS) -Production, History, Use, and Environmental Sources

- Production and History
  - Electrochemical Fluoridation
    - Developed in 1940s by 3M
    - Produces a mixture of linear and branched-chain isomers
  - Telomerization (telo = end [Greek])
    - Developed in 1970s
    - Produces exclusively linear PFAS with chain-length selectivity
- Uses
  - Products: textile coatings, paper products, food packaging, cookware, aqueous film-forming foams (AFFF) for firefighting
  - Applications: aerospace, photographic imaging, semiconductor, automotive, construction, electronics, aviation, chemical polymerization aids

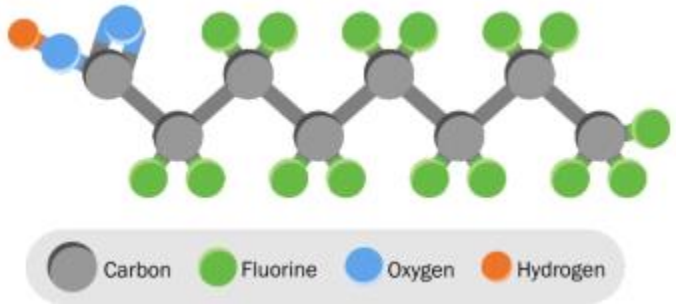

PFAS Cycle
PFAS TREATED MATERIAL
PFAS TREATED FOOD PACKAGING
RESIDENTIAL HOMES
Air
Landfill
PFAS PRODUCING/ USING INDUSTRIES
Leachate to WWTP
Sludge
SOIL/ FARMLAND
Food products
Drinking water
Biosolids
Wastewater to WWTP
WASTEWATER TREATMENT PLANT
Infiltrate into groundwater
Plant uptake
Wastewater direct discharge to stream
Wastewater direct discharge to stream
Firefighting foam
River
Groundwater
DEQ
MICHIGAN DEPARTMENT OF ENVIRONMENTAL QUALITY

Per and polyfluoroalkyl Substances (PFAS) - Production, History, Use, and Environmental Sources

- Known direct emitters to the environment
  - PFAS manufacturing facilities (e.g., 3M, DuPont/Chemours)
  - Wastewater treatment plants (municipal/domestic and industrial)
  - Wastewater biosolids
  - Drinking water residuals
  - Landfill leachate (municipal and hazardous)
  - AFFF (especially at military and fire-fighting training grounds)

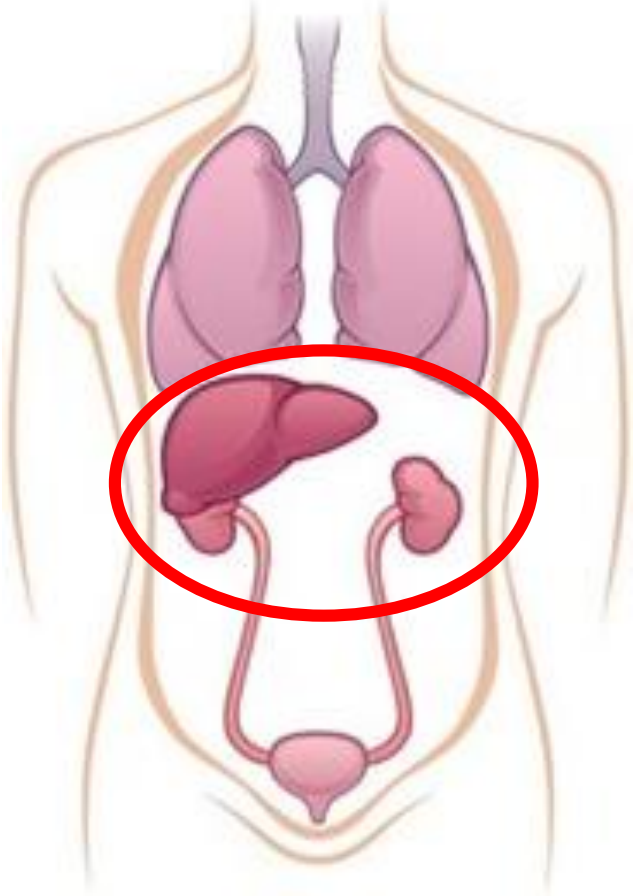
Per and polyfluoroalkyl Substances (PFAS) - Environmental Fate and Transport

