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Per- and Polyfluoroalkyl Substances (PFAS)

AN INTRODUCTION AND OVERVIEW

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AGENDA

- Introduction to PFAS
- Chemistry of PFAS
- Fate and Transport
- Regulatory Status
- Remediation

Introduction to PFAS

- Complex family of more than 4,500 anthropogenic fluorinated organic chemicals.
- First introduced in the 1930s.
- During late 1960s, PFAS-containing aqueous film-forming foam (AFFF) developed.
- Included in many different substances/products for their unique properties.
- Fluoropolymers (stable, durable, inert).
- Fluororepellents (water/oil repellency).
- Fluorosurfactants (detergents, wetting or foaming agents).

Fluoropolymers

- medical devices
- non-stick cookware
- electronics (cable insulation)

Fluororepellents

- Rain gear
- Upholstery/furniture
- Food packaging

Fluorosurfactants

- AFFF

- PFAS are produced via:
  - Electrochemical fluorination.
  - Telomerization.

PFAS[1]	Development Time Period							
	1930s	1940s	1950s	1960s	1970s	1980s	1990s	2000s
PTFE	Invented	Non-Stick Coatings			Waterproof Fabrics			
PFOS		Initial Production	Stain & Water Resistant Products	Firefighting foam				U.S. Reduction of PFOS, PFOA, PFNA (and other select PFAS[2])
PFOA		Initial Production	Protective Coatings					
PFNA					Initial Production	Architectural Resins		
Fluoro-telomers					Initial Production	Firefighting Foams		Predominant form of firefighting foam
Dominant Process[3]		Electrochemical Fluorination (ECF)						Fluoro-telomerization (shorter chain ECF)
Pre-Invention of Chemistry /			Initial Chemical Synthesis / Production			Commercial Products Introduced and Used		

- Significant source zones for PFAS include firefighting facilities or areas with high potential/history of fuel fires.

- Landfills and wastewater treatment plants also have PFAS concerns.

- PFAS present in all landfill leachate.

- PFAS can be detected in virtually all of the world population (blood serum).

- PFAS found virtually everywhere.

- Two classes of PFAS, PFOA (perfluorooctanoic acid) and PFOS (perfluorooctanesulfonate) have been linked to cancer (PFOA) and other illness.

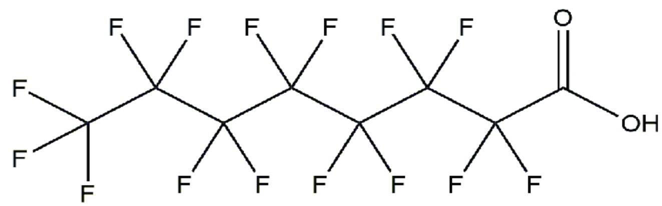
- Toxicological data still in development for human exposure.

Chemistry of PFAS

- C-4 to C-16 carbon chain lengths.
- Carbon to fluorine (F) bond is one of the shortest and strongest in nature.
- Structures contain a hydrophobic perfluoroalkyl backbone and a hydrophilic end group.
- PFAS divided into two general groups.

Perfluorinated

All H atoms in the alkyl chain are substituted by F atoms (PFOA and PFOS).

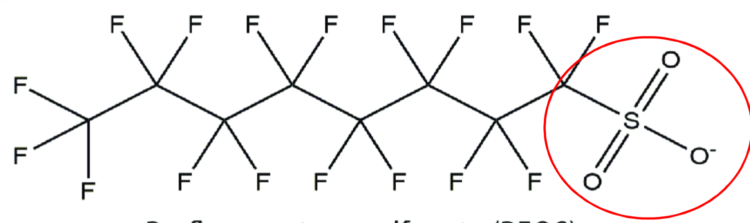


Perfluorooctanoic acid (PFOA)

Polyfluorinated

Partially fluorinated, the alkyl chain is not fully saturated with F atoms.

hydrophobic backbone



hydrophilic end group

Perfluorooctane sulfonate (PFOS)

Source: EPA.gov

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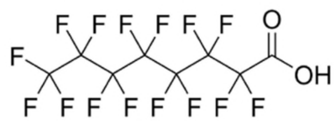
PFAS Precursors

- Many precursors can be degraded to perfluoroalkyl acids (PFAAS) of particular interest (PFOA and PFOS).

