



PFAS Overview and Water Quality Program Update

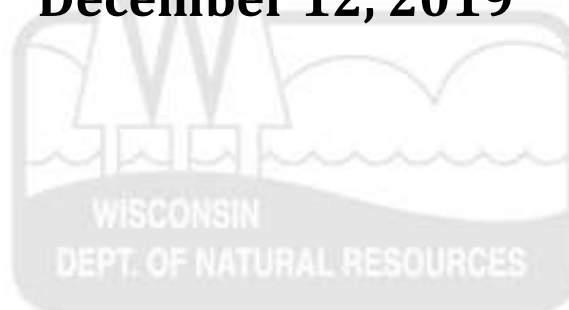
Nate Willis

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Wisconsin Dept. of Natural Resources

Lake Michigan District WWOA Meeting

December 12, 2019



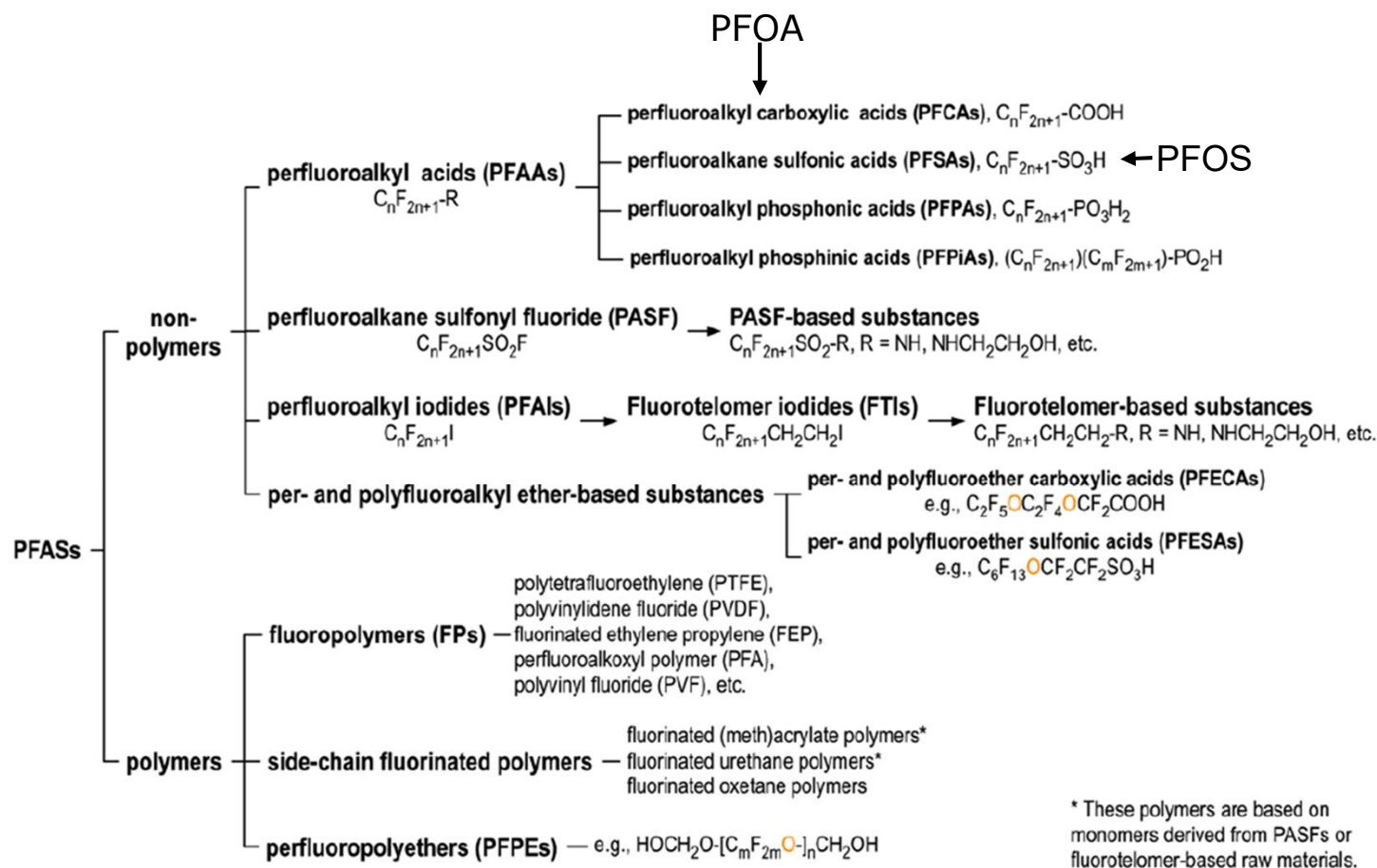


Topics

- PFAS Overview
 - What are they and where did they come from?
 - What's the problem?
- PFAS wastewater treatment options
- Water Quality Program Update
 - Monitoring Efforts
 - Rulemaking Efforts

What are PFAS and where did they come from?

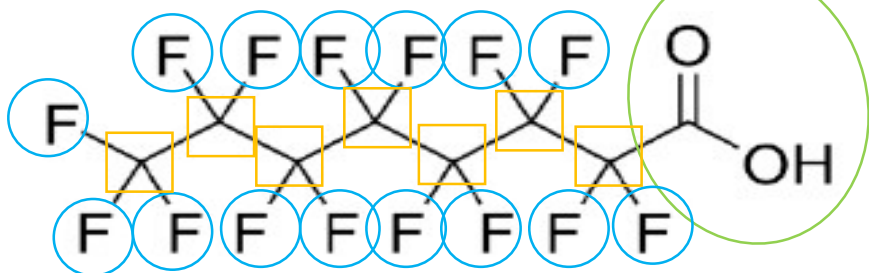
- Family of 4,000+ man-made organic compounds



