Per and Polyfluoroalkyl Substances: Making Informed Decisions about PFAS

Ray Wuolo – Barr Engineering Company

What are PFAS?

Properties

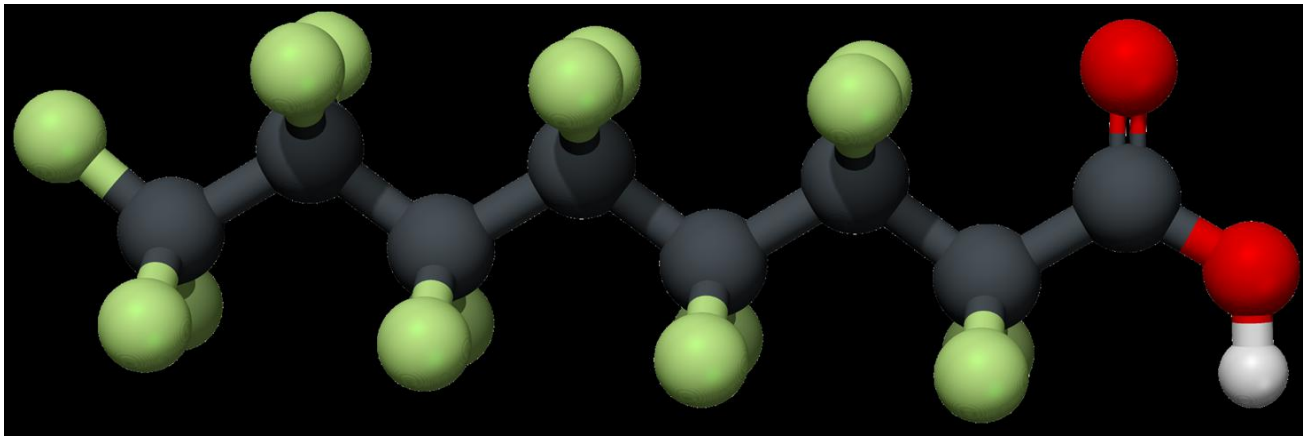
Health risks

Regulatory framework

Sources

Sampling and testing

Potential actions



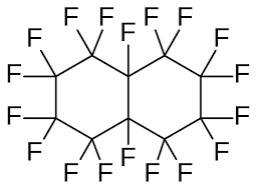
Per- and polyfluoroalkyl substances?

Perfluorcarbons
- Only carbon and fluorine atoms
- Potential green house gas

Perfluorinated chemicals

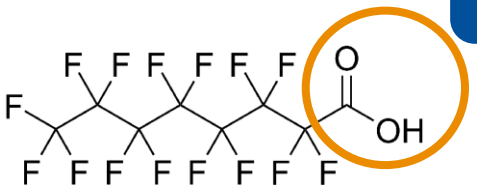
"PFCs"

Perfluorocarbons (also called "PFCs")



Per- and polyfluoroalkyl substances

"PFAS"



PFAS
- Oxygen, hydrogen, sulfur and/or nitrogen atoms in addition to carbon/fluorine
- PFOA, PFOS, and thousands more

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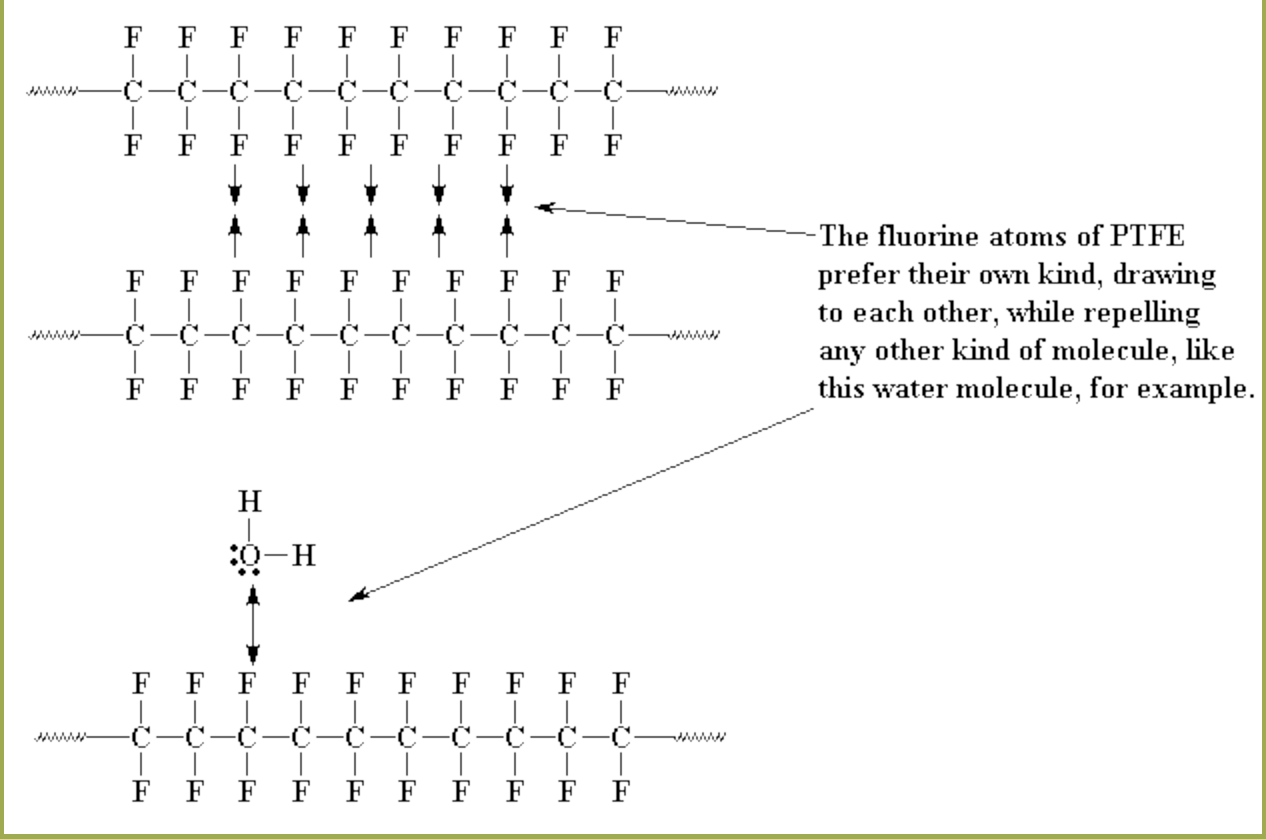
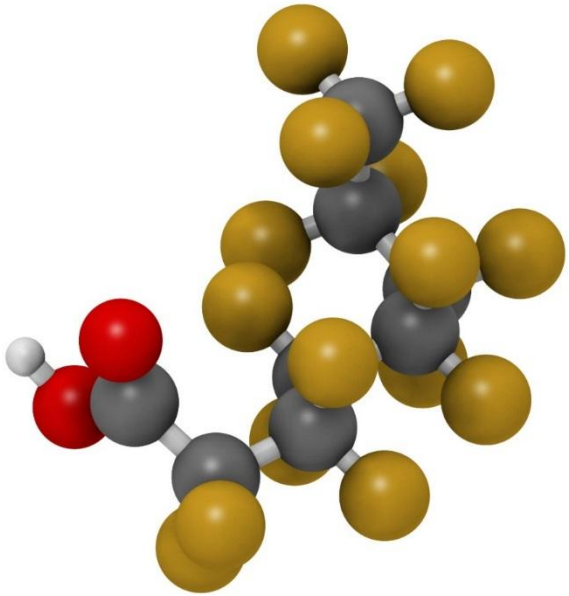
long-chains of carbon with 2 fluorine atoms attached to each carbon