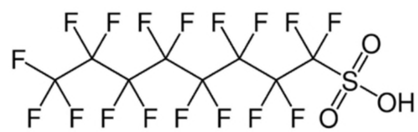
- PFAAS, which includes PFOS and PFOA are non-degradable, referred to as “terminal PFAS”.

Example of PFAAs

Perfluorooctanoic acid (PFOA)
$C_8HF_{15}O_2$

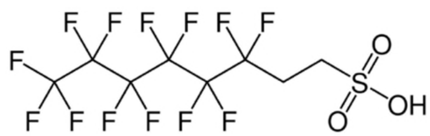


Perfluorooctanesulfonic acid (PFOS)
$C_8HF_{17}O_3S$

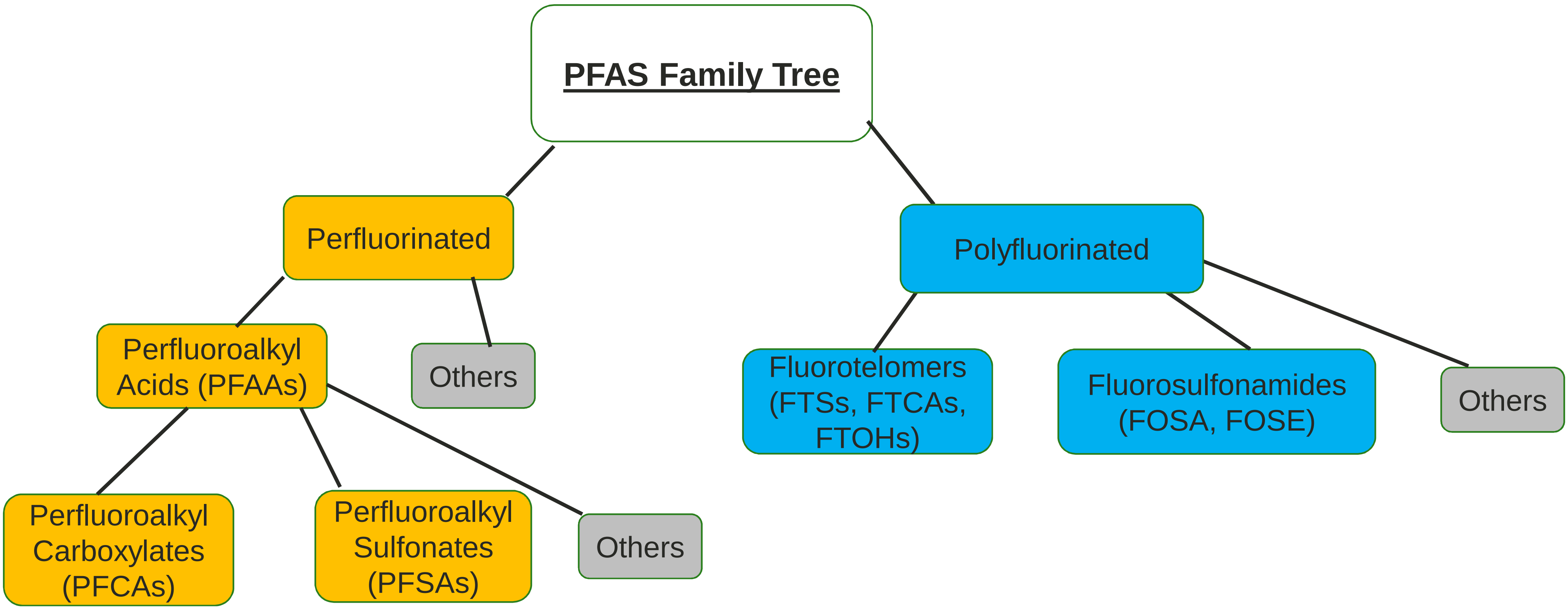


Example of PFAA Precursors

6:2 Fluorotelomer Sulfonate (6:2 FtS)
$C_8H_5F_{13}O_3S$



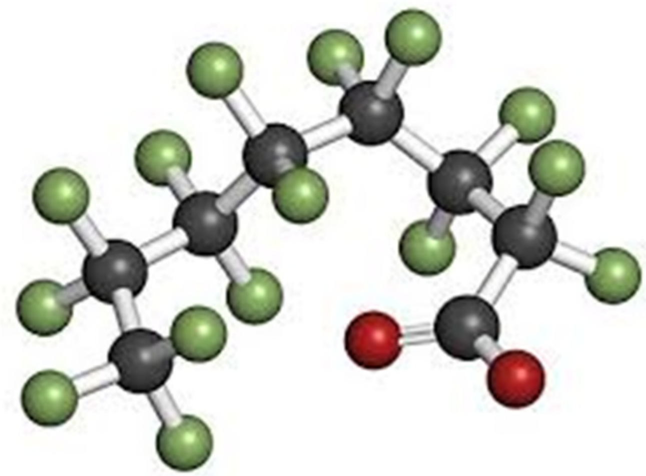
