PFAS Impacts on Solid Waste Landfills

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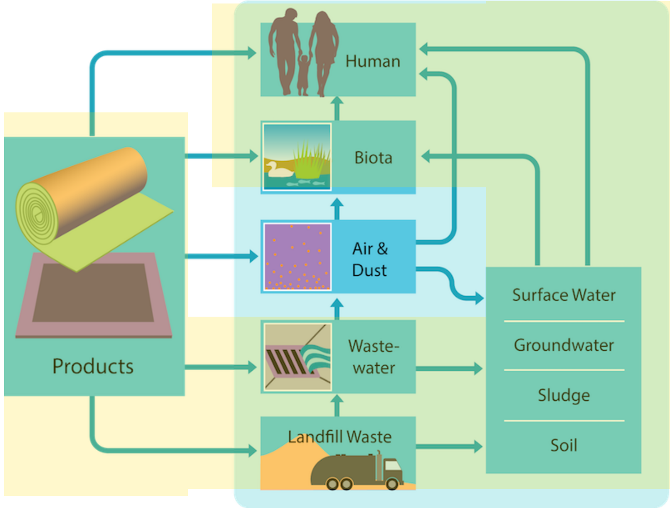
RemTech, Banff, AB – October 10-12, 2018

Outline

1. Background
2. PFAS concentrations in landfill leachate
3. Oxidizable precursors
4. Fate of PFAS in biological treatment systems
5. Potential treatment technologies