The C-F bond is the shortest and strongest in nature

PFAS properties

- **Manufactured chemicals** that are used in products that resist heat, oil, stains, and water
- Resistant to biodegradation
- Destroyed at high temperatures
- Semi-volatile
- Miscible in water
- *Slight* affinity for organic carbon/mineralization



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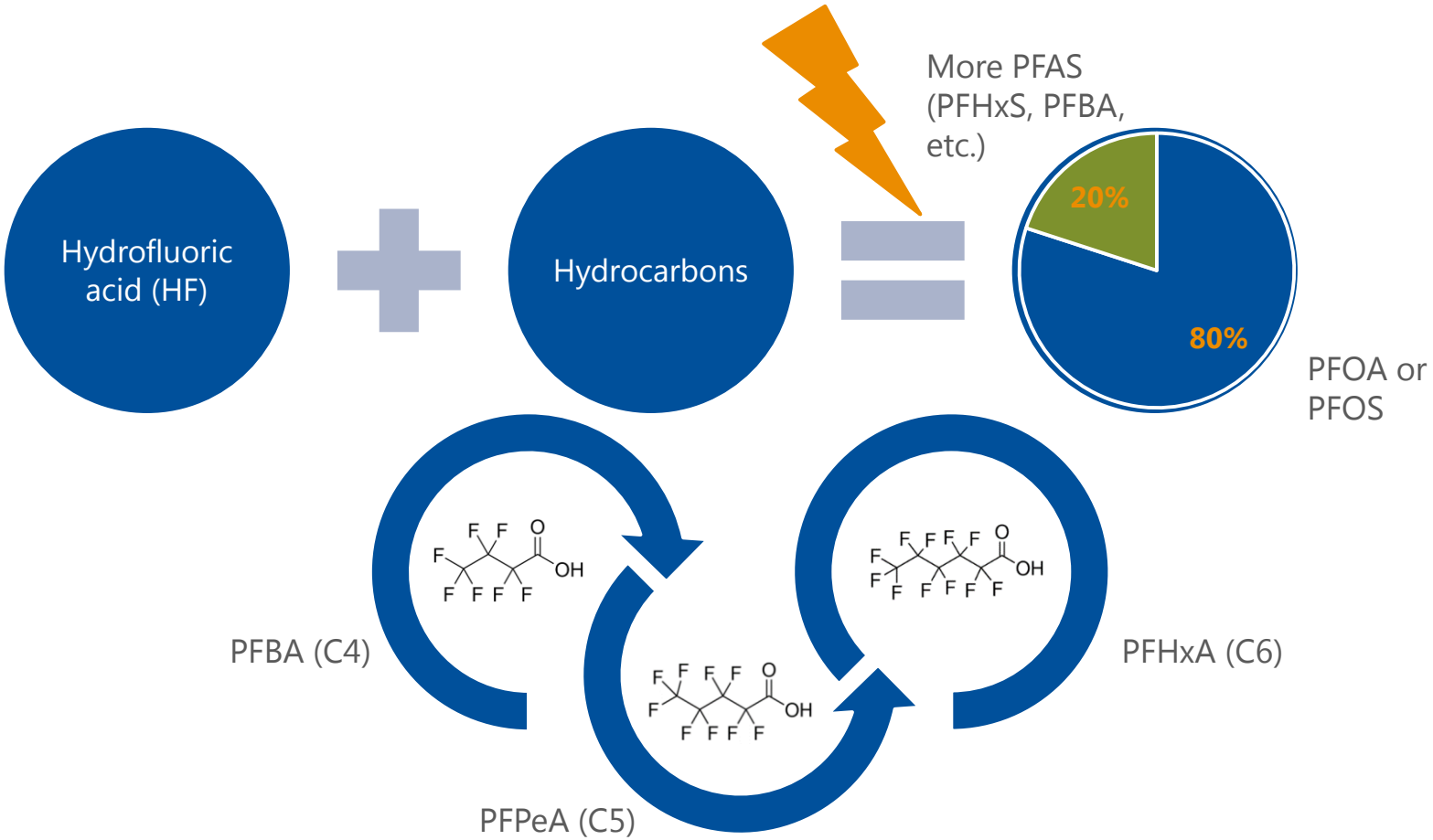
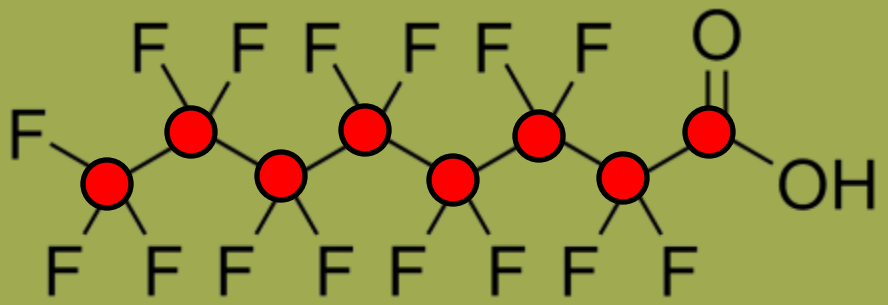
PFAS has historically been produced through two primary methods.



beginning @ 1951, DuPont began using perfluorooctanoic acid (**PFOA**) to manufacture Teflon®