Source: Chaing et al. 2019



Source: EPA.gov

Properties of PFAS

- Oil, stain, and water repellant.
- Very limited reactivity.
- Non-flammable, stable in acids, bases, oxidants, and heat.
- Soluble in water (shorter chain = more soluble)
- Low vapor pressure (most PFAS non-volatile).
- Not readily degradable.



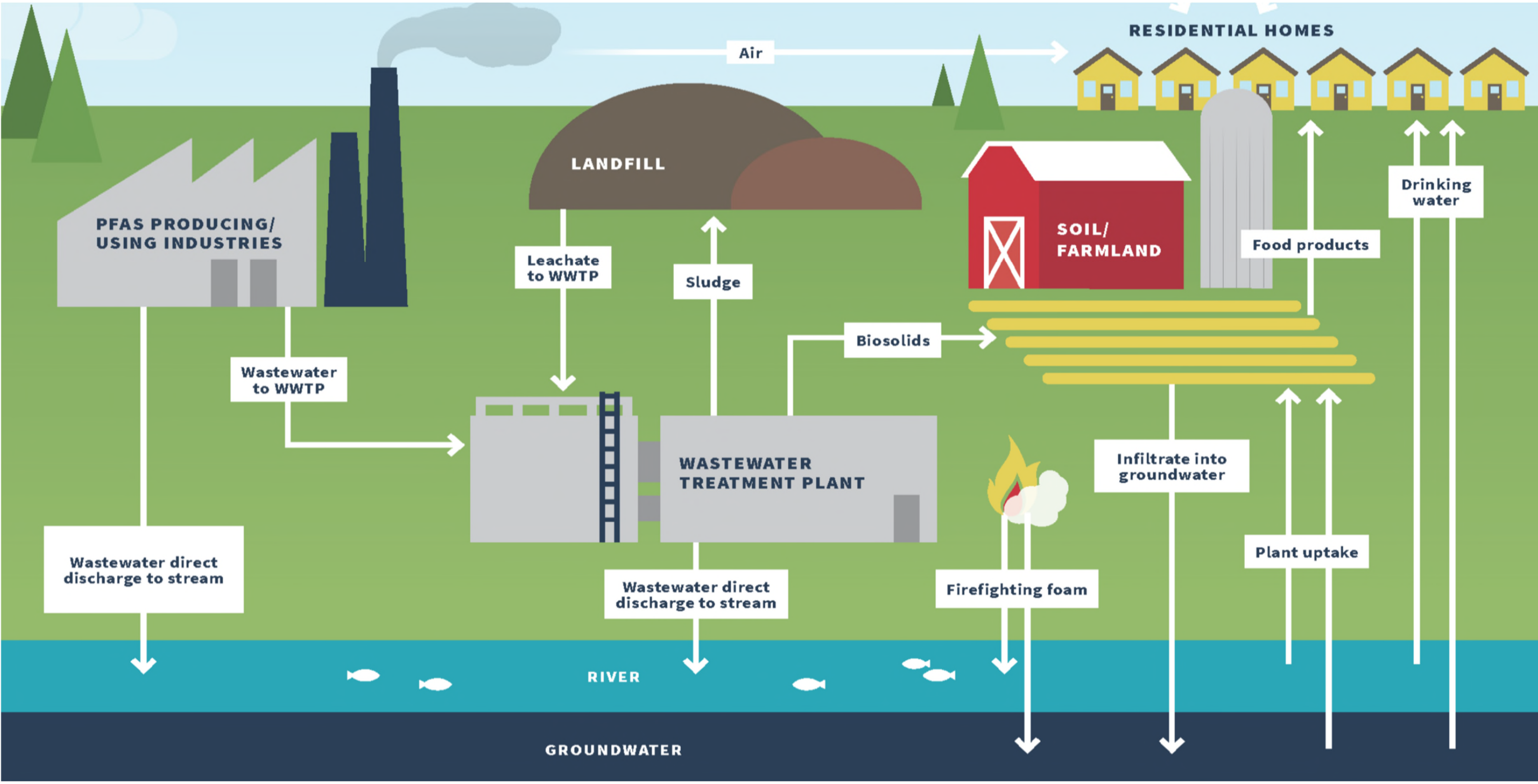
Drinking Water Analytical Method (EPA Approved/Validated)

- EPA Method 537 – drinking water matrices only (14 PFAS).

