PFAS:
Background, Risks, Monitoring, and Treatment

Wastewater Technical Advisory Group

Meghan Williams

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Today’s presentation

- What are PFAS and where did they come from?
- Why are PFAS a problem?
- What is Wisconsin doing about PFAS?

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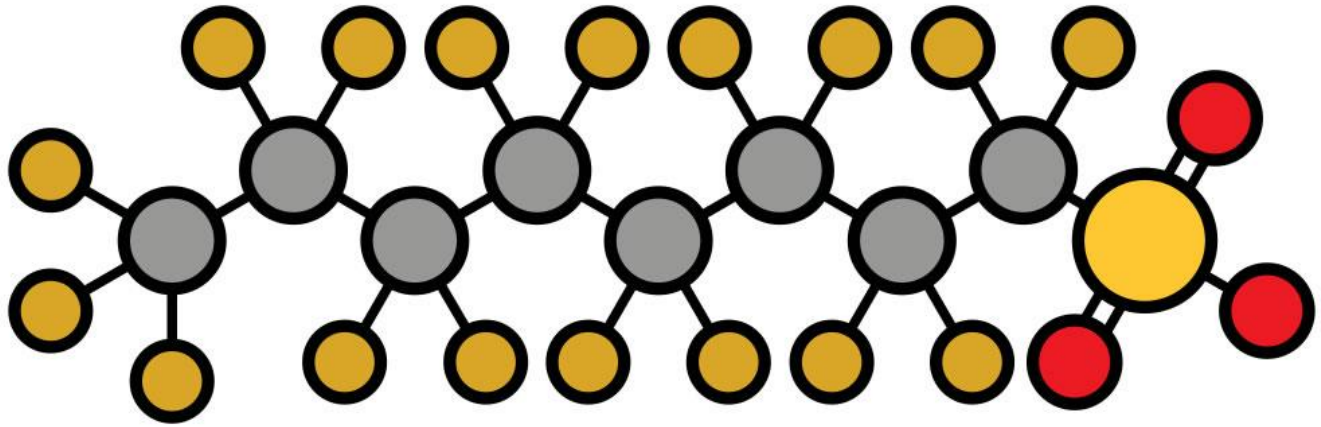
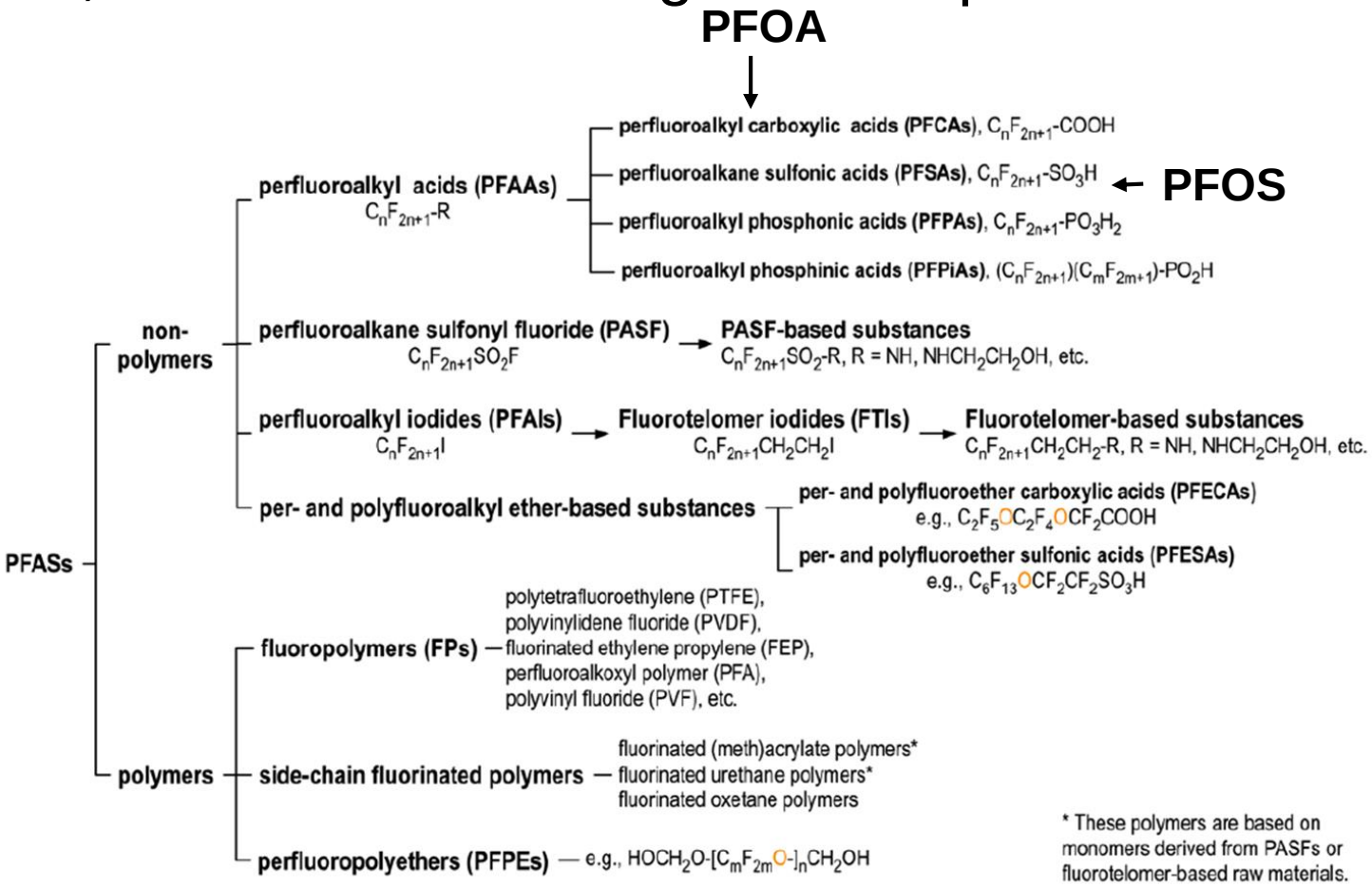


http://www.biocycle.net/wp-content/uploads/2018/07/20b.jpg

What are PFAS and where did they come from?