- Extremely Persistent – No effective conventional treatment methods for destruction/mineralization
- Essentially non-volatile at relevant environmental pH (anion form)
- Airborne sources are pure phase, or associated with aerosols or dust
- Longer chain PFAS tend to partition to soil organic (and mineral) phases, shorter chain PFAS partition to aqueous phase (large, dilute plumes)
- Precursors are generally less mobile than transformation products and can serve as on-going sources



Per and polyfluoroalkyl Substances (PFAS) - Human Exposure and Health Effects

- What Happens After Exposure?
  - PFAS are completely absorbed after oral exposure and distribute primarily in the blood serum, liver, and kidney with a half-life of 5-8 years
  - End products of degradation (e.g., PFOS and PFOA) are chemically inert and not metabolized
  - PFOS and PFOA are **protein**philic, and are **not stored in fat**
  - PFAS are circulated in the kidneys and eventually excreted through urine and feces over several years after chronic exposure
  - PFAS look like fatty acids to our bodies and interfere with lipid (fatty acid) metabolism in the liver (PPARα system)



Per and polyfluoroalkyl Substances (PFAS) - Human Exposure and Health Effects

- C8 Science Panel (Parkersburg, WV) is the most comprehensive single source of data regarding negative health effects of PFAS
- Health Effects Correlated to PFAS Serum Concentrations (C8 Science Panel)
  - High Cholesterol
  - Ulcerative Colitis
  - Thyroid Disease
  - Testicular Cancer
  - Kidney Cancer
  - Pregnancy-induced Hypertension (eclampsia, pre-eclampsia)

Per and polyfluoroalkyl Substances (PFAS) - Current Regulations

- Federal PFAS Regulations
  - Environmental Protection Agency (EPA)
    - 2002 – Voluntary Stewardship Program
    - 2009 – Short-term Provisional Health Advisory (200 ng/L PFOS, 400 ng/L PFOA)
    - 2016 – Lifetime Health Advisory (70 ng/L combined PFOS and PFOA)
    - 2018 – PFAS National Leadership Summit
    - 2019 – PFAS Task Force and Action Plan
- State-level Regulations
  - Currently 22 states have enacted some form of regulation of PFAS at state level (Ohio coming soon)

MCL v. LHA – Enforcement Matters

- MCL (Maximum Contaminant Level)
  - "Maximum level of a contaminant in drinking water at which no known or anticipated adverse effect on the health of persons would occur, allowing for an adequate margin of safety" (MCLG)
  - "The highest allowable concentration of a chemical in drinking water for a lifetime of exposure" (MCL)
  - Based on 70 kg adult consuming 2 L of water every day
- LHA (Lifetime Health Advisory)
  - "Reasonable, health-based hazard concentrations above which action should be taken to reduce exposure to unregulated contaminants in drinking water"
  - No recommended "actions", no direction on implementing a sampling and monitoring program, no information on how contaminated drinking water affects customers

States with Current and Proposed PFAS Regulations in Water – October 2018

LEGEND

STATE - First Year of Proposed Rules
PFAS Regulated
Matrices Regulated
PFAS Concentration Range (ppb)

ALABAMA - 2016
PFOS, PFOA
Drinking Water
0.07 ppb

ALASKA - 2016
PFOA, PFOS, PFBS, PFNA, PFHxS, PFHpA
Drinking Water, Groundwater and Surface Water/ Effluent
0.07 ppb - 2 ppb

ARIZONA - 2017
PFOS, PFOA
Drinking Water
0.07 ppb

CALIFORNIA - 2018
PFOA, PFOS
Drinking Water and Groundwater
0.013 ppb - 0.07 ppb

CONNECTICUT - 2016
PFOA, PFOS, PFHxA, PFHpA, PFNA
Groundwater
0.07 ppb

COLORADO - 2017
PFOA, PFOS
Drinking Water
0.07 ppb

DELAWARE - 2016
PFOA, PFOS, PFBS
Groundwater
0.07 ppb - 38 ppb

IOWA - 2016
PFOA, PFOS
Groundwater
0.07 ppb - 1 ppb

MAINE - 2016
PFOA, PFOS
Drinking Water, Groundwater and Recreational Water
0.05 ppb – 1.2 ppb

MASSACHUSETTS - 2017
PFOS, PFOA, PFBS, PFHxS, PFHpA, PFNA
Drinking Water
0.07 ppb - 2 ppb