EPA and ASTM Non-Drinking Water Methods (Not EPA Approved/Validated)

- SW-8327 – surface water, groundwater, wastewaters (24 PFAS).
- SW-8328 – surface water, groundwater, wastewater, biosolids (24 PFAS + GenX).
- ASTM D-7979 – water, sludge, influent, effluent, wastewater (21 PFAS).
- EPA Method 537M (using isotopic dilution) – groundwater, leachate, surface water, wastewater (MI list of 24 PFAS).

Fate and Transport


RESIDENTIAL HOMES
Air
LANDFILL
PFAS PRODUCING/ USING INDUSTRIES
Leachate to WWTP
Sludge
SOIL/ FARMLAND
Food products
Drinking water
Wastewater to WWTP
Biosolids
WASTEWATER TREATMENT PLANT
Infiltrate into groundwater
Wastewater direct discharge to stream
Wastewater direct discharge to stream
Firefighting foam
Plant uptake
RIVER
GROUNDWATER

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- Not readily degradable (precursors are the exception).
- Long hydrolysis half-life (low reactivity with water).
- Long photolysis half-life (stable when exposed to light).
- Low retardation factor (highly mobile in groundwater).
  - Shorter chain length = more mobile.

= **persistent, can travel long distances**

- Bioaccumulative.

Atmosphere

- PFAS can occur in gas and particle phases or other aerosols suspended in air.
- PFAS commonly found in precipitation.
- Transformation of precursors (such as volatile FTOHS) to other PFAS can occur in atmosphere via reaction with O_2 / O_3.

Soil and Sediment

- PFAS found in soil and sediment due to atmospheric deposition, direct discharge, or exposure to impacted media.

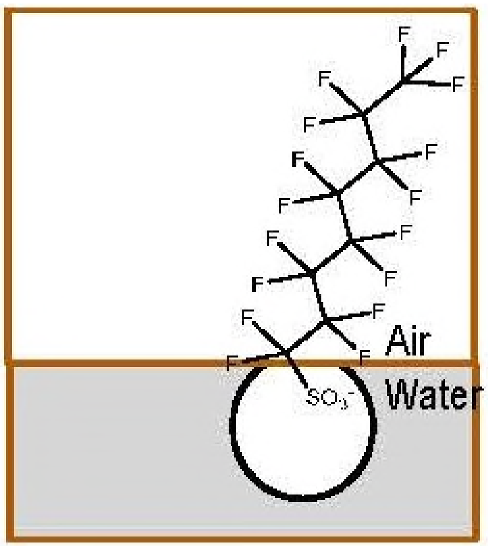
- PFAS distribution in soils is complex, affected by site-specific factors such as TOC, particle surface charges, and phase interfaces.

- Shorter chain PFAS have low sorption rate to soil particles.

- PFAS present in unsaturated soils are subject to downward leaching.

Groundwater

- Numerous sources of PFAS in groundwater.
- PFAS readily exist in aqueous phase and will not exist as NAPLs.
- Persistence and mobility of PFAS can cause large plumes.
- PFAS mass balance and fate and transport not fully understood.



Surface Water

- PFAS in surface waters typically depend on proximity to release/source.
- Groundwater impacted with PFAS can recharge surface water bodies (wetlands) and vice versa.