- Family of 4,000+ man-made organic compounds

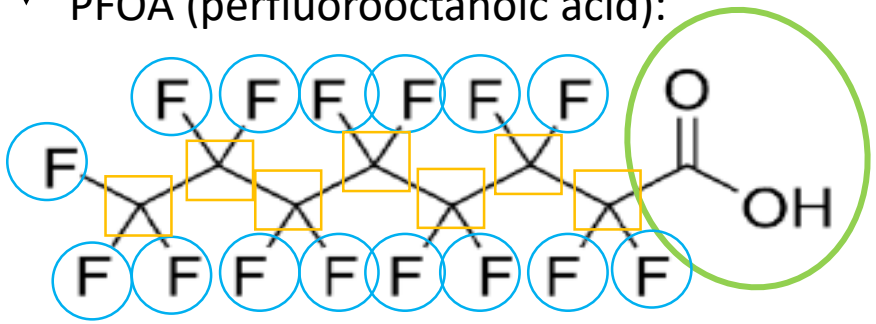


What are PFAS and where did they come from?

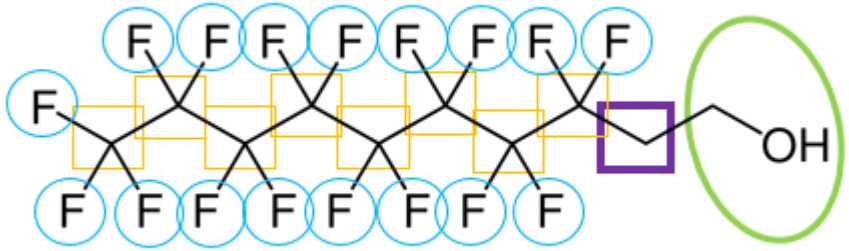
- General structure: **fluorinated carbon** chain (tail) attached to **functional group** (head)

- **Per**fluoroalkyl Substances: fully-fluorinated tail
  - Stable, resistant to degradation
- **Poly**fluoroalkyl Substances: not fully-fluorinated (at least one carbon is **not attached** to a fluorine)
  - Polyfluoroalkyl substances can transform into to perfluoroalkyl substances

PFOA (perfluorooctanoic acid):

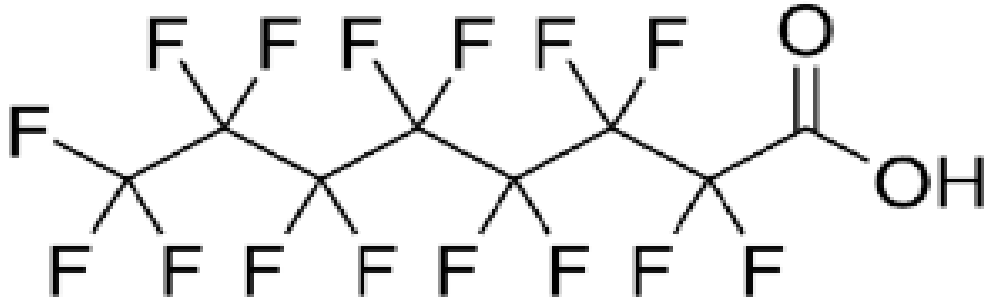


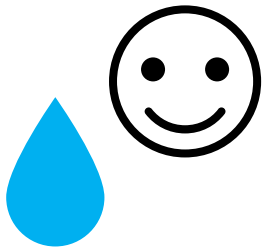
8:2 FTOH (fluorotelomer alcohol):



What are PFAS and where did they come from?

- Many PFAS are surfactants
  - Tail is hydrophobic and lipophobic, head is polar and hydrophilic
  - Readily form films, water soluble
  - Unique structure means they have excellent water- and oil-repelling properties





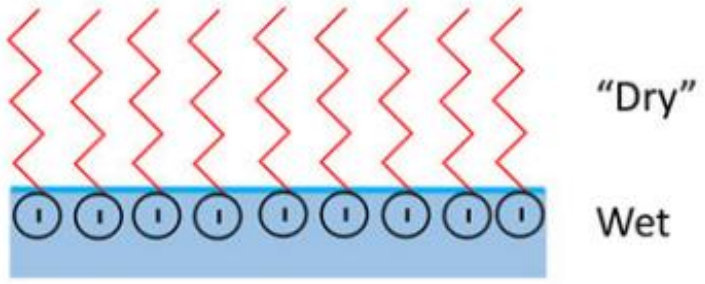


Image from: Hatton et al. 2018. Remediation (28): 89-99.

What are PFAS and where did they come from?

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		

Interstate Technology Regulatory Council (https://pfas-1.itrcweb.org/wp-content/uploads/2017/11/pfas_fact_sheet_history_and_use__11_13_17.pdf)

What are PFAS and where did they come from?

- Manufactured since 1940s for use in:
  - Non-stick coatings
  - Waterproof fabrics
  - Firefighting foams
  - Protective coatings
  - Stain/water resistant products
  - Chrome plating
  - Food packaging
  - Personal care products

https://www.flickr.com/photos/yourbestdigs/32948842081
https://commons.wikimedia.org/wiki/File:US_Navy_021022-N-5362A-011_Fire_fighting_training_during_Diligent_Warrior_2003.jpg
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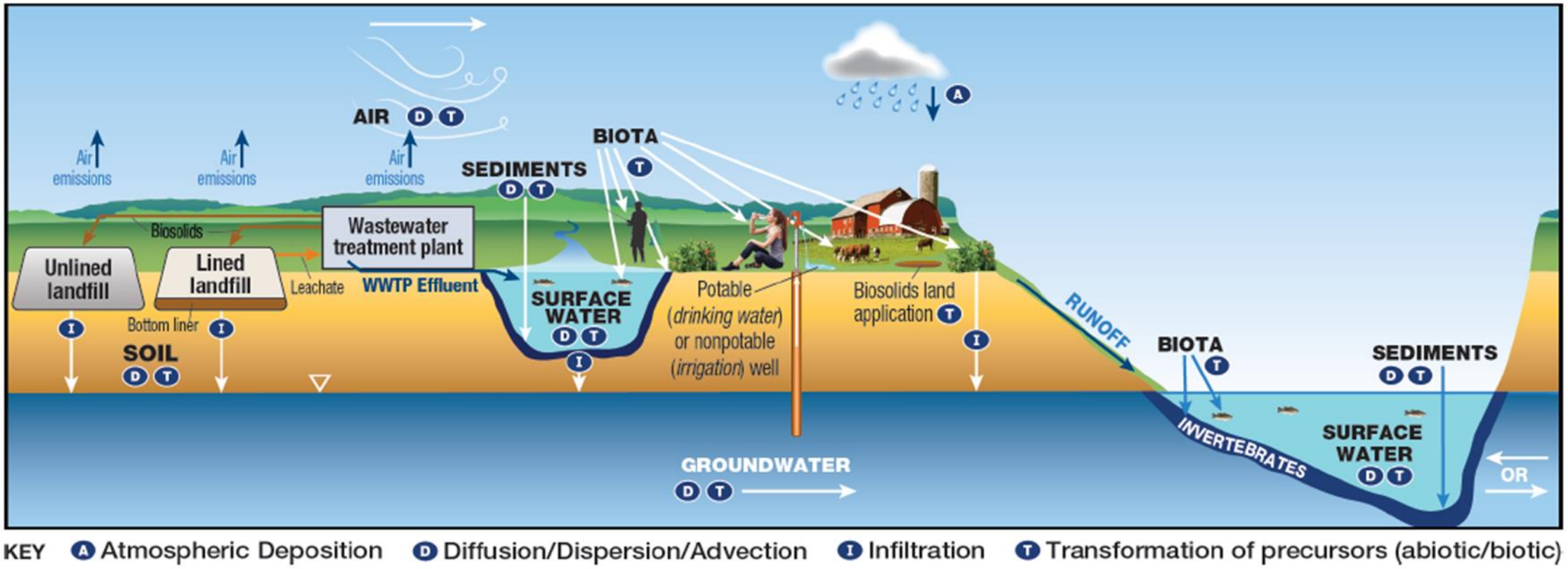
What are PFAS and where did they come from?