MICHIGAN - 2015
PFOS, PFOA
Drinking Water, Groundwater, Surface Water/Effluent
0.011 ppb - 0.42 ppb

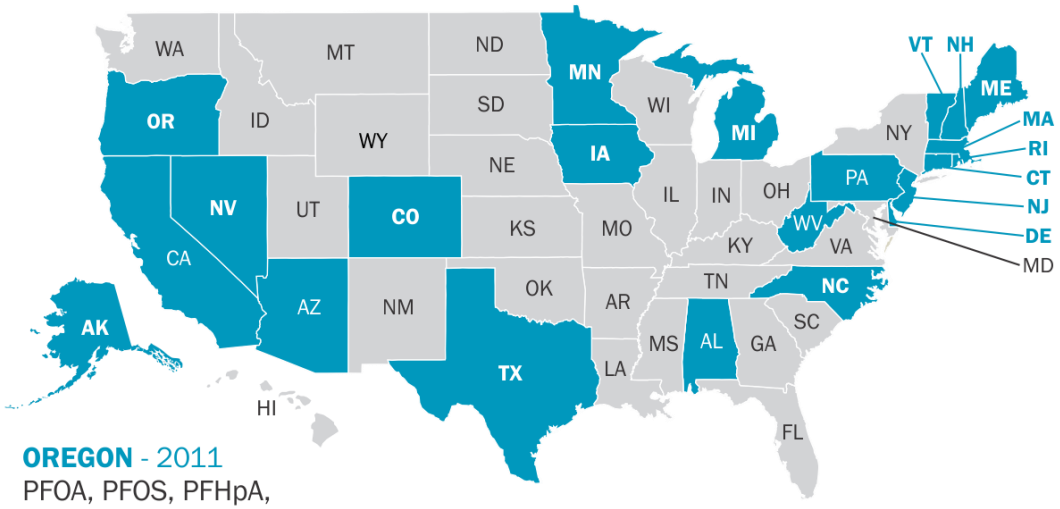
MINNESOTA - 2017
PFOA, PFOS, PFBA, PFBS, PFHxS
Drinking Water and Groundwater
0.027 ppb – 7 ppb

NEVADA - 2015
PFOA, PFOS, PFBS
Drinking Water
0.667 ppb - 667 ppb

NEW HAMPSHIRE - 2016
PFOA, PFOS
Groundwater
0.07 ppb

NEW JERSEY - 2015
PFOA, PFOS, PFNA
Drinking Water and Groundwater
0.013 ppb -0.014 ppb

NORTH CAROLINA - 2006
PFOA, GenX
Drinking Water and Groundwater
0.14 ppb - 2 ppb



OREGON - 2011
PFOA, PFOS, PFHpA, PFOSA, PFNA
Surface Water/Effluent
0.2 ppb - 300 ppb

PENNSYLVANIA - 2018
PFOS, PFOA
Drinking Water
0.07 ppb

RHODE ISLAND - 2017
PFOS, PFOA
Drinking Water
0.07 ppb

TEXAS - 2017
PFOA, PFOS, PFBA, PFBS, PFPeA, PFHxA, PFHxS, PFHpA, PFOSA, PFNA, PFDA, PFDS, PFUnA, PFDoA, PFTrDA, PFTeDA
Groundwater
0.093 ppb - 71 ppb

VERMONT - 2016
PFOA, PFOS, PFHxS, PFHpA, PFNA
Drinking Water and Groundwater
0.02 ppb

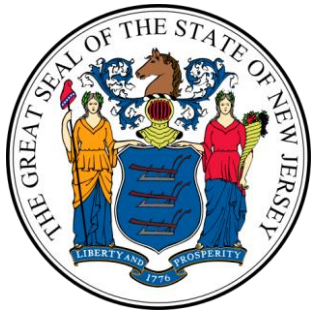
WEST VIRGINIA - 2016
PFOS, PFOA
Drinking Water
0.07 ppb