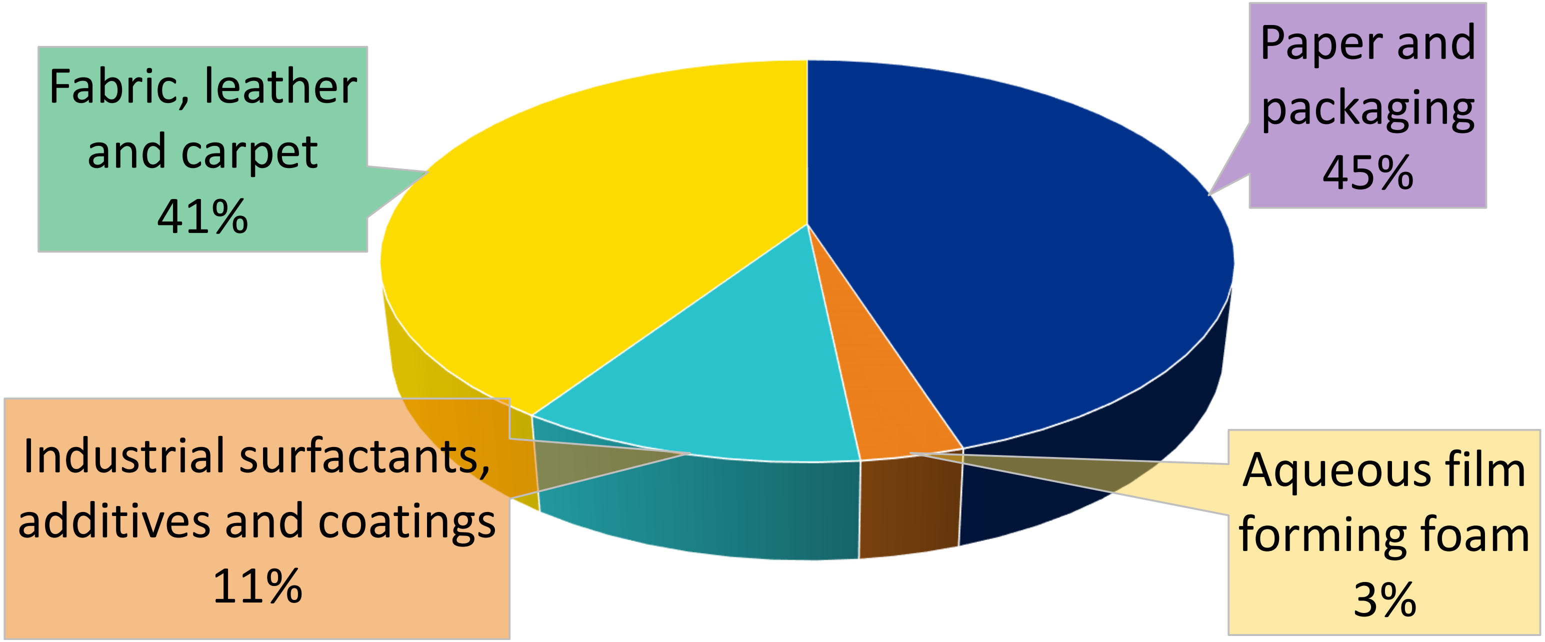


Source: www.buildinggreen.com

PFAS Uses & Products

- Heat, oil, stain, and grease resistant coatings
- Clothing
- Furniture
- Carpet stain protection
- Food packaging
- Paper coating
- Non-stick cooking surfaces
- Electrical wire insulation
- Chromium plating mist suppressants
- Photolithographic chemicals
- Many other uses

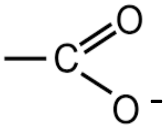
Pre-2003 North American PFAS Production



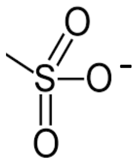
(Schultz, et al, 2003)

PFAS

- Naming convention by
  - Number of carbons
  - Functional group
- Perfluoro Carboxylic Acids (PFCA)



- Perfluoro Sulfonic Acids (PFSA)



C4	**Bu**tane
C5	**Pen**tane
C6	**Hex**ane
C7	**Hep**tane
C8	**O**ctane
C9	**N**onane
C10	**D**ecane
C11	**U**nodecane
C12	**Do**decane
C13	**Tr**idecane
C14	**Te**tradecane

Perfluorooctanoic acid (PFOA)

Perfluorooctane sulfonate (PFOS)

Perfluorobutane sulfonate (PFBS)

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Fluorotelomers

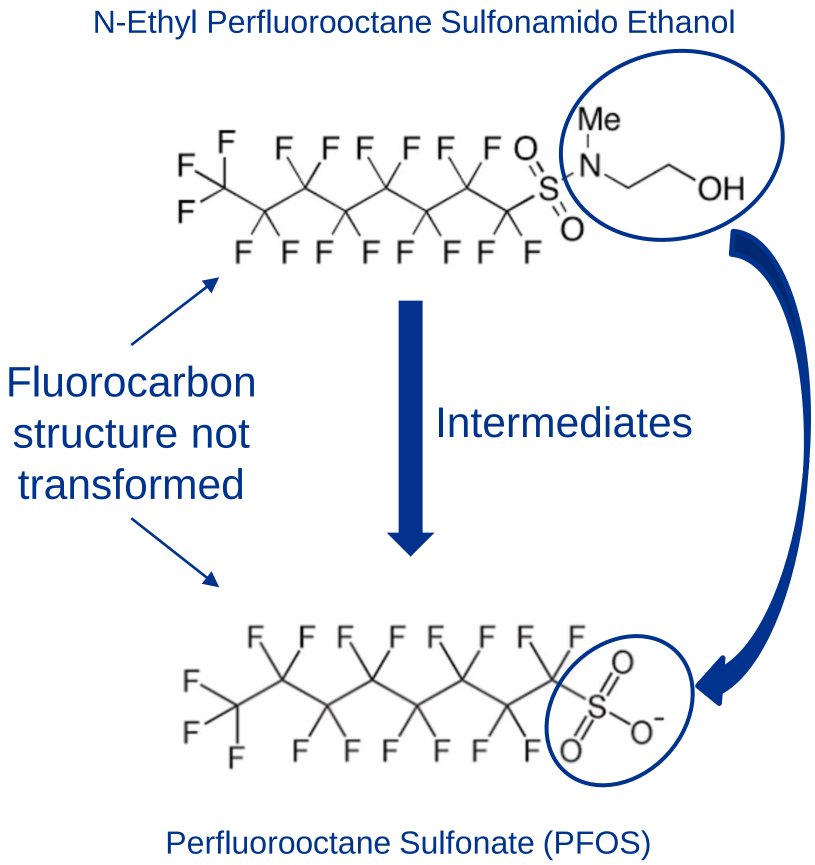
- “Telomer” small polymer (usually 2 to 5 monomer units)