Interstate Technology Regulatory Council (https://pfas-1.itrcweb.org/wp-content/uploads/2018/03/pfas_fact_sheet_fate_and_transport_3_16_18.pdf)

What are PFAS and where did they come from?

- Fate and transport
  - Longer chains tend to adsorb to organic carbon in soils
  - Shorter chains are more mobile in groundwater
  - Highest concentrations at the air-water interface
  - Mobile through air by adsorbing onto particulates
- More studies needed!

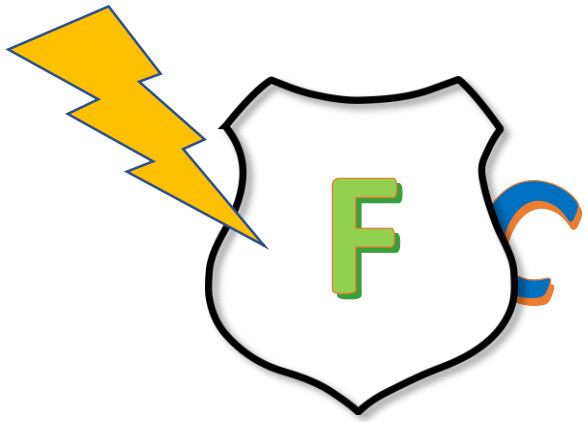
Today’s presentation

- What are PFAS and where did they come from?
- Why are PFAS a problem?
- What is Wisconsin doing about PFAS?

https://magentafp.com/wp-content/uploads/2018/02/questions.png

Why are PFAS a problem?

- Carbon-fluorine bond is incredibly strong
  - Fluorine atoms “shield” carbon from chemical reactions
  - PFAS do not undergo biotic or abiotic degradation
  - Thermally degrade only at high temperatures
  - Very persistent!



Why are PFAS a problem?

- Persistence = global distribution
  - PFAS have been found in wildlife on all continents

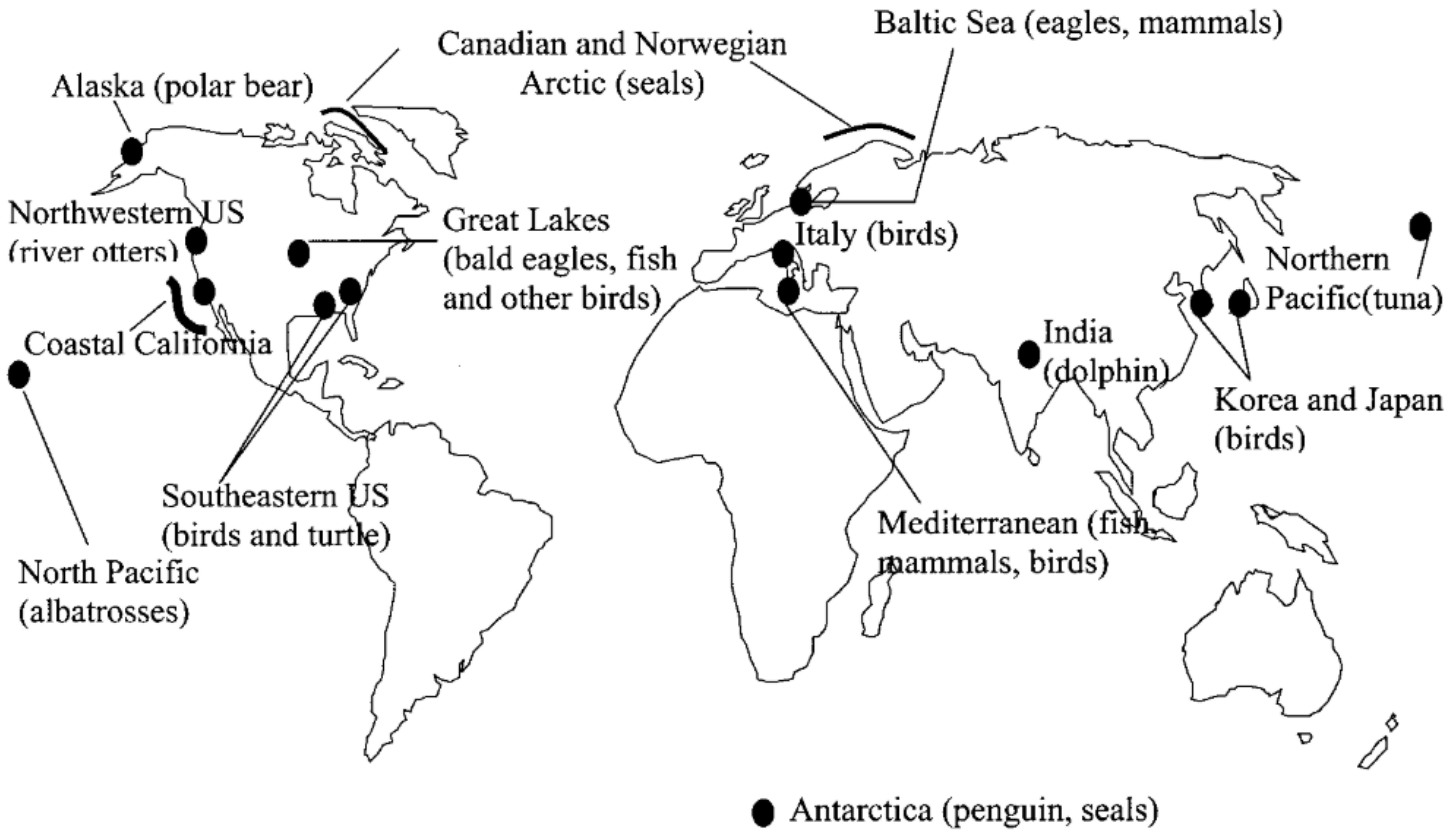


Image from Giesy and Kannan 2001. ES&T 35(7): 1339-1342.