PFOA = perfluorooctanoic acid (C8)
PFOS = perfluorooctane sulfonic acid (C8)
PFBA = perfluorobutyric acid (C4)
PFBS = perfluorobutane sulfonic acid (C4)
PFPeA = perfluoropentanoic acid (C5)
PFHxA = perfluorohexanoic acid (C6)
PFHxS = perfluorohexane sulfonic acid (C6)
PFHpA = perrfluoroheptanoic acid (C7)
PFOSA = perfluorooctane sulfonamide (C8)
PFNA = perfluorononanoic acid (C9)
PFDA = perfluorodecanoic acid (C10)
PFDS = perfluorodecane sulfonate (10)
PFUnA = perfluoroundecanoic acid (C11)
PFDoA = perfluorododecanoic acid (C12)
PFTrDA = perfluorotridecanoic acid (C13)
PFTeDA = perfluorotetradecanoic acid (C14)
Gen-X = ammonium hexafluoropropylene oxide-dimer acid

Data are from ITRC https://pfas-1.itrcweb.org/fact-sheets/ accessed October 30, 2018

Recent Actions at the State Level

- Pennsylvania (setting an MCL)
  - Statewide sampling plan to identify impacted drinking water supplies
  - More than 300 public water supplies based on proximity to common sources of PFAS, such as military bases, fire training sites, landfills, and manufacturing facilities
- Maine (convening a task force)
  - All biosolids will have to be tested for the presence of PFAS before being used as fertilizer or applied to land
  - Dairy farmers seeing PFAS in finished milk products have blamed biosolids applied to their land
- New Jersey (quarterly testing for PFAS)
  - The Department of Environmental Protection proposed drinking water limits of 14 ppt for PFOA and 13 ppt for PFOS
  - The regulation would put 39 public water systems over the limit for PFOA and 19 for PFOS
- North Carolina (PFAS testing network)
  - A bill banning their use in AFFF used for training
  - Repeal the so-called Hardison Amendment that prohibits the state from enacting laws that are more stringent than the federal government's



PFAS National Leadership Summit (May 2018)

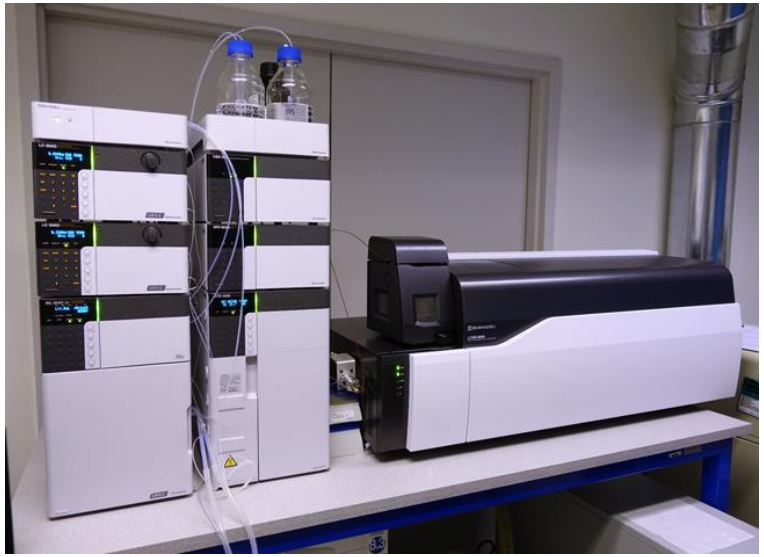
- Four Action Items Announced
  - Initiate steps to evaluate the need for a MCL
  - Beginning the necessary steps to propose designating PFOS and PFOA as hazardous substances through one of the available federal statutory mechanisms (CERCLA, RCRA, TSCA, CWA, CAA)
  - Develop groundwater cleanup recommendations
  - Develop toxicity values (oral reference doses) for Gen-X and PFBS

EPA PFAS Action Plan (February 14, 2019)

- EPA Priority Actions
  - Announced at PFAS National Leadership Summit
- Short-term Actions
  - Understanding an Addressing PFAS Toxicity and Occurrence
  - Identifying and Addressing PFAS Exposures
  - Risk Communication and Engagement
- Long-term actions
  - Listing PFAS on Toxic Release Inventory (TSCA)
  - Ambient Water Quality Criteria (CWA)
  - Regulation of Industrial Sources' Effluent (NPDES)
  - Nationwide Drinking Water Monitoring (UCMR)
  - Others
- State Actions (Collective Federalism)