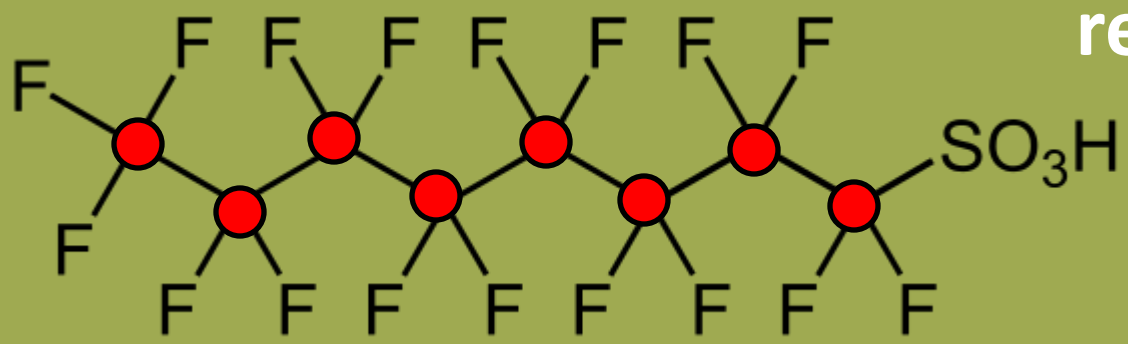
- purchased from 3M
- 3M began PFOA production in 1947 using an electrochemical fluorination process – ceased in 2002
- DuPont began PFOA production (on a small scale) in 1970s using telomerisation process – ramped up in 2002
- 8 manufacturers phased out production by 2010



$C_8HF_{15}O_2$
8 carbon atoms
referred to a “C8”

The other perfluorinated alkylated substance (PFAS) - **PFOS**

- **PFOS** – perfluorooctane sulfonate, manufactured from 1949-2002
- **3M** made PFOA and PFOS directly through electrochemical fluorination



also referred to a "C8"

PFOA and PFOS are not pure products

Table 3 Impurities and branched isomer content in 3M ECF PFOS and PFOA

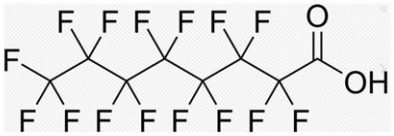
Impurity in 3M ECF PFOS (lot 217)	%Impurity (wt)	%Branched of the impurity	Impurity in 3M ECF PFOA (lot 332)	%Impurity (wt)	%Branched of the impurity
PFBS	1.2[a]	0[b]	PFHxA	0.73[c]	18[d]
PFPeS	1.3[a]	N/A	PFHpA	3.7[c]	N/A
PFHxS	4.7[a]	18[e]	PFNA	0.2[f]	65[f]
PFHpS	1.1[a]	28[g]	PFDA	0.0005[f]	54[f]
PFDS	N/A	75[h]	PFUnA	0.0008[f]	28[f]
PFOA	0.79[f]	19[f]	PFDoA	0.0008[f]	32[f]
PFNA	0.002[f]	70[f]			
PFDA	0.0005[f]	51[f]			
PFUnA	0.0002[f]	46[f]			
PFDoA	0.0004[f]	33[f]			

"C7"

PFAS – uses and history

- Used in **coating** and **waterproofing** processes, **fire suppression** and to reduce surface tension
- Production of PFOA and PFOS phased out
  - Current products have different chemical makeup
- Historical chemicals were found to be persistent

perfluoroctanoic acid (PFOA)



perfluoroctane sulfonate (PFOS)

PFAS can be found in consumer products, and municipal and industrial sources.