Why are PFAS a problem?

- Persistence = global distribution
  - PFAS have been found in surface waters globally

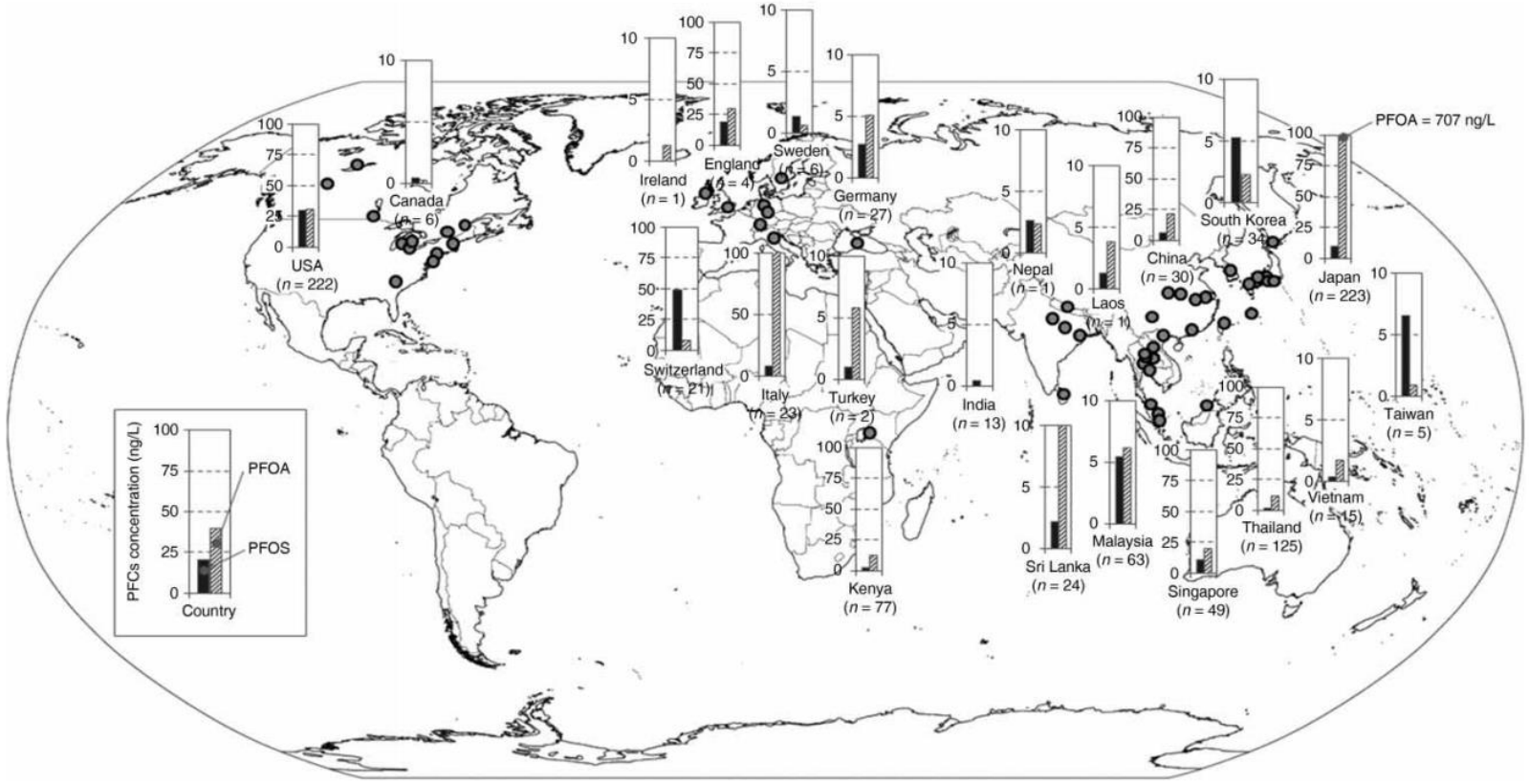
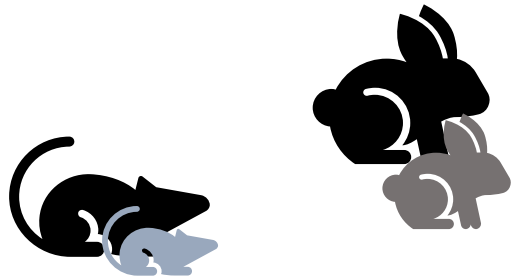
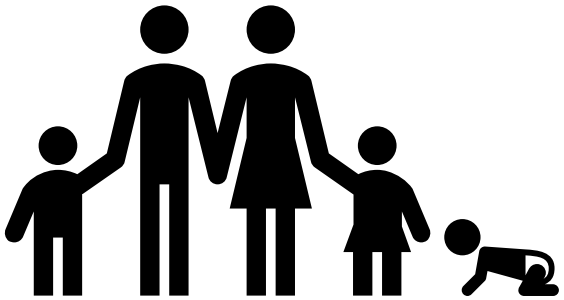


Image from Kunacheva et al. 2012. WS&T 66: 2764-2771.

Why are PFAS a problem?

