EMERGING CONTAMINANTS:
POLY- AND PERFLUOROALKYL SUBSTANCES AND YOUR WATER SUPPLY

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Why the Interest in PFAS?

- Found widely distributed in the environment
  - Persistent and resistant to degradation
  - Potential human toxicity
- Used in a wide range of industrial and commercial applications;
  - Non-stick cookware
  - Fabric protectors
  - Paints and coatings
  - Ski wax
  - Microwave popcorn bags and pizza boxes
  - Aqueous Film Forming Foam (AFFF)

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Agenda

- What are PFAS?
- Where are they used?
- History of use
- Toxicology and Potential Health Effects
- Regulatory Framework
- Major Sources and Entrance into Water Supplies
- Site Characterization Considerations
- Fate and Transport in Groundwater
- Treatment Options

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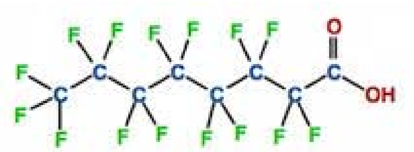
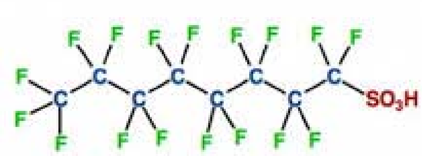
What Are Poly – and Perfluoroalkyl Substances (PFAS)?

- PFAS have been around for ~ 60 years
- Complex family of >3,000 chemicals
  - Long chain and short chain molecular structure
    - Greater than 8 C atoms – Long Chain
    - Less than 8 C Atoms – Short Chain
- Two currently regulated PFAS molecules
  - Perfluorooctane sulfonic acid (PFOS) and
  - Perfluorooctanoic acid (PFOA)
    - Sometimes referred to as C8



PFOA – Perfluorooctanoic acid



PFOS – Perfluorooctanesulfonic acid

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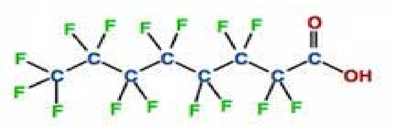
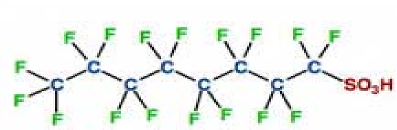
What Are Poly – and Perfluoroalkyl Substances (PFAS)?

- Unique physical and chemical properties drive the end uses
- C-F Bond is very strong



PFOA – Perfluorooctanoic acid



PFOS – Perfluorooctane sulfonic acid

From Steinle-Darling, 2016

Properties	Desirable		Less Desirable
Extreme Chemical inertness	Firefighting (AFFF)		Difficult to Destroy
Hydrophobic and Lipophobic	Repels Stains and water. Prevents wrinkles		Accumulates in protein tissues and blood
Surface Active	Nonstick coating material		Environmentally Stable.

History of PFAS

- **1940s Production** - 3M PFOS and PFOA; Dupont uses to make Teflon products
- **1960s - Wide spread use** - Food packaging, water-repellent products, AFFF developed
- **1978 - Health Effects** - 3M finds PFOA in blood samples from workers
- **1980s - Environmental Impacts** - Dupont finds PFOA in drinking water near WV Teflon Manufacturing Plant
- **2002 - 3M Phases out production** - of PFOS (2002) & PFOA (2008)
- **2015 - All other PFOS & PFOA producers in US phase out production**

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			

Notes:
1. This table includes fluoropolymers, PFAAs, and fluorotelomers. PTFE (polytetrafluoroethylene) is a fluoropolymer. PFOS, PFOA, and PFNA (perfluorononanoic acid) are PFAAs.
2. Refer to Section 3.4.
3. The dominant manufacturing process is shown in the table; note, however, that ECF and fluorotelomerization have both been, and continue to be, used for the production of select PFAS.