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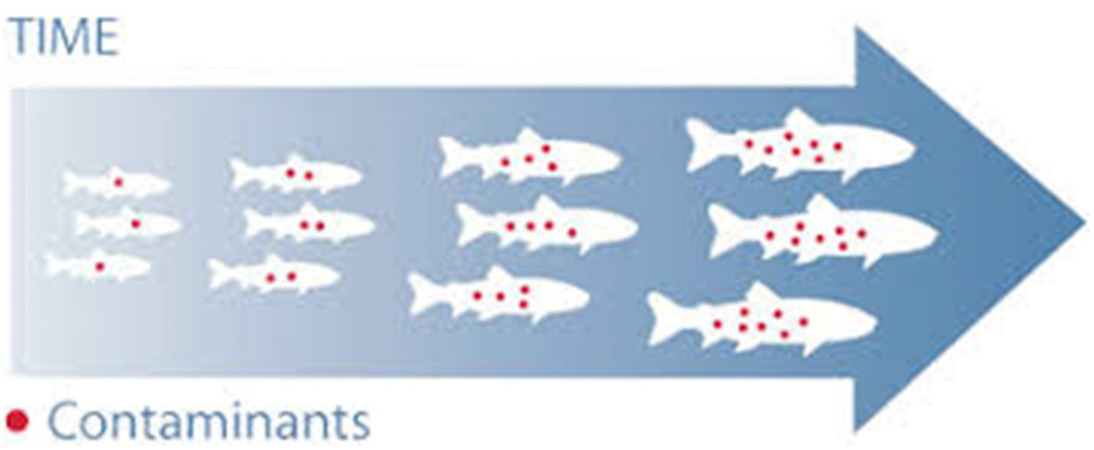
Biota and Bioaccumulation

- PFAS may be introduced to plants from soil, water, and air.
- Invertebrates are main component of food chain base, and play large role in biomagnification.
- In higher trophic level organisms, PFOS has been found as the dominant PFAS, with concentrations increasing up the food chain.
- In terrestrial systems, research indicates that the bioaccumulation of PFOS is low.

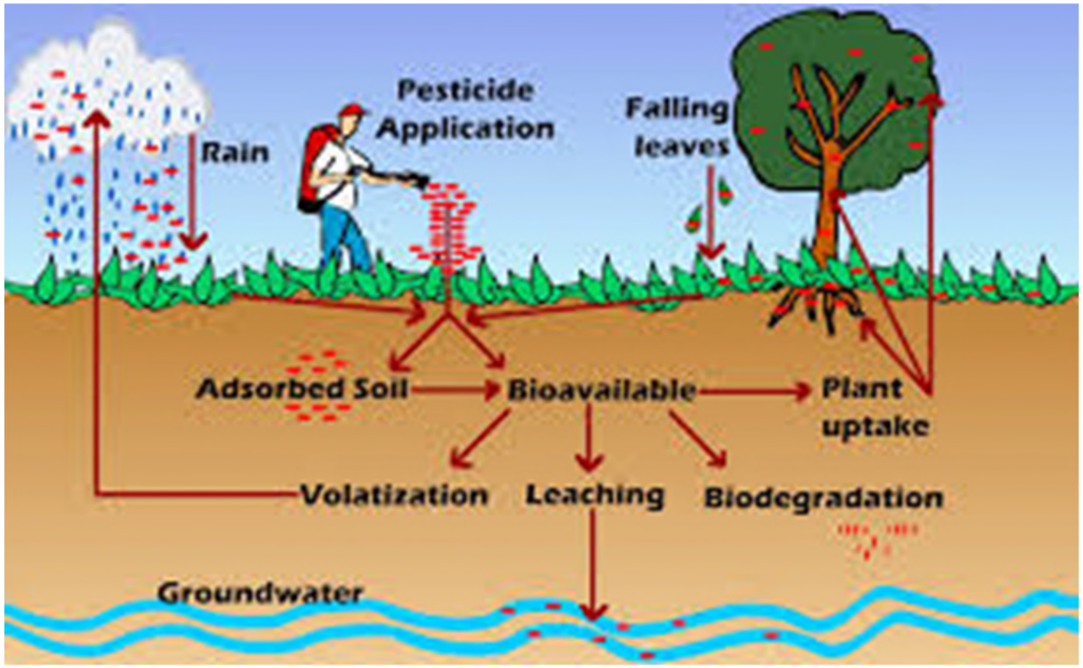


Biota and Bioaccumulation

- Accumulation of PFAS in fish is well documented, particularly for PFOS.
- Shorter chain PFAS are not as readily bioconcentrated or accumulated.
- PFOS tends to partition to the tissue of the highest protein density.

Department of Defense Study of Plant Uptake

- PFAS concentration – the higher the concentration of PFAS in water, the higher the uptake into the plant tissue.
- Plant type.
- Water Quality.
- Soil Type.
- Carbon chain length of PFAS.