- Fluorotelomer acrylate (FTA) polymers are used to coat a wide range of textiles, paper, and carpet
  - water, oil, and stain repellency

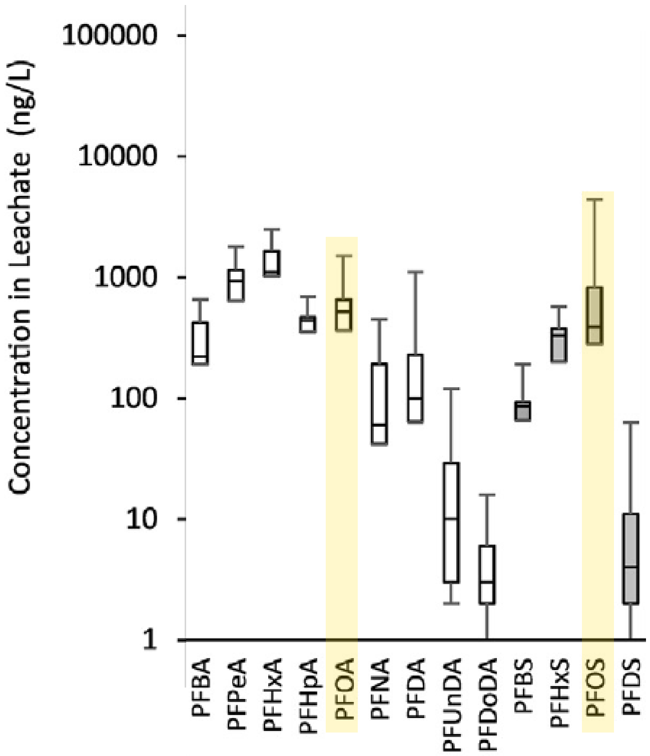
- FTA products expected to end up in landfills leading to long-term presence in the environment of a potential source of PFOA

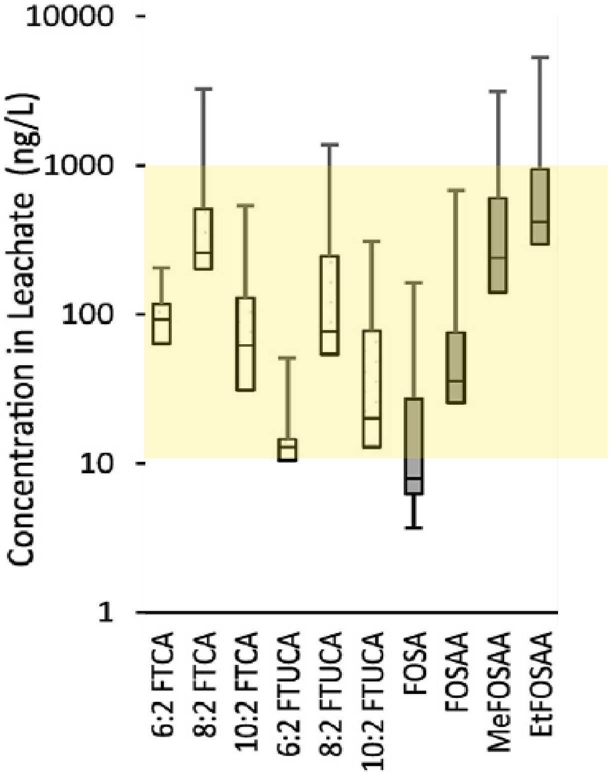
Precursors

- 1000's of PFAS compounds created – very few quantified analytically
- Precursors may be <u>transformed</u> through biological treatment
- Generates stable end-products of PFOA or PFOS
- Treatment of PFOA & PFOS not feasible with current observed biology



PFAS Concentrations – Canadian Leachate Study





Source: Benskin et. al., 2012 ES&T, as presented in Humid et. al., 2018 Environmental Pollution.