Sampling and Analysis

- EPA 537.1 released in 2018 includes 18 PFAS compounds measurable in *drinking water*
- Modified EPA 537 includes other matrices such as soil and biosolids
- Other Methods
  - Particle-induced Gamma-ray Emission (PIGE)
  - Total Oxidizable Precursor (TOP Assay - UC Berkeley)
  - Total Organofluorine Methods (TOF - Battelle, UN-Reno)
- Analytical Method is LC MS/MS
- Restrictions on Sampling (develop a QAPP!)
  - Clothing (boots, gloves, rain gear)
  - Cosmetics
  - Sunblock and Insect Repellant
  - Food and Drink
  - Detergent
  - Sampling Bottles and Tubing
  - Field Supplies

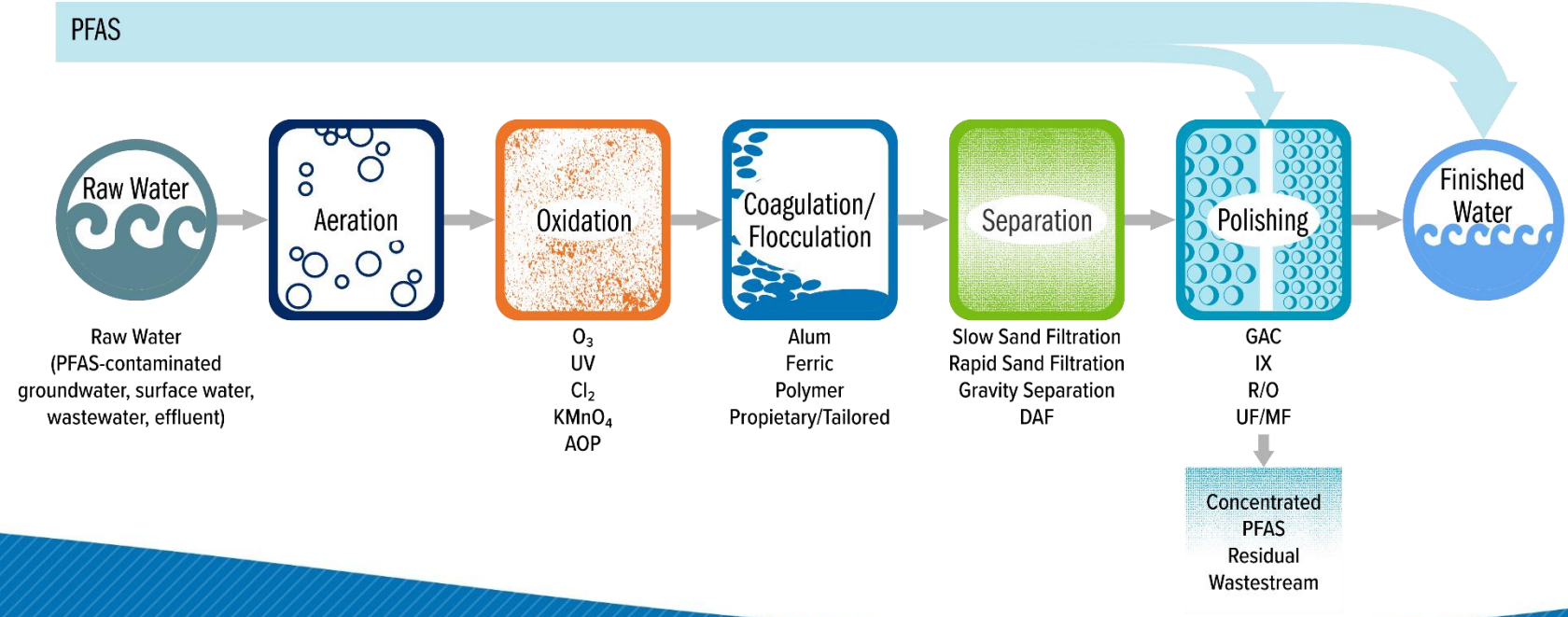


The McCrone Group

Almance County

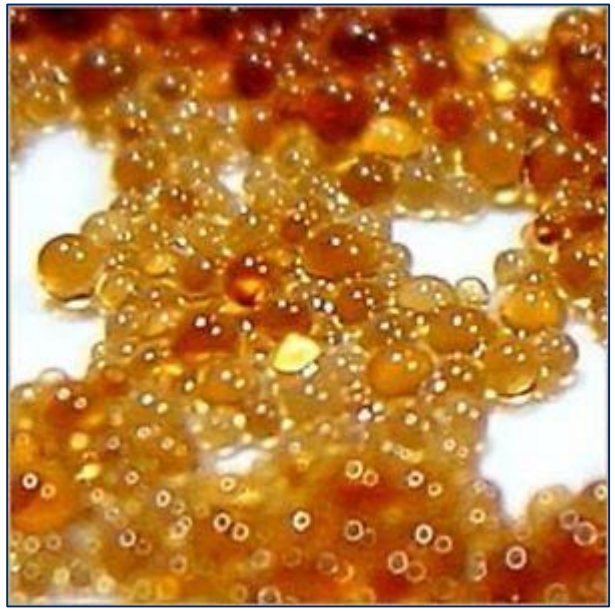
Per and polyfluoroalkyl Substances (PFAS) - Treatment Options