- PFAS have documented toxicity
  - Animal studies have shown negative effects on:
    - Liver
    - Immune system
    - Reproduction and development
    - Thyroid (endocrine system)
    - Cancers
  - Probable links to human health effects*:
    - Childhood growth and development
    - Pregnancy-related hypertension
    - Hormone regulation
    - Increased cholesterol levels
    - Immune system effects
    - Cancer risk

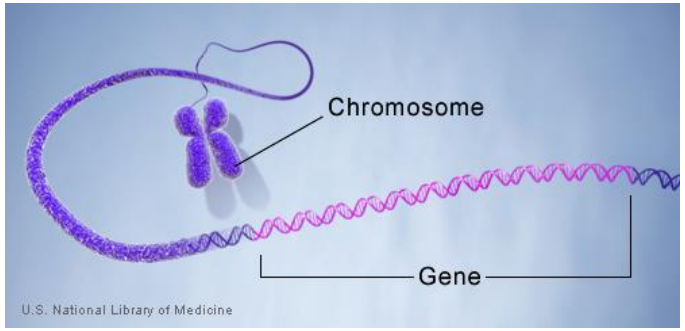


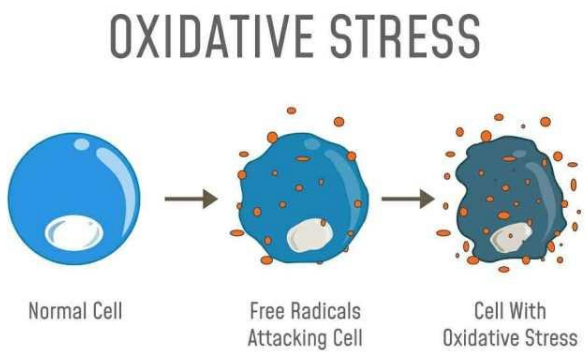


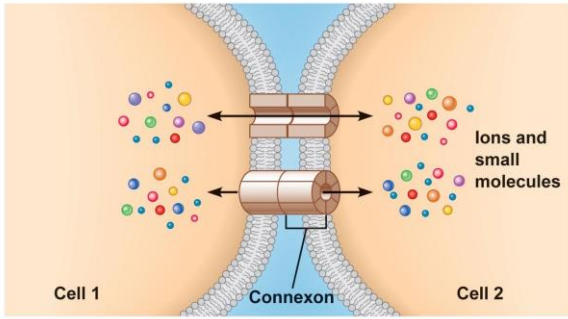
*Human health effects were often found in highly exposed populations (i.e., Dupont workers in Ohio River Valley)

Why are PFAS a problem?

- How are PFAS toxic?
  - Proposed mechanisms
    - Gene expression changes
    - Increased oxidative stress
    - Disruption of mitochondria (powerhouse of cell)
    - Inhibited intercellular communication







https://kasturisem2biochem.files.wordpress.com/2013/10/figure_05_01a_labeled1.jpg

https://i0.wp.com/alternativemedicine.com/wp-content/uploads/2018/12/oxidative-stress.jpg?resize=678%2C381&ssl=1

Today’s presentation

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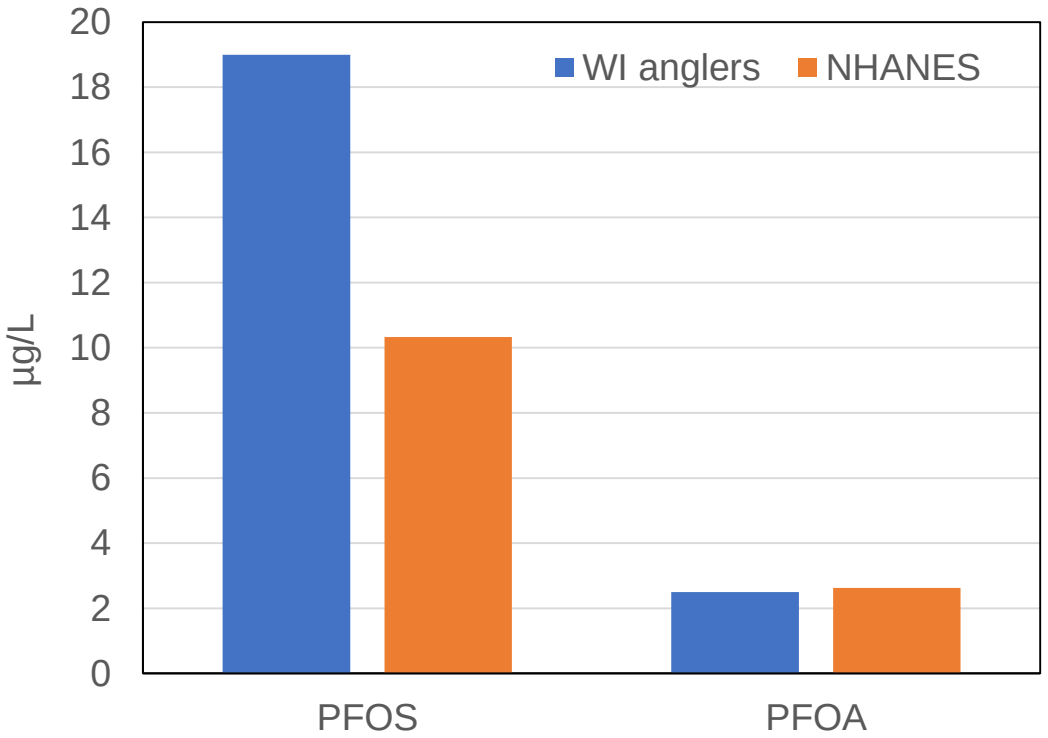
- Why are PFAS a problem?

- What is Wisconsin doing about PFAS?
  - Past monitoring efforts
  - Treatment strategies

Monitoring efforts - anglers

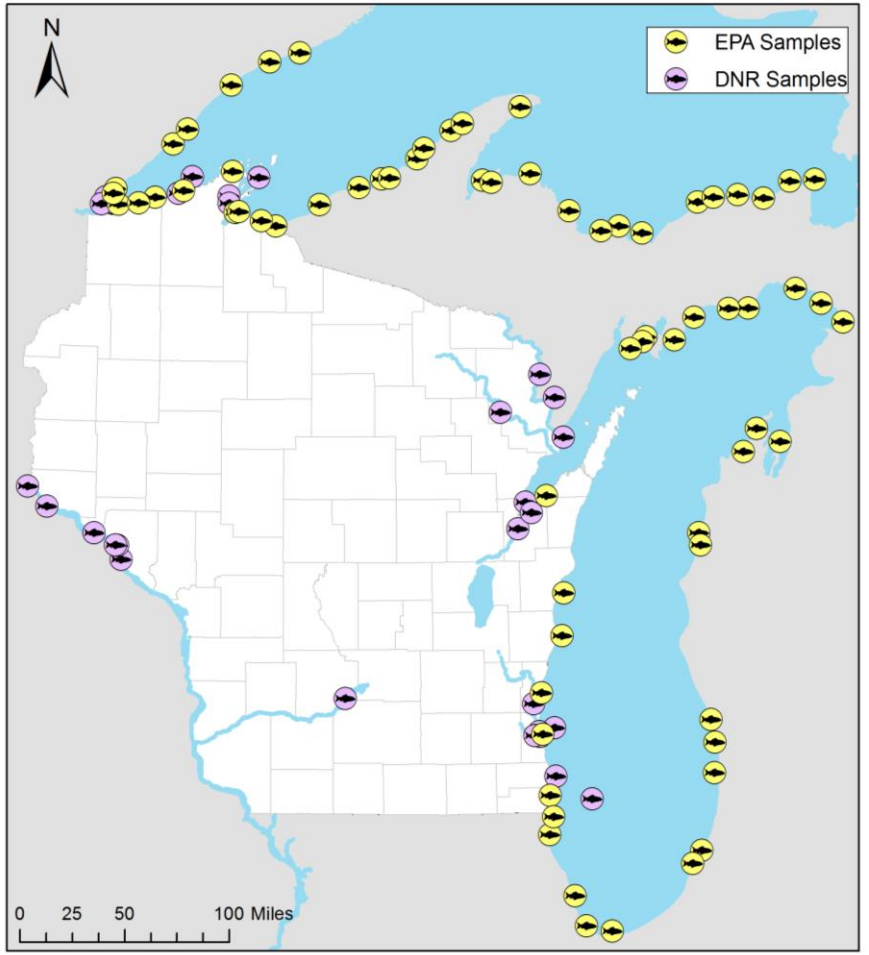
- 2012-13 DHS biomonitoring study of older male anglers
  - PFOS in all samples, median 19 µg/L
  - PFOA in >97% of samples, median 2.5 µg/L
  - PFOS in WI anglers > PFOS in comparable population surveyed in National Health and Nutrition Examination Survey