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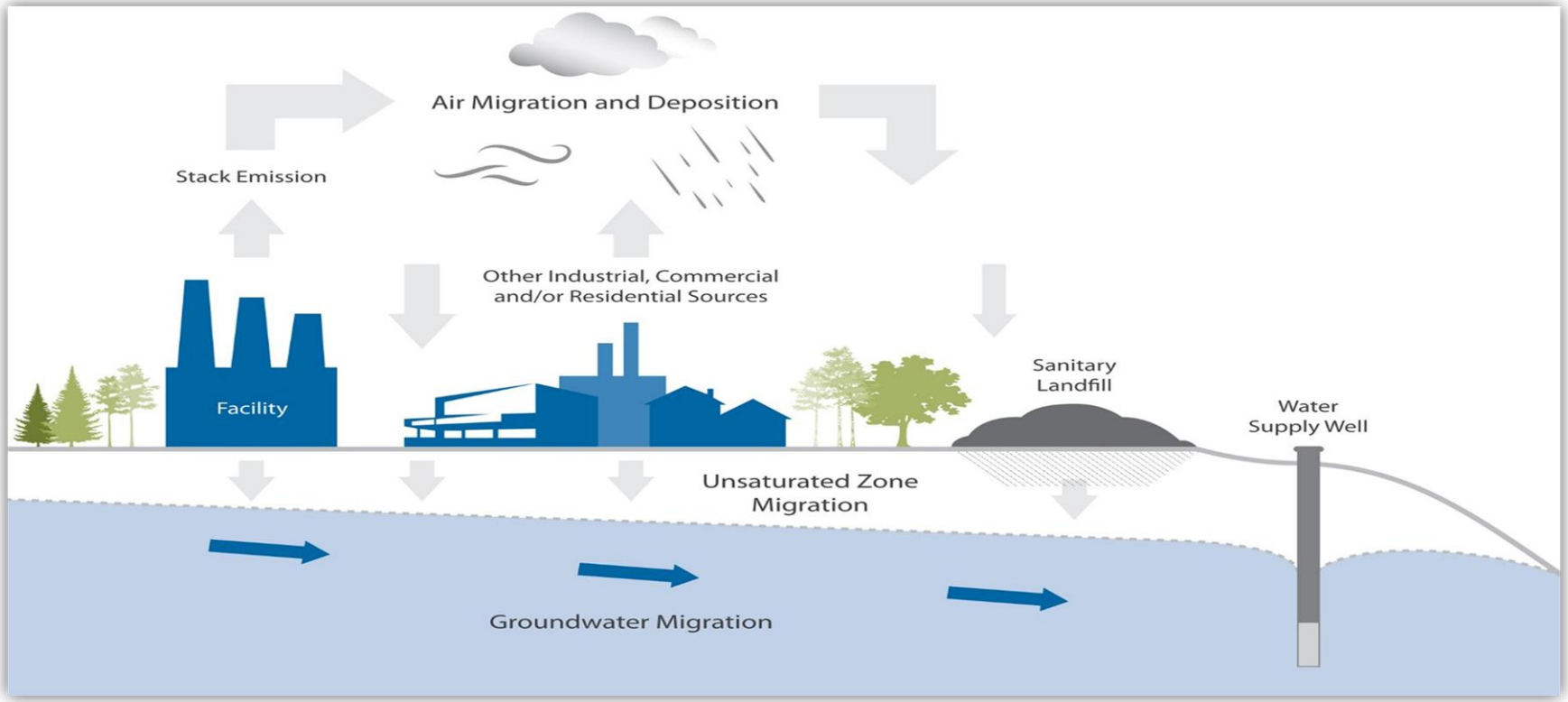
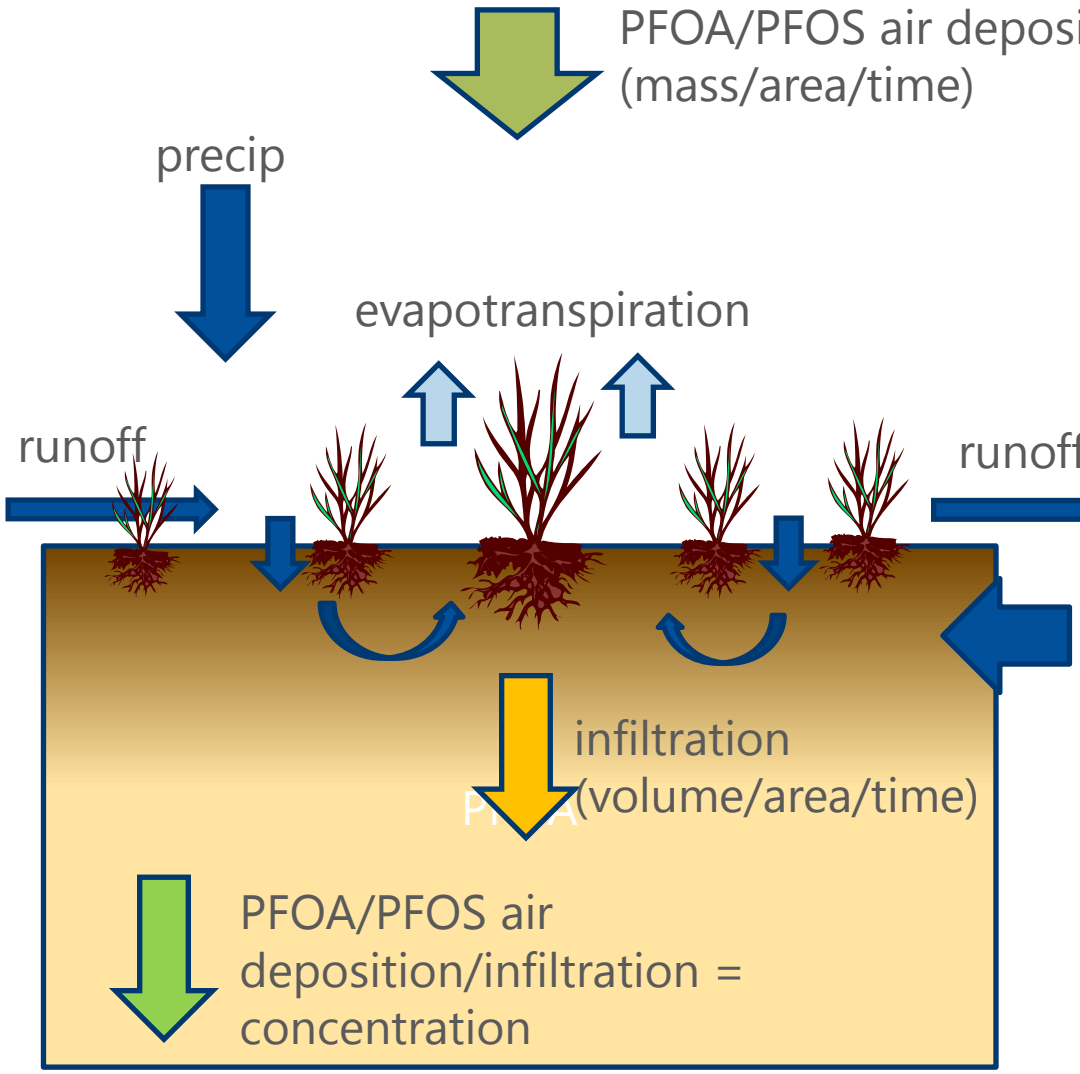
where is PFOA (and PFOS) found in the environment?

- in vicinity of manufacture and use (air-borne deposition) – by far the largest source
- manufacturing facilities that use fluoropolymers
- fire-fighting training locations (especially airports and refineries)
- landfills
- wastewater treatment plant outfalls
- treatment sludge application areas
- plating facilities

Fate and transport in the environment



PFOA and PFOS likely have a global background concentration



PFOA & PFOS soil concentrations correlated with total organic carbon in shallow soils

Global air deposition likely results in a **ubiquitous** background concentration in soil