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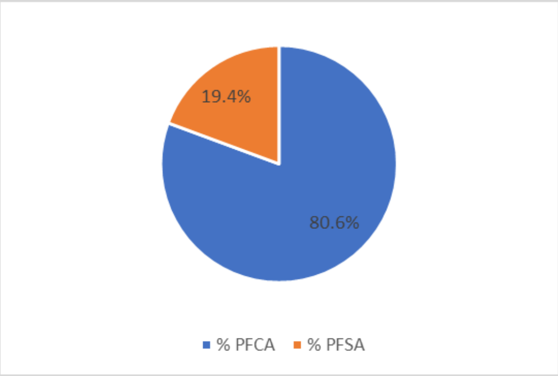
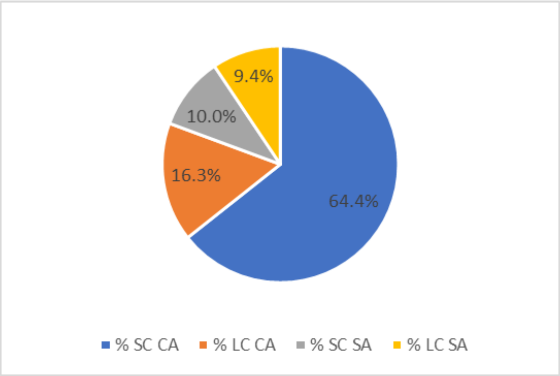
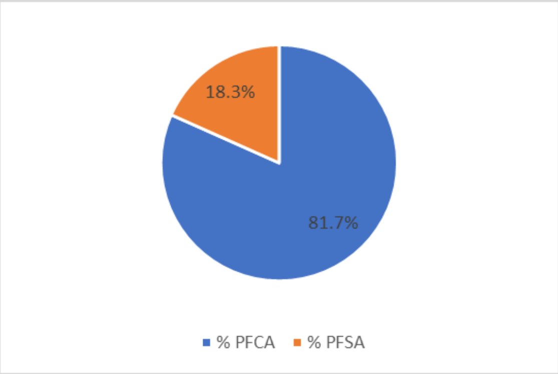
PFAS Distribution - Landfill Leachate