Monitoring efforts – fish

*May be an artifact of analysis method

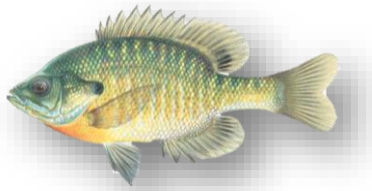
- 2006-2012 – subset of contaminant monitoring samples analyzed for PFAS, combined with PFAS data from EPA
  - WDNR sampled fish from rivers with high industrial use, Great Lakes AOCs
  - PFOS found in >99% of samples
  - Other PFAS detected varied by location*
  - PFOS variation:
    - Species: highest in fillets of white bass, crappie, and bluegill
    - Location: highest in fillets from Mississippi River, lowest in fillets from Lake Superior



Fish consumption advisories

- Locations within the Mississippi river have PFOS-based advisories
  - Pool 3 – bluegill, crappie
  - Pool 4 – bluegill
  - Pools 5, 5A, and 6 – bluegill, crappie

- PFAS levels detected in fish from other locations were not high enough to supersede advisories already in place for PCBs



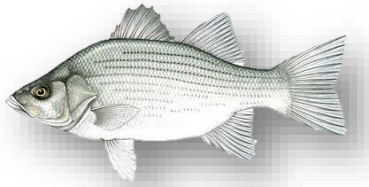
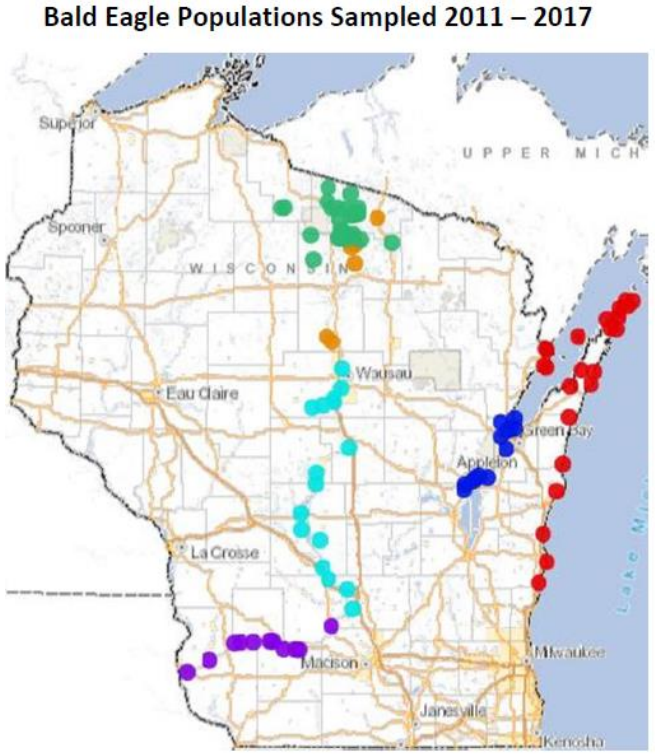


Image: https://www.umesc.usgs.gov/rivers/upper_mississippi/reach_1/images/reach1.jpg, UW Zoology Museum

Monitoring efforts – bald eagles

- WDNR statewide biosentinel program (2011-2017)
  - Sampled in 6 regions, measured total PFAS
  - Highest concentrations (>600 µg PFAS/L) in Middle & Lower Wisconsin River
  - Lowest concentrations in Northern Highlands



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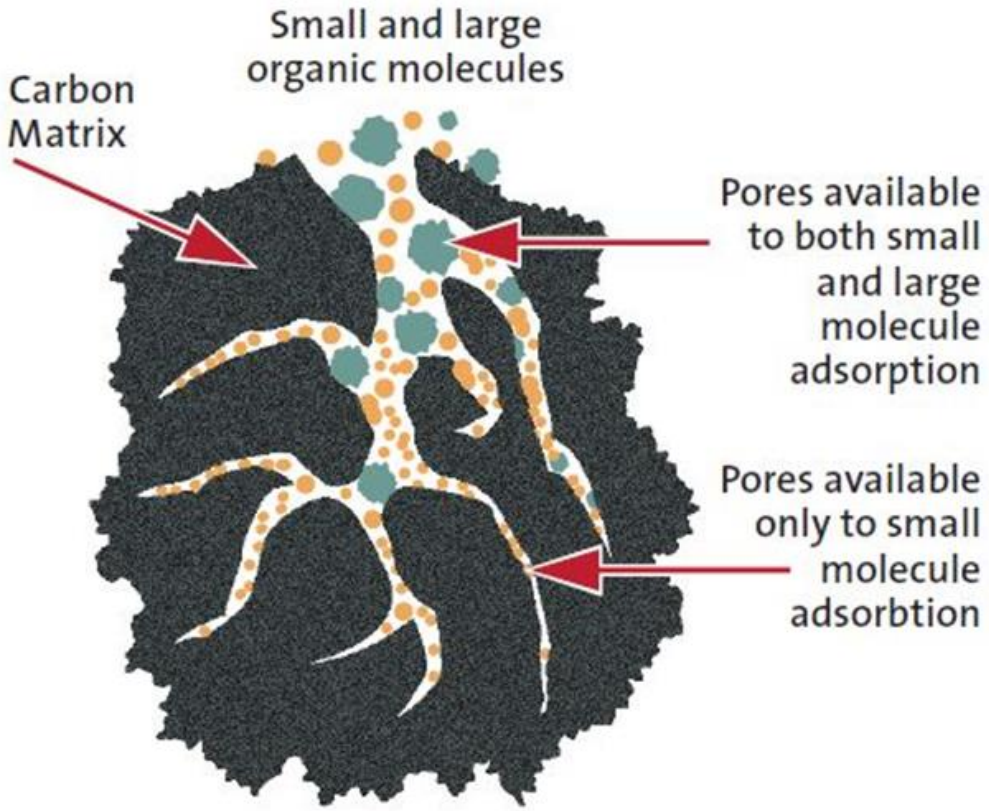
PFAS Wastewater Treatment