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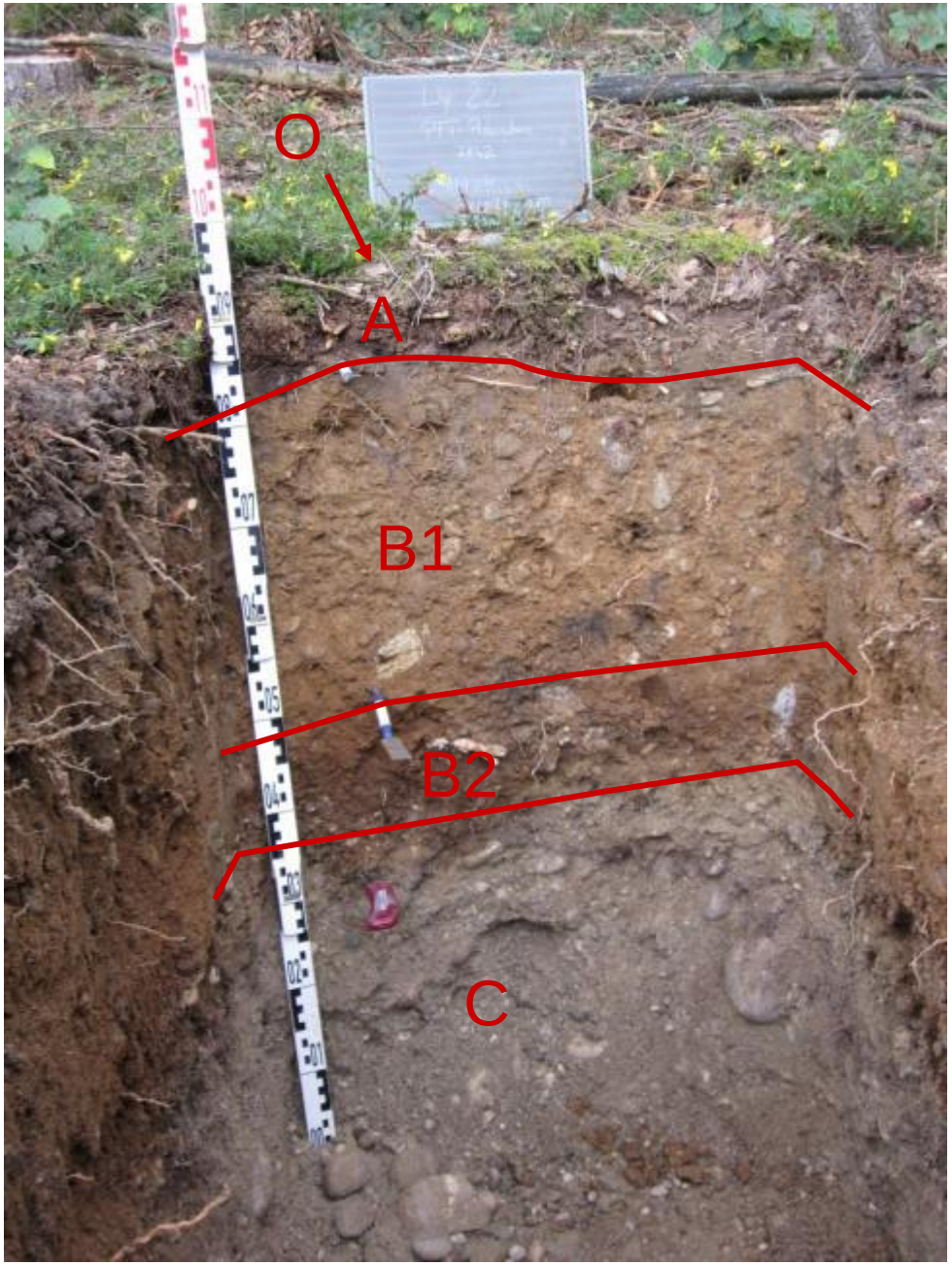
PFOA and PFOS accumulate in the O and A soil horizons (higher TOC)



Research on the health effects of PFAS is evolving.

National median blood: 2 - 6 ppb

- 2016: EPA released **health advisory levels** for PFOA/PFOS
- 2018: ATSDR draft report on PFAS listed additional affects for PFOA and PFOS and also **added health concerns** for PFNA, PFHxS, and PFHpA
  - Industry disputes ATDSR methodology and approach
  - ATSDR acknowledges that "…cause and effect relationships have not been established for any of the effects, and the effects have not been consistently found…"

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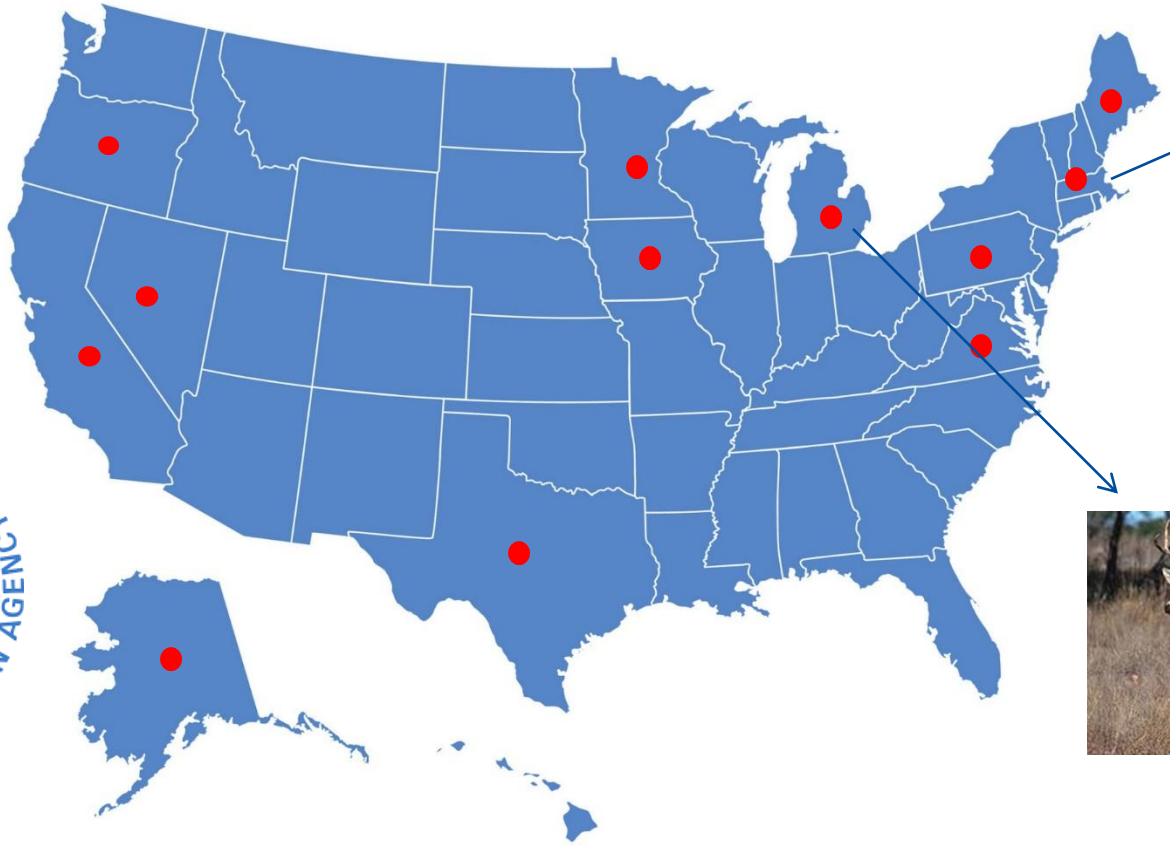
18 states in the U.S. have established PFAS guidance or limits.

State has adopted EPA criteria (PFOA and PFOS) and/or has released revised state-specific criteria



Connecticut
Delaware
Massachusetts
New Jersey
New Hampshire
Rhode Island
Vermont

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

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Standards and guidance values for PFAS in groundwater, drinking water, surface water and wastewater are changing rapidly.