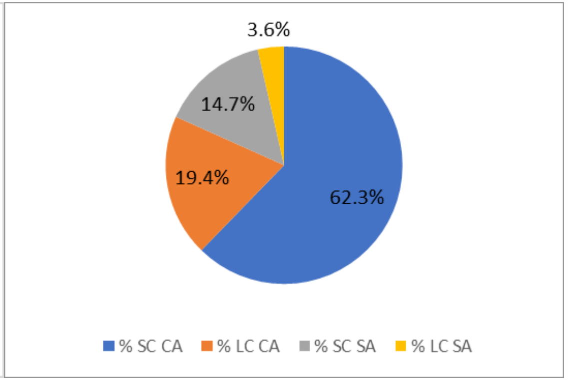
United States





Canada





Source: Huset et. al., 2011 Chemosphere; Benskin et. al., 2012 ES&T

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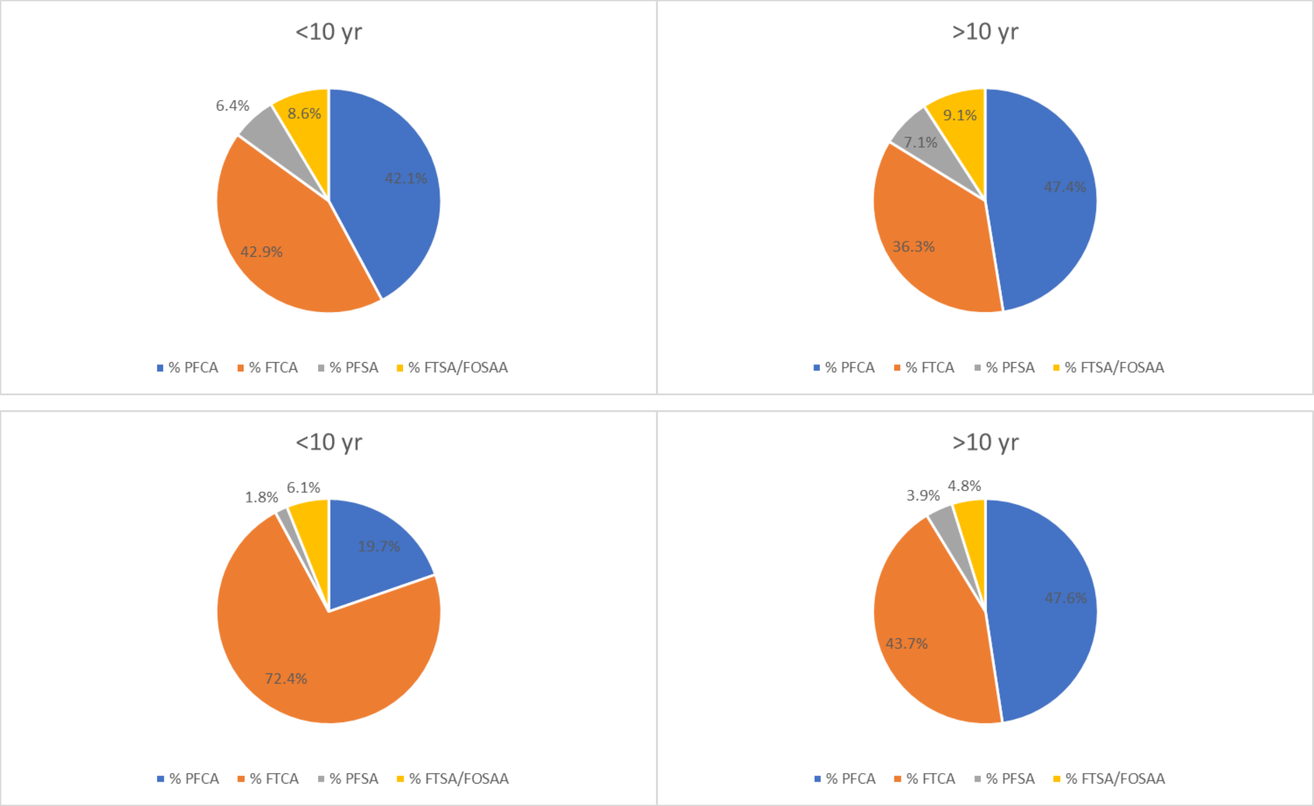
PFAS Distribution - Landfill Leachate

Wet Climate

Temperate Climate



Source: Lang et. al., 2017 ES&T

Total Oxidizable Precursor (TOP) Assay

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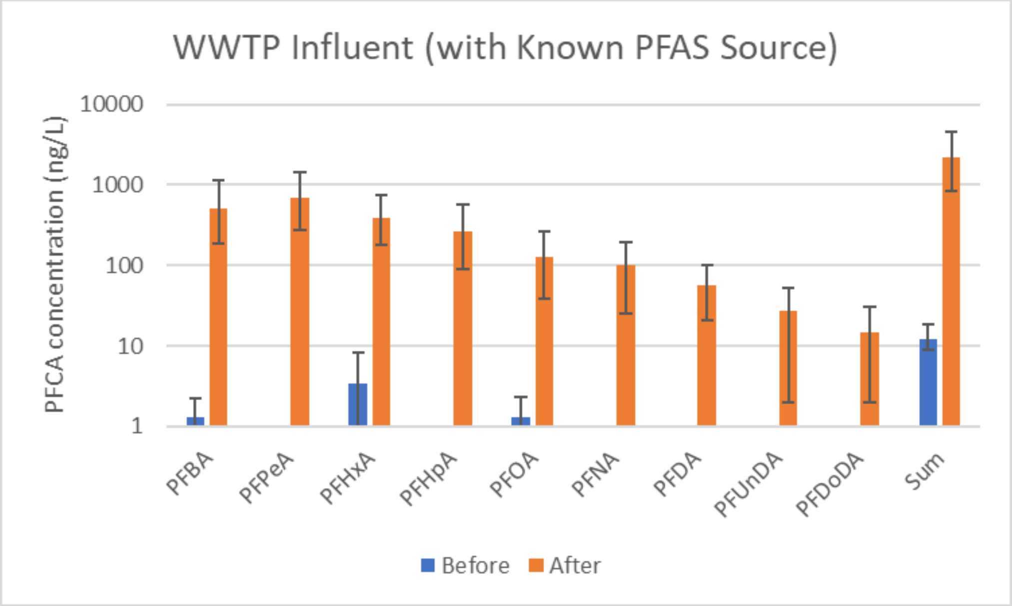
- Undefined potential precursors to PFOA/PFOS
- Best offered technique to towards “total PFAS”
- Allows for analysis utilizing traditional PFAS methodologies