- Ineffective Conventional Treatment Processes
  - Conventional and Advanced Oxidation (with some exceptions)
  - Coagulation/Flocculation/Sedimentation (with some exceptions – PerfluorAD)
  - Slow and Rapid Sand Filtration
  - Dissolved Air Floatation (with some exceptions)
  - Microfiltration/Ultrafiltration



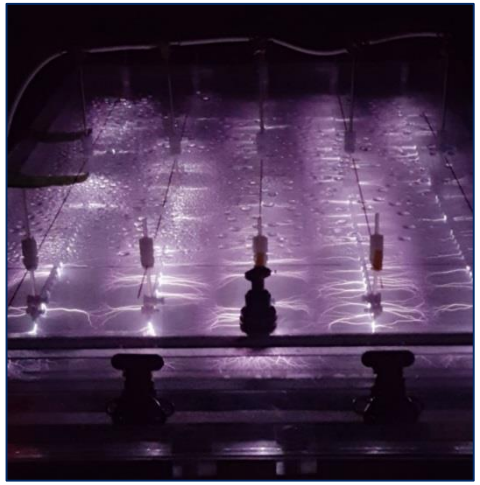
Per and polyfluoroalkyl Substances (PFAS) - Treatment Options

- Partially-effective Conventional Treatment (Concentration) Processes
  - Activated Carbon (GAC/PAC)
  - Ion Exchange (IX)
  - Reverse Osmosis (R/O)



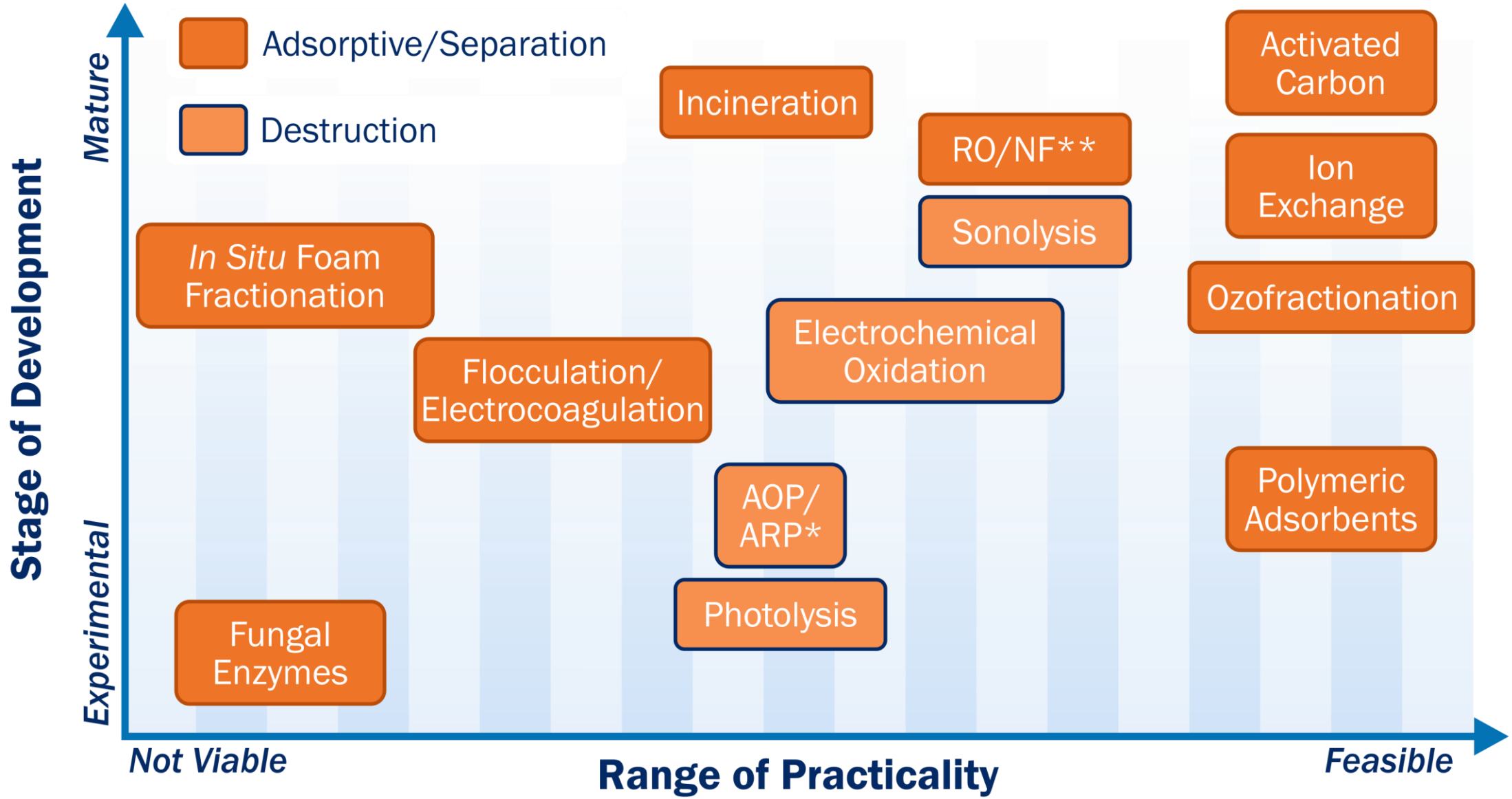
Per and polyfluoroalkyl Substances (PFAS) - Treatment Options