Sources: Prevedouros et al. 2006; Concawe 2016; Chemours 2017; Gore-Tex 2017; US Naval Research Academy 2017

Toxicology and Potential Health Effects

+95%

of individuals sampled detected PFAS

- Appear to be widespread across the globe
- Contacts primarily through
  - Food, Food packaging, drinking water
  - Breathing air that contains contaminated dust from carpets, upholstery, clothing, etc.
- Will build up in body until exposure stops
- PFAS Reach the fetus or nursing infants of mothers who are exposed
- Are not significant through skin contact when bathing or showering

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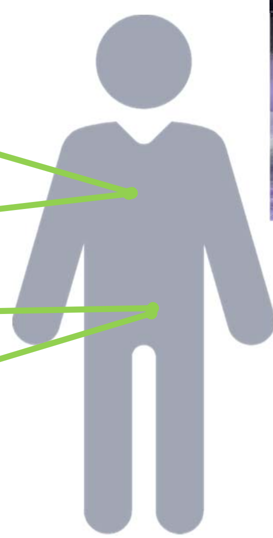
In the Body

Readily absorbed Bio accumulative
Not metabolized

Distributed predominantly to the liver and blood

Leaves the body as waste

Reabsorbed to the body to an extent after excretion



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Potential Health Effects

- Animal studies indicate impacts to the liver, changes in hormone levels and adverse developmental outcomes
- Possible health effects include the following:
  - Increased cholesterol levels?
  - Increased risk for high blood pressure?
  - Liver disease?
  - Auto immune diseases?
  - ulcerative colitis?
  - thyroid disease?
  - Possibly carcinogenic?

There is still uncertainty regarding the toxicology effects in humans

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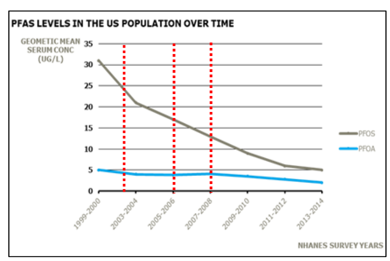
Regulatory Framework

2014 EPA Progress Report – US Operations
(all 8 manufacturers reporting)

- %Reduction, PFOA Emissions: >91%
- %Reduction, PFOA Product Content: >94%



- 1990s - EPA receives information on PFOS & PFOA blood levels in general population
- 2006 - EPA launches PFAS Stewardship Program
  - Commit to achieve 95 percent reduction in emissions and product content by 2010
    - PFAS and precursor chemicals
    - Complete elimination by 2015
- 2009 - EPA establishes drinking water **Health Advisory Levels** of **400 ng/L** for PFOA and **200 ng/L** for PFOS
- 2012 - EPA initiates requirement for public drinking water supply monitoring of PFAS compounds through UCMR 3
- 2016 EPA lowered drinking water **Health Advisory Level** to **70 ng/L** for combined PFOA & PFOS
- No Federal MCL established under Safe Drinking Water Act…yet

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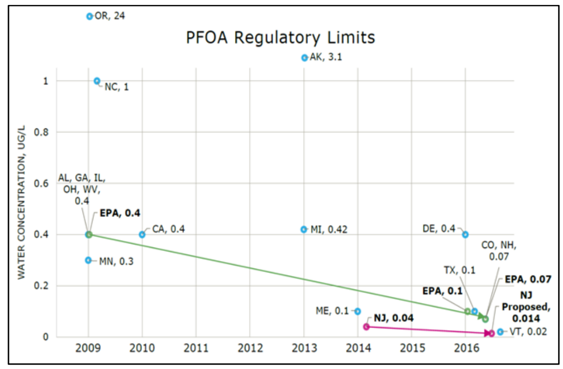
Regulatory Framework

- Current Regulatory focus is on PFOS and PFOA at the Federal Level
- Most states do not yet regulate PFAS in groundwater
  - Defer to EPA's drinking water health advisory level of 70 ng/L
- Some states have adopted lower criteria levels
  - NJ; 14 ng/L and VT ; 20 ng/L
- As regulatory focus shifts to other PFAS compounds, changes in regulatory cleanup levels will occur
  - Will impact characterization and treatment requirements



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Major Sources of PFAS Soil and Groundwater Contamination

- Fire Training and Fire Response Sites that use AFFF
- Manufacturing Facilities and Industrial Sites
- Landfills
- Waste Water Treatment Plants