Source: DoD, 2017

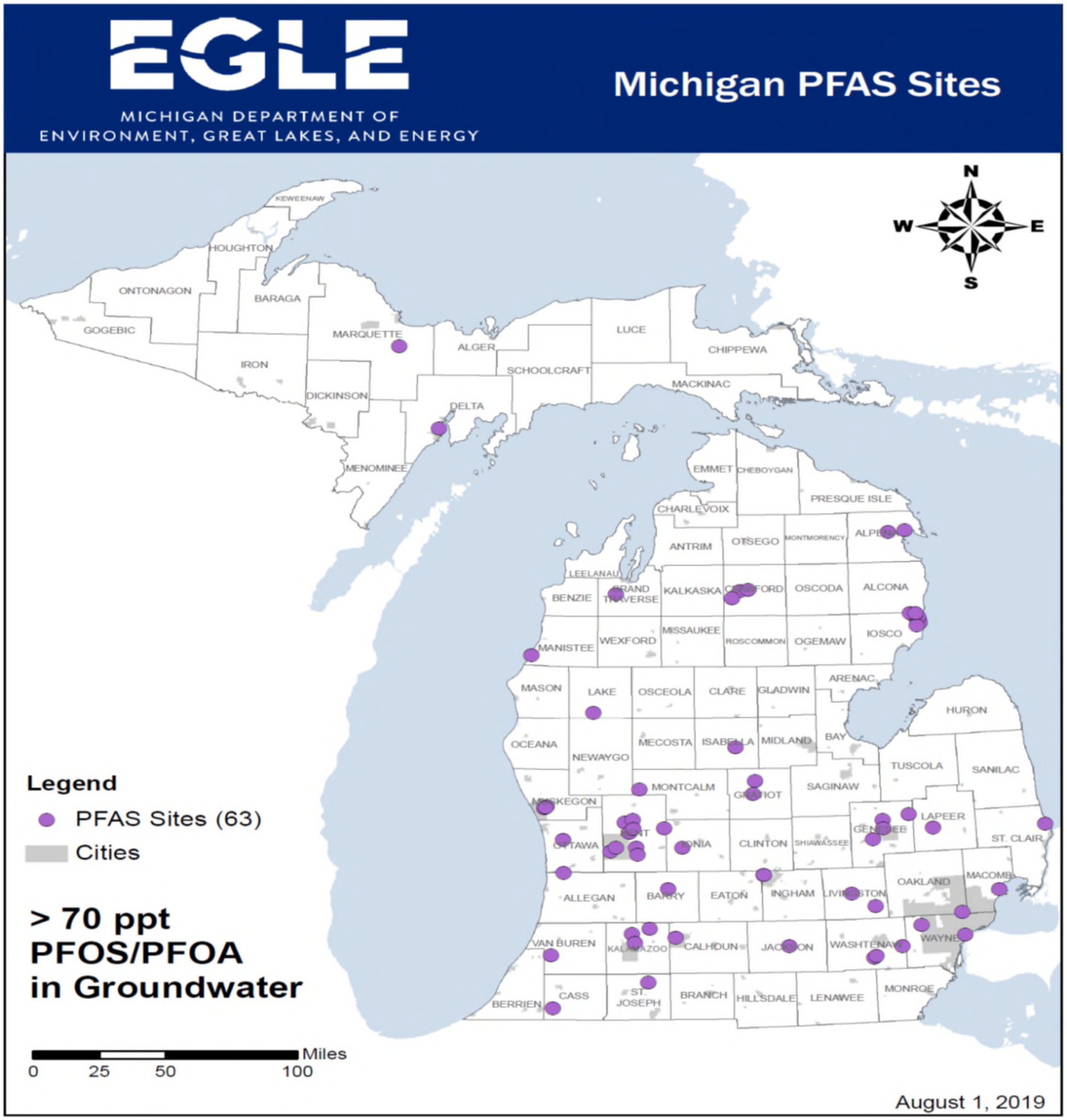
Biota and Bioaccumulation (humans)

- Dominant route of PFAS exposure in humans is ingestion of PFAS in water and consumption of food.
- Long chain PFAS are excreted very slowly in humans.
- As with other organisms, PFAS in humans tend to bind to and accumulate in protein-rich tissues.