	USEPA (PPT)	Minnesota (PPT)	Vermont (PPT)	New Jersey (PPT)	California (PPT)	Nevada (PPT)
Standard/ Guidance	Health advisory levels (2016)	Health based guidance values (2017/2019)	Health advisory levels (2018)	Maximum contaminant levels (2017/2018)	Response level (SWRCB, 2018)	Basic comparison level (2015)
PFOS	70	15	20	13	70	667
PFOA	70	35	20	14	70	667
PFOA + PFOS	70	--	20	--	70	--

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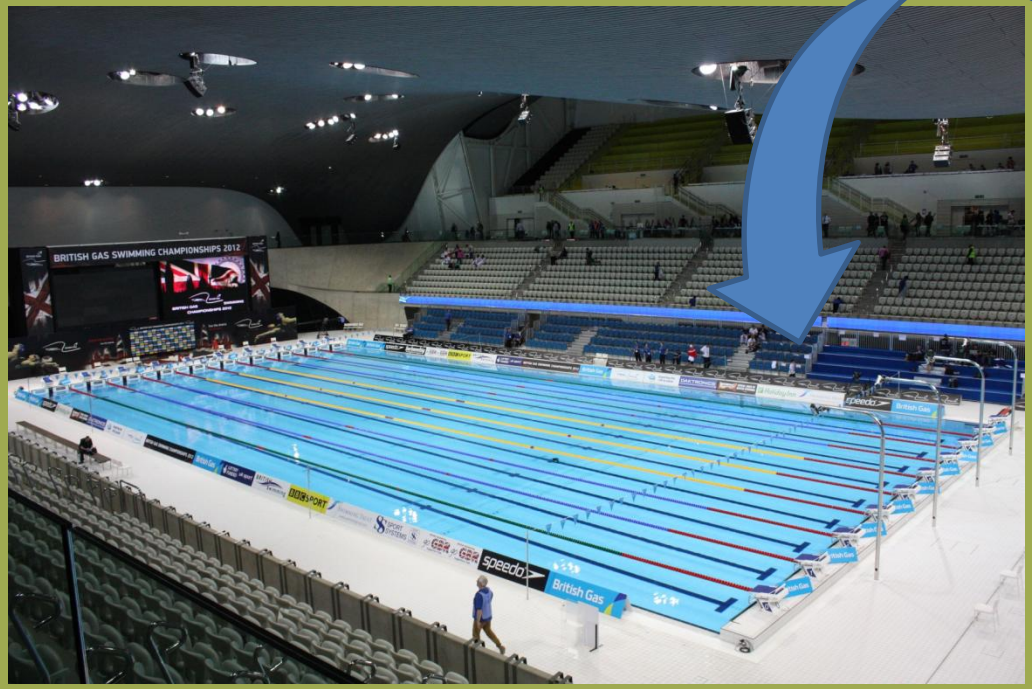
how much is 40 parts per trillion (ppt)?



1 pea

Olympic swimming pool =660,430 gallons of water

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Many challenges exist in sampling and analyzing for PFAS.

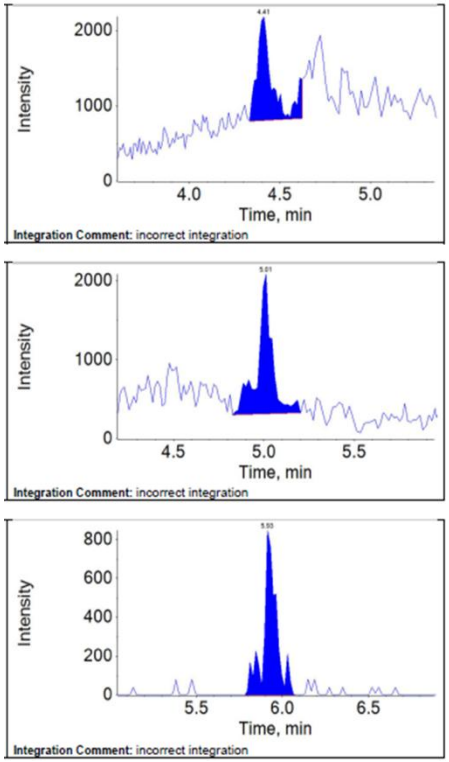
- Rinse/equipment blanks are necessary
- Multiple materials commonly-used in investigations may contain PFAS
  - Bentonite, lube oil for drilling tools, pipe dope, plumbing tape
  - Teflon™ bailers, tape
  - Tyvek®, Nomex®
  - Blue ice packs
  - Field books
  - Performance fabrics, rain gear

USEPA Method 537.1 is currently the only promulgated method for analyzing PFAS

US EPA 537.1 – drinking water method

- state lists continue to grow
- replacement chemicals (4 carbon chains/GenX)
- data validation

EPA developing new methods



Fire-Fighting Foams: potential sources at many facilities

- Aqueous film-forming foam (AFFF)
  - Not all foams contain PFAS
- Lignite, subbituminous, and brown coal piles where AFFF may have been used
- Other manufactured/general use items
  - Paints, coatings, hydraulic fluids
- Long-term wire storage yards

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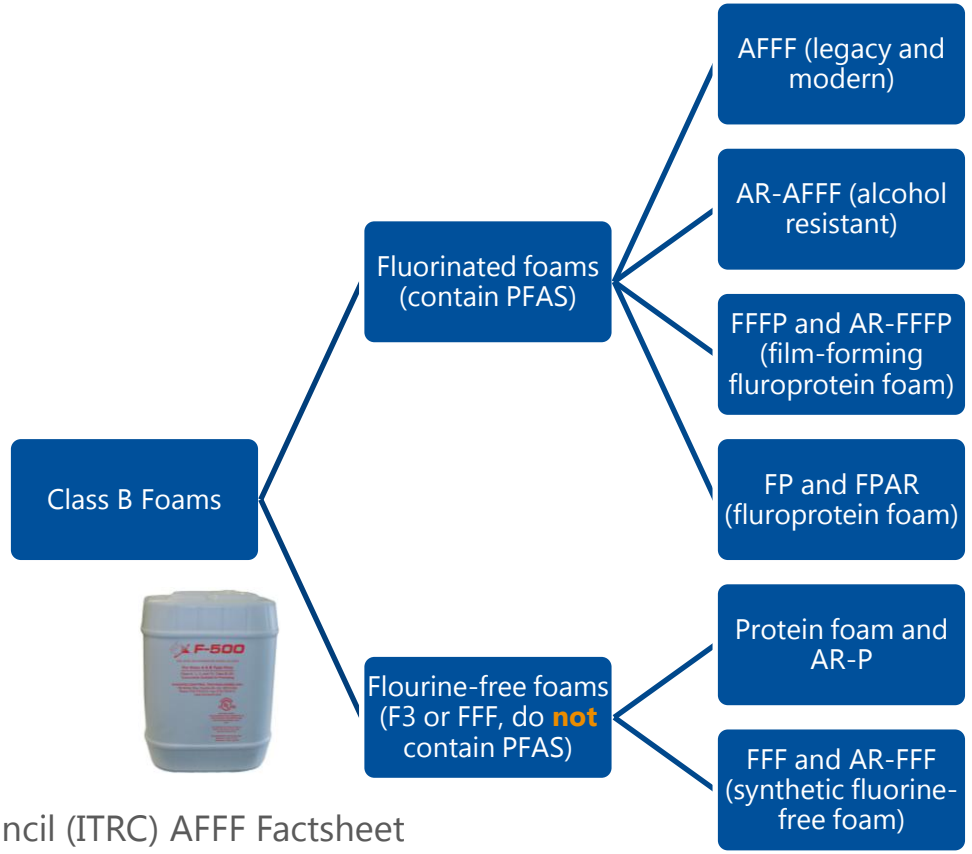
AFFF: Class B foam