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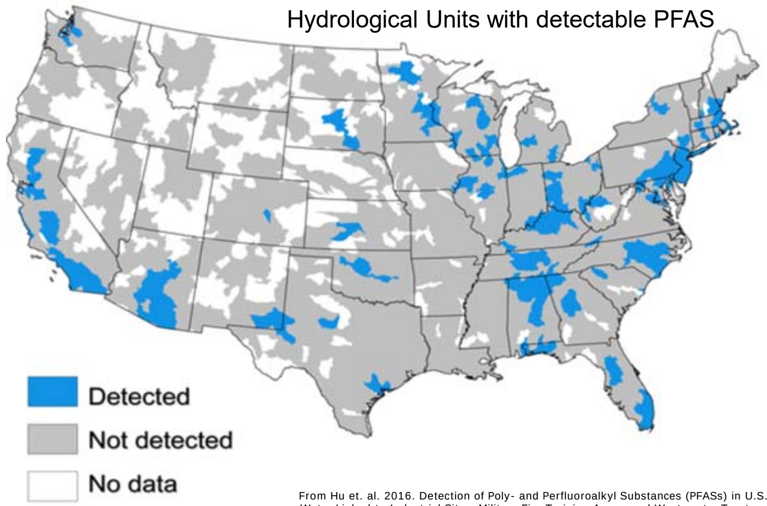
Detections of PFAS in Drinking Water



From Hu et. al. 2016. Detection of Poly- and Perfluoroalkyl Substances (PFASs) in U.S. Drinking Water Linked to Industrial Sites, Military Fire Training Areas, and Wastewater Treatment Plants.

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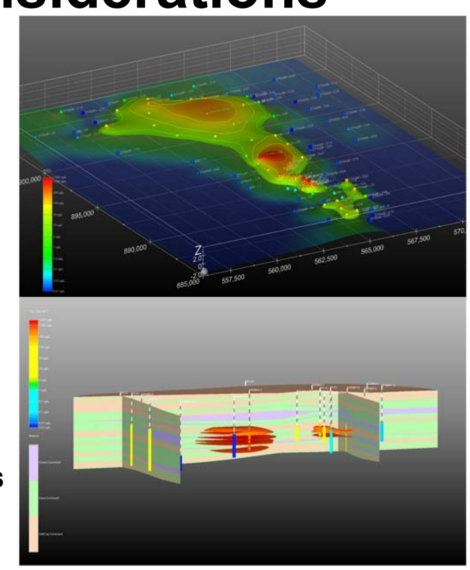
Site Characterization Considerations

Conceptual Site Model Development

- Site History
- Source Identification
- Nearby receptors
- Other potential Sources
- Hydrogeologic Framework
  - Aquifer characteristics and architecture
  - Geochemical characteristics
  - Surface and groundwater interaction
- Contaminant mass distribution
- Groundwater flow directions and velocities
- Vertical gradients mass flux movement
- CSM is a living document

Goal: Develop understanding of known/potential distribution of PFAS contamination in context of hydrogeological conditions to help identify data gaps and uncertainties



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Site Characterization Considerations

Investigative Strategies

- Drilling and sampling methods
- High resolution characterization
  - Geoprobe
  - Continuous core
- Monitor well installation
- Hydropunch samples
- Other comingled contaminants
- Contaminant mass distribution

Equipment and Supply Considerations

- Need to be mindful about sampling equipment that contains PFAS.
- MSDS Review of all materials that will be used in sampling

Goal of characterization is to define extent of contamination. Fill in data gaps to help guide remedial investigations.

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Laboratory Testing

- EPA Method 537 using LC-MS/MS is only commonly accepted laboratory analysis in US for groundwater
- Soil and sediment can also be analyzed via modified Method 537
- Cost per sample - $250 to $500
  - Includes suite of 24 compounds, including PFOS & PFOA
  - Detection limits typically in low ppt range

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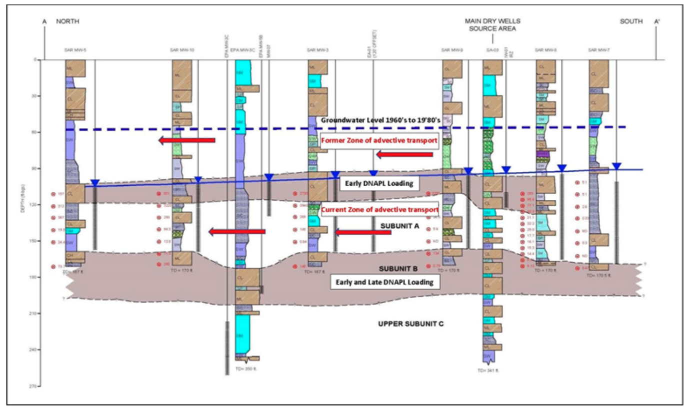
Groundwater Fate and Transport