TOP Analysis Results

- Leachate TOP analysis conducted
  - 100,000 ng/L of detectable PFOA
  - 1,300,000 ng/L of potential precursor material from TOP



Graphical data: Dauchy et. al., 2017 Sci Total Env

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PFAS Distribution & Fate – Municipal WWTP

Location	PFHxA	PFHpA	PFOA	PFHxS	PFOS	Total
Influent	59	13	206	24	134	444
Effluent	60	13	200	28	240	560
Influent	9.7	2.2	3.1	6.6	12	35
Effluent	31	3.7	14	48	22	120

- Precursors discharged to WWTP cause PFAS increase across aeration
- Measured PFAS pass through WWTP with limited/no reduction
- PFAS also leave plant through biosolids

Source: Gallen et. al., 2018 Chemosphere

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PFAS in Biosolids

- Annual biosolids generation
  - 660,000 tons in Canada (land application varies by province)
- PFAS concentrations in biosolids have remain relatively constant [1]
- Biosolids increased PFAS in soil and bioaccumulate in earthworms [2]
  - PFAS concentrations 9.88 to 99.9 ng/g (d.w.) compared to control 1.76 ng/g (d.w.)
- Limited data on crop uptake groundwater
  - Some data show translation to crops [3]
- Rainfall can cause leaching to groundwater
  - One study showed GW concentrations < Health Canada Screening Values [4]

Sources: 1. Armstrong et. al., 2016 Journ Env Management; 2. Navarro, 2016 Env Research; 3. Blane et. al., ES&T 2013;
4. Gottschall et. at., 2017 Sci Tot Env

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Adsorption

- Granular Activated Carbon (GAC) well demonstrated
  - Bituminous-based GAC: increasing number of full-scale installations
  - Regenerated agglomerated shows better performance
- Ion Exchange Resin is becoming more demonstrated
  - IX generally outperforms GAC -- becomes cost-benefit exercise
  - Not effectively regenerable (ECT2 is focused on on-site regen)
- Generally more effective for
  - Long chain versus shorter chain
  - Sulfonates versus carboxylic acids of same length

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Leachate-specific considerations for adsorption

- Many competing constituents
  - Slows transport kinetics (speed that constituents adsorb)
  - Limits adsorption capacity (how much PFAS can be adsorbed)
- GAC
  - Background organics
- IX
  - Background organics
  - Anions (chlorides, sulfates)
- Batch Application
  - Standalone
  - PACT