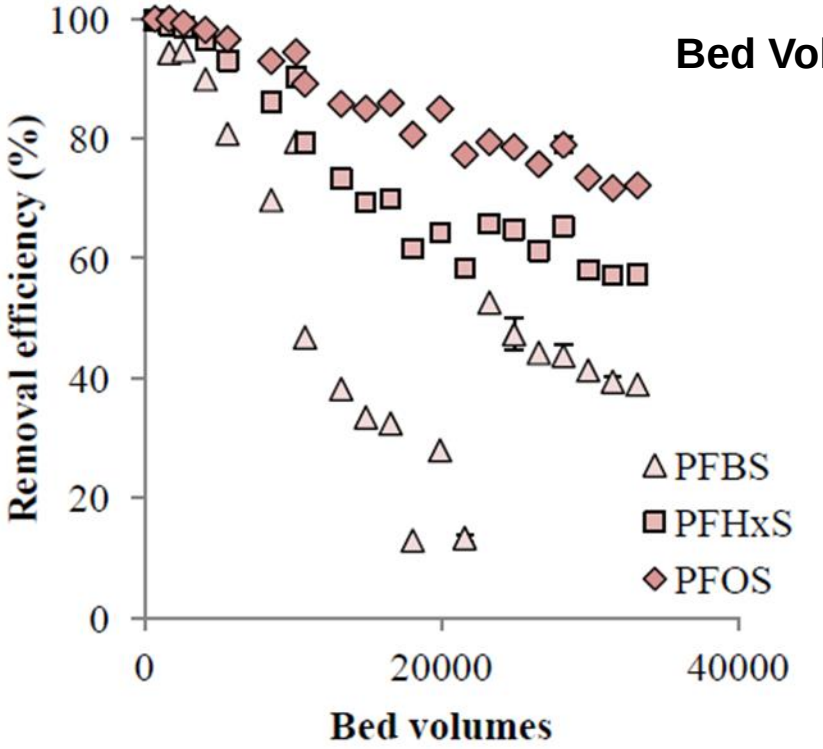
- GAC (Granular Activated Carbon)
  - Pollutants adsorb to surface of activated carbon
  - Carbon material (wood, coconut shells, coal, etc.,…)
    - Diameter = 0.5 to 3mm
    - Surface Area = 1000 – 1500 m^2/gram
  - Once adsorption capacity reached, carbon is either regenerated or replaced



(https://www.elgalabwater.com/technologies/activated-carbon)

PFAS Wastewater Treatment

- GAC Column Experiment Example



$$\text{Bed Volume} = \frac{\text{Volume of treated water}}{\text{Volume of the adsorbent (carbon)}}$$

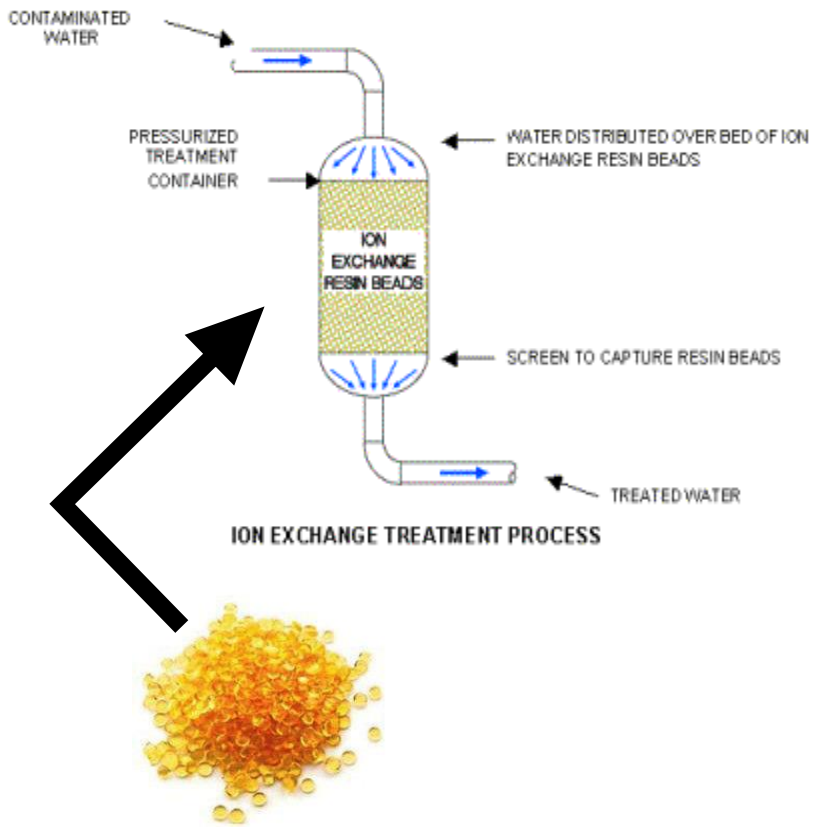
Source: (https://stud.epsilon.slu.se/8158/13/ostlund_a_150709.pdf) Ostlund, Anna; *Evaluation of granular activated carbon and anion exchange using column tests, and the effect of dissolved organic carbon*, Swedish University of Agricultural Sciences

PFAS Wastewater Treatment

- GAC
  - Most widely-used/studied treatment for PFAS
  - High removal efficiency (89 - 99%) of long-chained PFAS (≥C8; PFOA, PFOS)
  - **Poor removal of smaller-chained PFAS (<C6; PFBS)**
  - Background organics negatively impact efficiency
  - What to do with spent carbon?!
    - Incinerate!