- PFAS are relatively mobile in groundwater
- Less volatile than other contaminants such as chlorinated solvents
- PFOS & PFOA molecular structure can lead to widespread distribution
- Partitioning Mechanisms
  - Hydrophobic effects
  - Associations with organic content in soils
  - Sorbed into finer grained deposits followed by matrix back diffusion



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Ex-Situ Treatment Options

1. What doesn't work
2. What we know works

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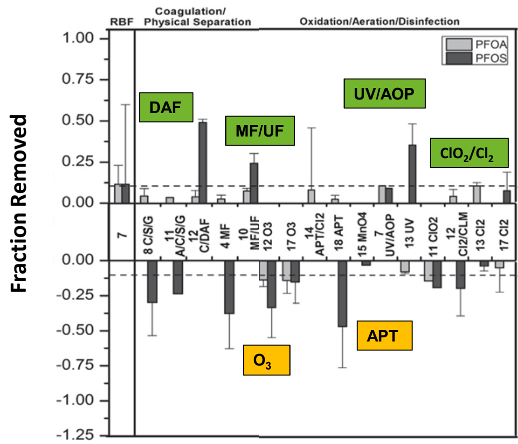
Ex-situ PFAS Treatment – What Doesn't Work

From Steinle-Darling, 2016



Limited or no Removal

Detection Limits

Formation

Edited from Appleman et.al, 2014, Water Research, 51, 246-255

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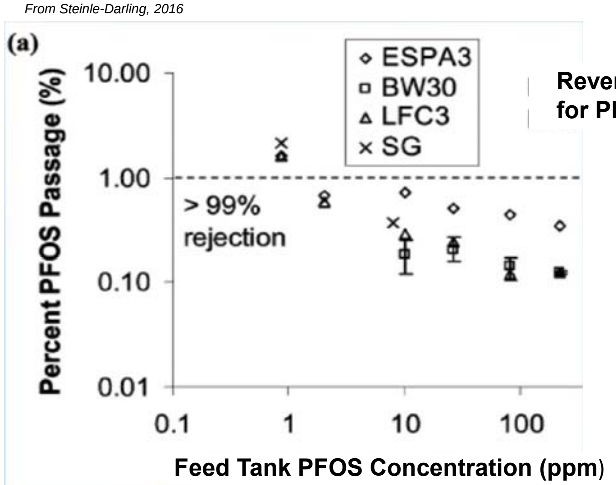
Ex-situ PFAS Treatment – What Works

From Steinle-Darling, 2016



Reverse Osmosis works well for PFOS Removal

99% Rejection or better

Edited from Fig 3a, Tang et al, Environ.Sci.Tech., 40(23), 7343-7349

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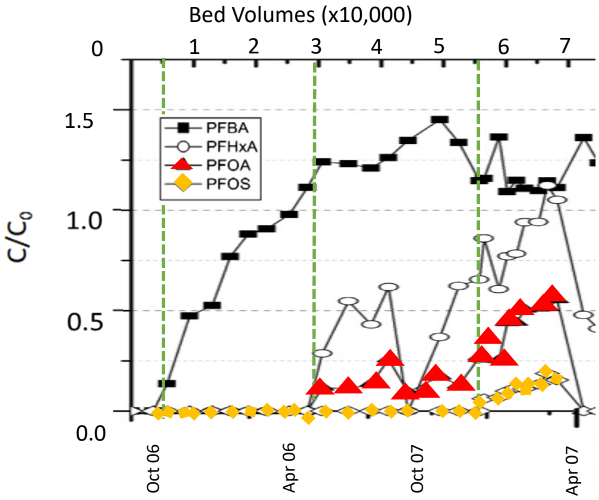
Ex-situ PFAS Treatment – What Works



Edited from Fig 3a, Tang et al, Environ.Sci.Tech., 40(23), 7343-7349

Granular Activated Carbon works well for PFOS Removal

- Smaller chain PFAS (PFBA) compounds break through sooner – 5000 bed volumes
- PFOA break through at ~ 30,000 bed volumes
- PFOS breakthrough at ~ 55,000 bed volumes