- Underwriters Laboratories **(UL) Standard 162**
- Department of Defense MILSPEC MIL- PRF-24385 (military applications/ airports)

AFFF: contingency planning and risk management

- Identify **appropriate storage** and consider unplanned **release impacts**
- Prepare to **manage fire fighting water** as hazardous material
- Reconsider on-site, live **fire training**, train with fluorine-free foam



Interstate Technology Regulatory Council (ITRC) AFFF Factsheet

AFFF: ongoing risk management approach

- Incorporate **fire fighting water management** into emergency response plans
- Evaluate conveyances and storage to find and address potential off-site or unlined **containment impacts**
- Pre-plan treatment approach as **PFAS water treatment** may be required depending on containment capacity

3. Composition/information on Ingredients

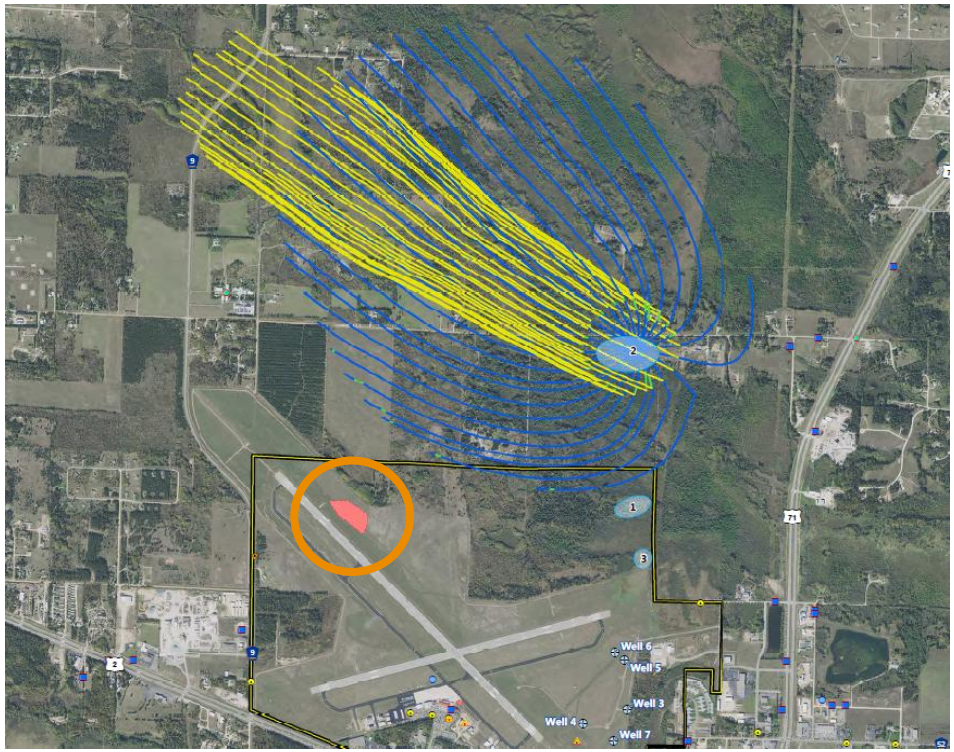
3.1. Mixture

The following component(s) in this product are considered hazardous under applicable OSHA(USA)

Chemical name	CAS No	weight-%
2-(2-Butoxyethoxy)ethanol	112-34-5	10 - 30
Sodium Decyl Sulfate	142-87-0	1 - 5
Perfluorinated Amphoteric Surfactant	Proprietary	1 - 5
Sodium Octyl Sulfate	142-31-4	1 - 5
Perfluoro Telomer	Proprietary	1 - 5

AFFF: current risk evaluation

- Existing fire training or historic fire areas
  - identify potential risks (proximity to drinking water sources)
  - evaluate **fate and transport**
  - plan for public/ regulator reaction



Remediation: techniques and challenges

- **In-situ** techniques include groundwater cutoff and containment and activated carbon injection.
- **Soil treatment** techniques include stabilization and thermal destruction (>950 °C)

PLUME STOP®
Liquid Activated Carbon

ITRC Remediation Technologies and Methods for PFAS Factsheet

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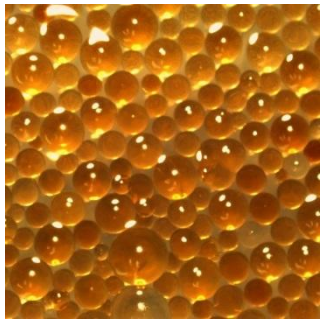
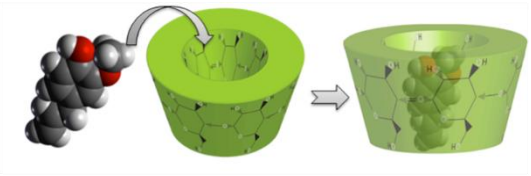
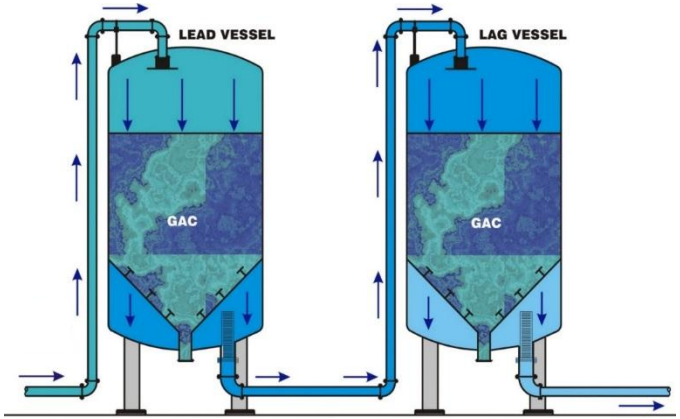
Water treatment: primary treatment technologies