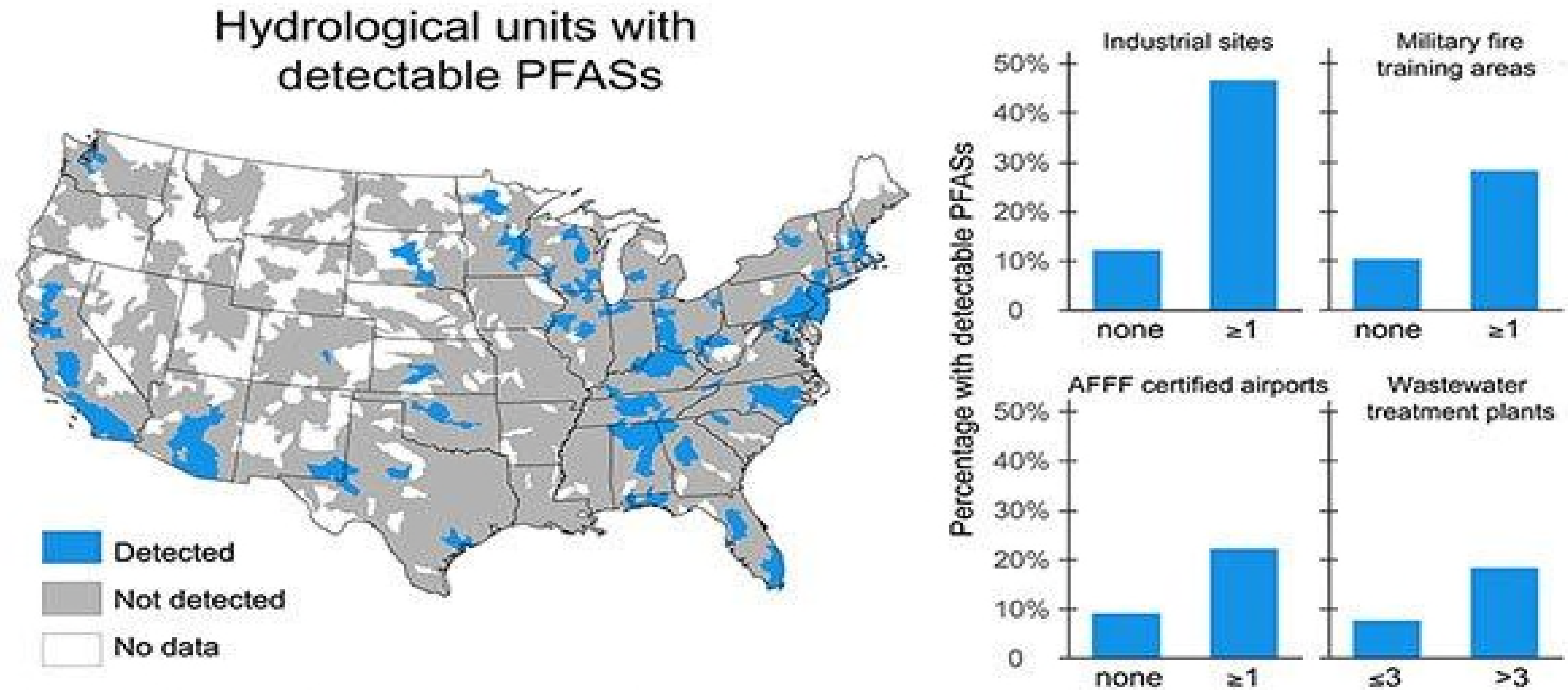
Regulatory Status

Michigan PFAS Standards

- Surface water
  - PFOS: 11 ppt (or ng/L) for surface water (e.g. streams) used as drinking water source and 12 ppt for those not used as a source.
  - PFOA: 420 ppt for surface waters used as a drinking water source and 12,000 ppt for those not used as a source.
- Groundwater
  - 70 ppt for PFOA/PFOS combined total.
  - GSI per surface water quality standard.
- Drinking water
  - 70 ppt for PFOA/PFOS combined total.



- Prioritized investigations based on known or suspected sources, potential for exposure.
- Numerous other investigations underway.



Credit: Hu et al, *Environmental Science & Technology Letters*

Remediation

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PFAS Remediation Challenges

- The same chemical properties that make PFAS so effective and useful make them difficult to remediate.
- Clean-up goals.
- Lack of biodegradation and persistence in the environment = MNA not feasible.
- Sorption using carbon is currently the only full-scale treatment option.
- Excavation and disposal of impacted soils.
- Risk to make the site worse by generating more terminal compounds and more mobile species.
- Some alternative remedial technologies are being developed.

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Thank You

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