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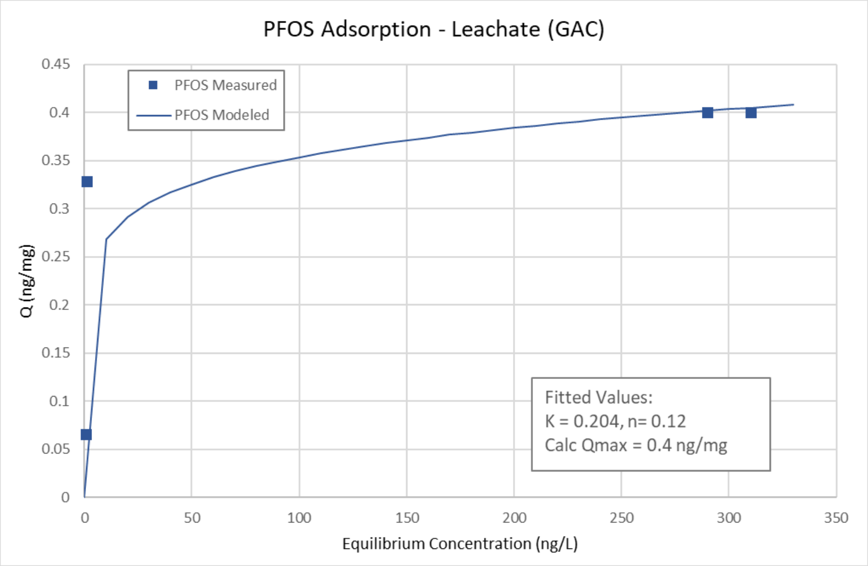
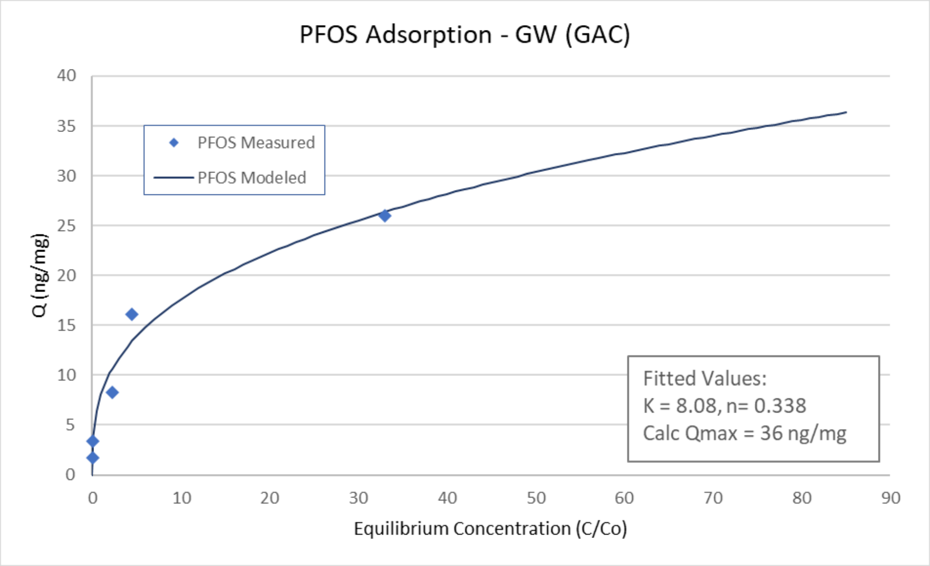
Adsorption – Leachate vs DW



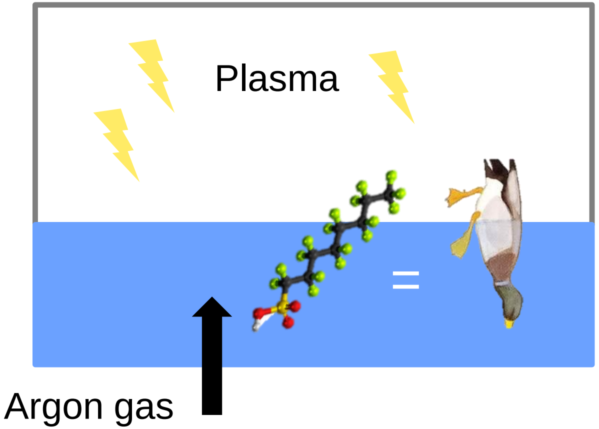


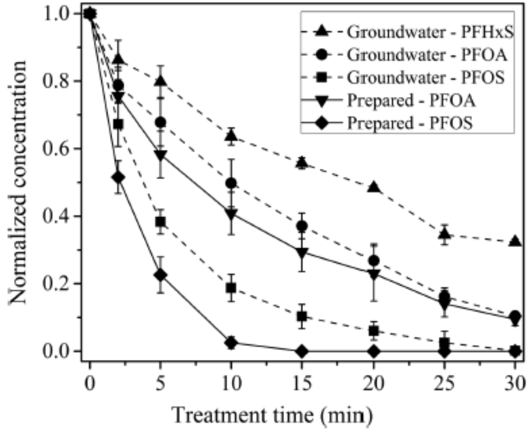
Reverse Osmosis

- Effective for removal
  - Both long and short-chain PFAS
- Concerns
  - Managing liquid concentrates
  - Application in leachate
    - Usually require pretreatment (i.e., MBR)
- Areas of development
  - Effectiveness of precursor removal
  - Lower pressure NF applications