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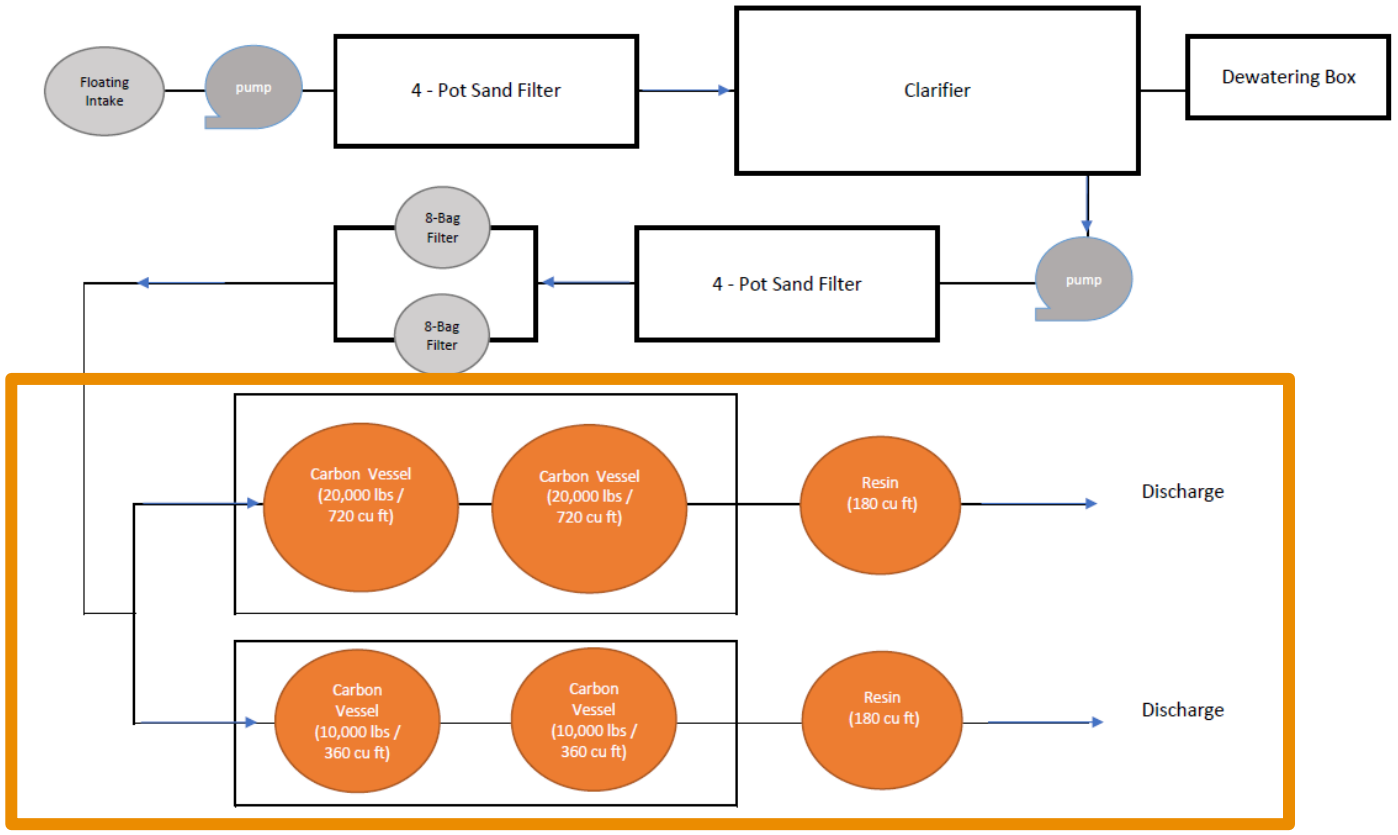
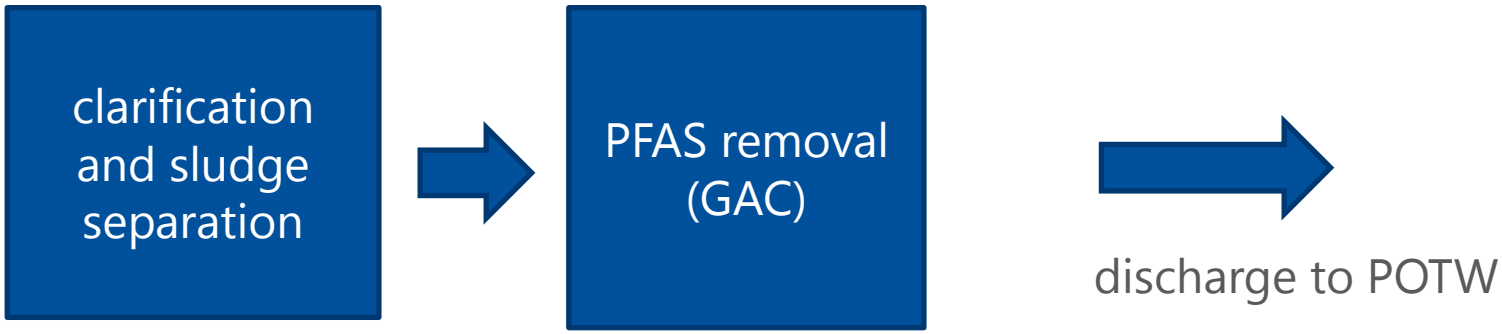
Water treatment: surface water treatment example process flow



treatment of industrial waste before discharge POTW

- remove PFAS from waste stream before discharge to sanitary sewer
- sludges and heavy mixed waste streams require thoughtful pre-treatment
- separating in-plant waste streams may be necessary
  - allows for collection and batch treatment



Takeaways

- Understand that there may be many sources of PFAS

- Examine and understand risks, take prudent action

- Ensure appropriate sampling and analysis procedures are followed

- Proven remedial options are limited

- Emergency response planning should include PFAS impacts

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Thank you!

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