PFAS Wastewater Treatment

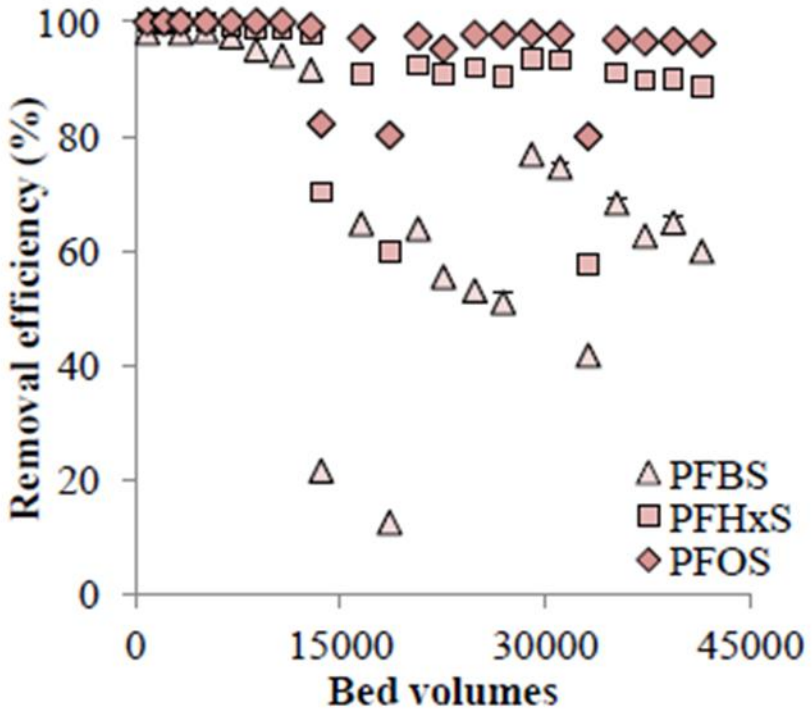
- Anion-Exchange Resins
  - Anions in resin exchange with PFAS anions
  - Binds PFAS with resin
  - Operated in series or individually
  - Like GAC, must be regenerated



Resin Image: (https://www.indiamart.com/proddetail/ion-exchange-resin-7318500655.html) Ion-Exchange Process Image: (http://onlineresize.club/news-club.html)

PFAS Wastewater Treatment

- Anion-Exchange Resin Column Experiment Example



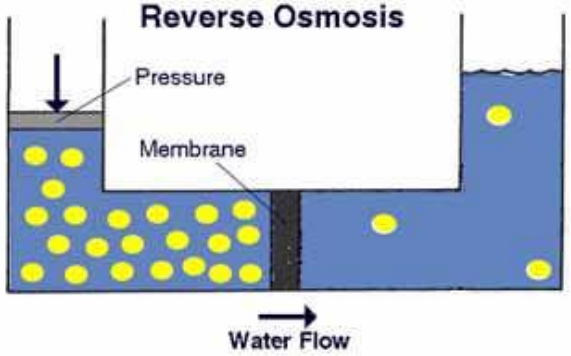
Source: (https://stud.epsilon.slu.se/8158/13/ostlund_a_150709.pdf) Ostlund, Anna; *Evaluation of granular activated carbon and anion exchange using column tests, and the effect of dissolved organic carbon*, Swedish University of Agricultural Sciences

PFAS Wastewater Treatment

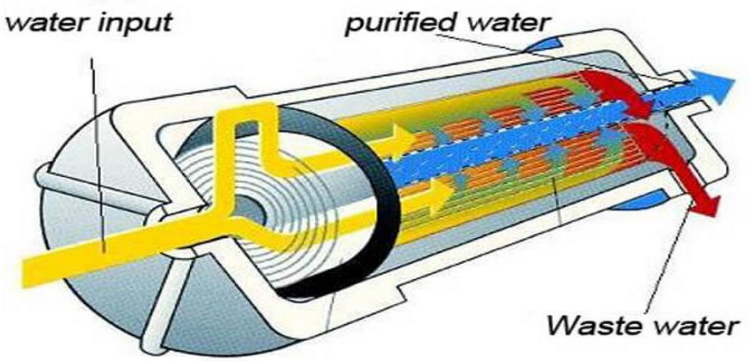
- Anion-Exchange Resin
  - Higher removal rates of longer-chained PFAS at higher Bed Volumes than GAC
  - Same issues as GAC:
    - Breakthrough of smaller-chained PFAS
    - Organic matter reduces efficiency

PFAS Wastewater Treatment

- Reverse Osmosis Filters
  - Water is pushed through a spiralized semipermeable membrane under pressures that exceed the osmotic pressure
  - 93-99% Removal efficiencies
  - Contaminants are captured by the membrane and contained in a more **concentrated solution**
  - More initial capital costs than GAC



Source: (http://www.csun.edu/~vchsc006/356b/ro.html)



Source: (http://www.ionicsystems.com/us/reverse-osmosis/)

PFAS Wastewater Treatment

- Ineffective Removal Technologies (for PFAS)

Treatment	% Removal
Conventional Treatment	0
Low Pressure Membranes	0-23
Biological Treatment (including slow sand filters)	0-15
Disinfection – Chloramines	0
Oxidation – Permanganate	1-53**
Oxidation – Hydrogen Peroxide	0-2*
Oxidation – Ozone	0-7
Advanced Oxidation: UV - TiO_2	15
Advanced Oxidation: UV – Ozone	0*
Advanced Oxidation: Ozone - Peroxide	9

**Bench-scale with up to 18 days of exposure

*Bench-scale data

Source: EPA (https://cfpub.epa.gov/si/si_public_record_report.cfm?Lab=NRMRL&dirEntryId=341079&simpleSearch=1&searchAll=Perfluorochemicals+OR+Perfluoroalkyl+OR+Perfluorinated+OR+Polyfluorinated+OR+Polyfluoroalkyl+OR+pfas+OR+pfoa+OR+pfc+OR+pfos)

Questions?

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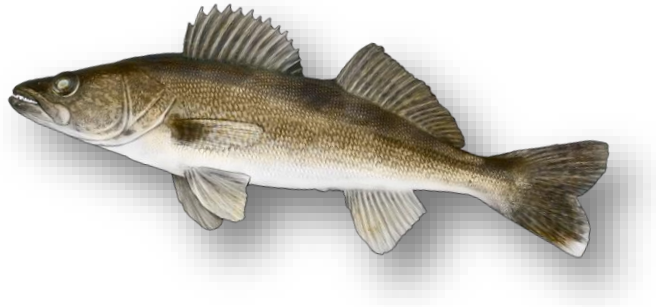

Images: UW Zoology Museum