Advanced Reduction Processes

- Non-Thermal Plasma
- “Solvated electron” (e^{-}_{aq})
  - Free electron
  - In water unstable, short lifetime
  - Research shows liquid penetration of ~2.5 nm
- Highly reductive species
  - Reduction is gain of electrons
    - Net increase in C-H bonds
    - Net decrease in C-F bonds





Data Source: Stratton et. al., 2017 ES&T

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Zero Valent Iron

- Another means of chemical reduction – generation of electrons

$$Fe \rightarrow Fe^{2+} + 2e^{-} \ (\text{anode})$$

$$2H^{+} + 2e^{-} \rightarrow 2[H]_{abs} \rightarrow H_2 \ (\text{cathode})$$

- Cathode indicates low pH is preferred
- PFAS attracted to surface-liquid boundaries
- pKa of PFAS << 7 (anion in solution)
  - Positive surface charge

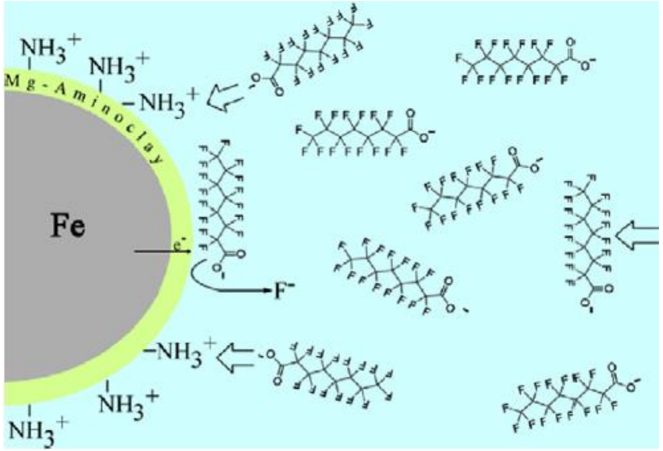

Figure Source: Arvaniti et. al., 2015 Chem Eng Journ

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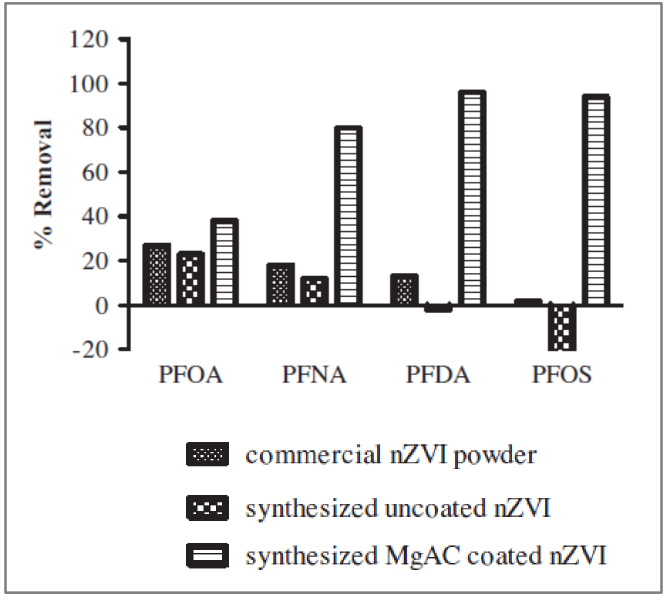
Zero Valent Iron

- Nano or colloidal ZVI much more reactive (higher surface area)
- Surface modifications
  - Improve adsorption of PFAS to surface
  - Limits passivation of reactive iron surface
    - Amino-clay
    - Sulfidation
    - Noble metals
    - Manganese



Data Source: Arvaniti et. al., 2015 Chem Eng Journ

Thank you for your time
Questions?

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