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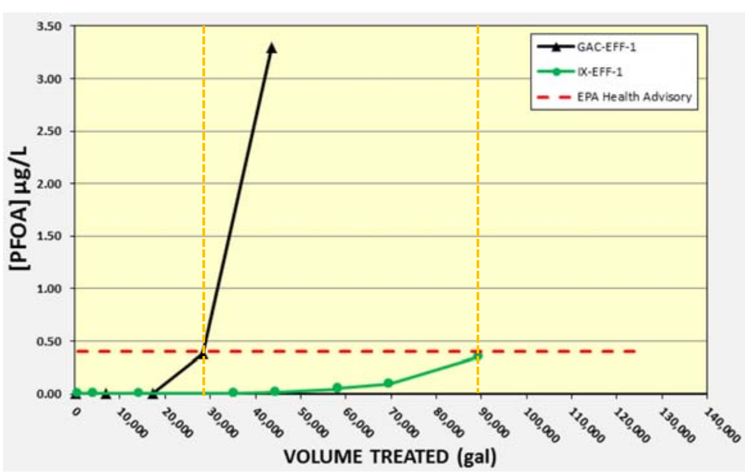
Ex-situ PFAS Treatment – What Works

From Steinle-Darling, 2016



Edited from Amec Foster Wheeler, 2016

Anion Exchange Resins work well for PFAS removal

- IX resins can be designed for removal of short and long chain PFAS compounds
- More effective and efficient than GAC - GAC breakthrough at ~28,000 gallons
- IX Resin breakthrough at 90,000 gallons or 10,000 bed volumes

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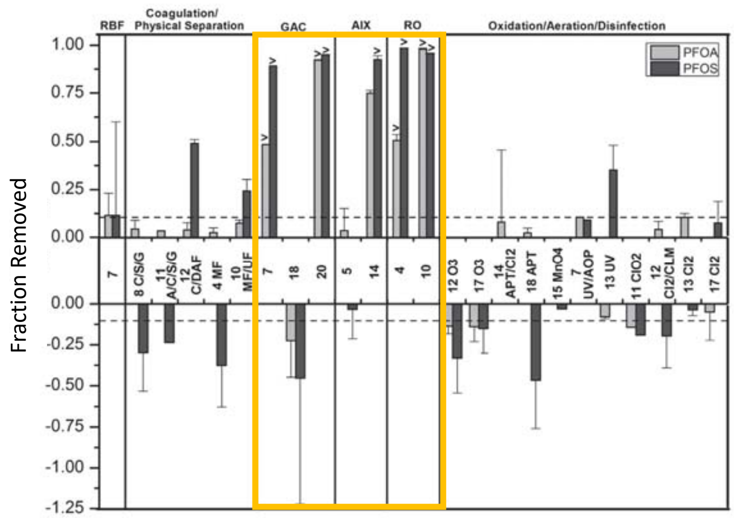
Summary Groundwater Treatment Options



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Process Selection Depends on Treatment Goals

From Steinle-Darling, 2016

Process	Effective For…	Capital Costs	O&M Costs	Residual
GAC	Long chain PFAS	Lower	Low-Med	Spent Carbon/regeneration ($)
AIX	Depends on Resin	Lower	Low-Med	Spent Resin/Regeneration ($)
RO	Long and short chain PFAS	High	Med-High Range	Liquid Concentrate ($$$)

Fundamental Flaw in these treatment options: Sequestration and not Destruction of PFAS

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In situ Groundwater Treatment

- Many different In-situ remediation methods have been attempted with limited success
  - Thermal Treatment
  - Bio Remediation
  - Chemical Oxidation - Persulfate
  - Injection of activated carbon slurry

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Some Takeaways

- Unique physical properties drive their end uses
  - Chemically stable, mobile, and degradation resistant
  - Bioaccumluative
- Found in waste water and groundwater in areas near landfills, manufacturing sites, and/or near fire training sites that use AFFF.
- Exposure predominantly via food or in drinking water in areas with impacted drinking water supplies.
- Site characterization efforts need to be mindful of sampling equipment.
- Regulatory Standards are changing - State agencies are adopting their own standards.
- Proven *ex-situ* treatment technologies are currently limited to GAC, IX, and RO.
- Proven *insitu* treatment technologies are continuing to evolve.

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Questions

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