- Emerging Treatment Processes
  - Advanced Oxidation Processes (Oxidizing Free Radicals)
  - Advanced Reduction Processes (Reducing Free Radicals)
  - Sonolysis
  - Plasma Treatment
  - Next Generation Adsorbents (e.g., Carbon Nanotubes, Graphene, Polymeric Adsorbents)
  - Biodegradation?



Clarkson University

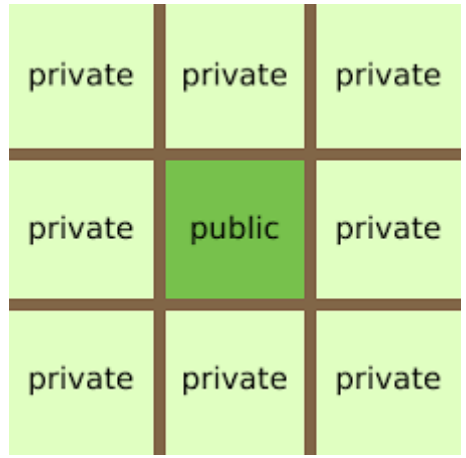
Jurassic World, Legendary Entertainment



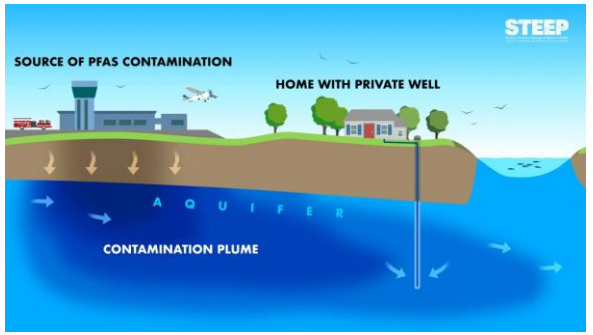
*AOP/ARP: Advanced oxidation processes/advanced reduction processes | **RO/NF: Reverse osmosis/nanofiltration

Adapted from Ross, et al., 2018

What Should Utilities Be Doing About It?



- There is no one-size-fits-all solution
- Balancing risk (financial, legal, customer)
- To sample or not to sample?
- Inclusion of PFAS in industrial pretreatment programs
- Evaluation of potential PFAS sources within sewershed
- OEPA will begin to request sampling of specific sites (e.g., triage of known users of AFFF and industrial users of PFAS)
- Certain large Ohio cities have begun testing industrial discharges from suspected PFAS emitters



BURGESS & NIPLE

Engineers ■ Planners ■ Environmental Scientists

Questions or (PFAS) Concerns?

Brian Yates, P.E.
brian.yates@burgessniple.com
614-459-2050 x 1416 (O)
614-558-2689 (C)