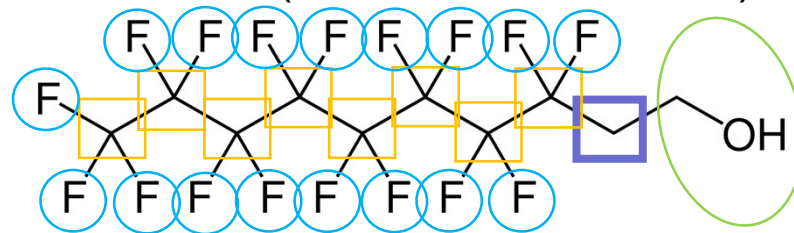
What are PFAS and where did they come from?

- General structure: **fluorinated carbon** chain (tail) attached to **functional group** (head)
- **Perfluoroalkyl** Substances: fully-fluorinated tail
- **Polyfluoroalkyl** Substances: not fully-fluorinated (at least one carbon is **not attached** to a fluorine)

PFOA (perfluorooctanoic acid):



8:2 FTOH (fluorotelomer alcohol):



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		

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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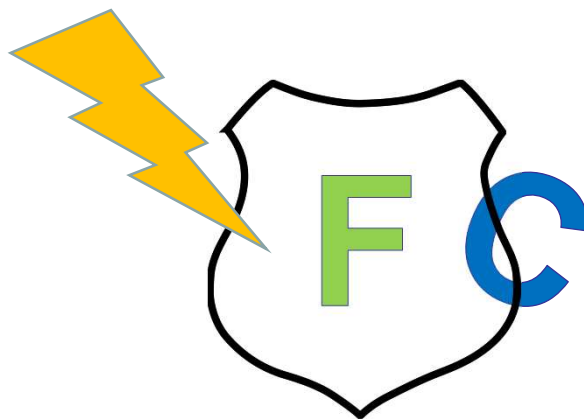


What's the problem?

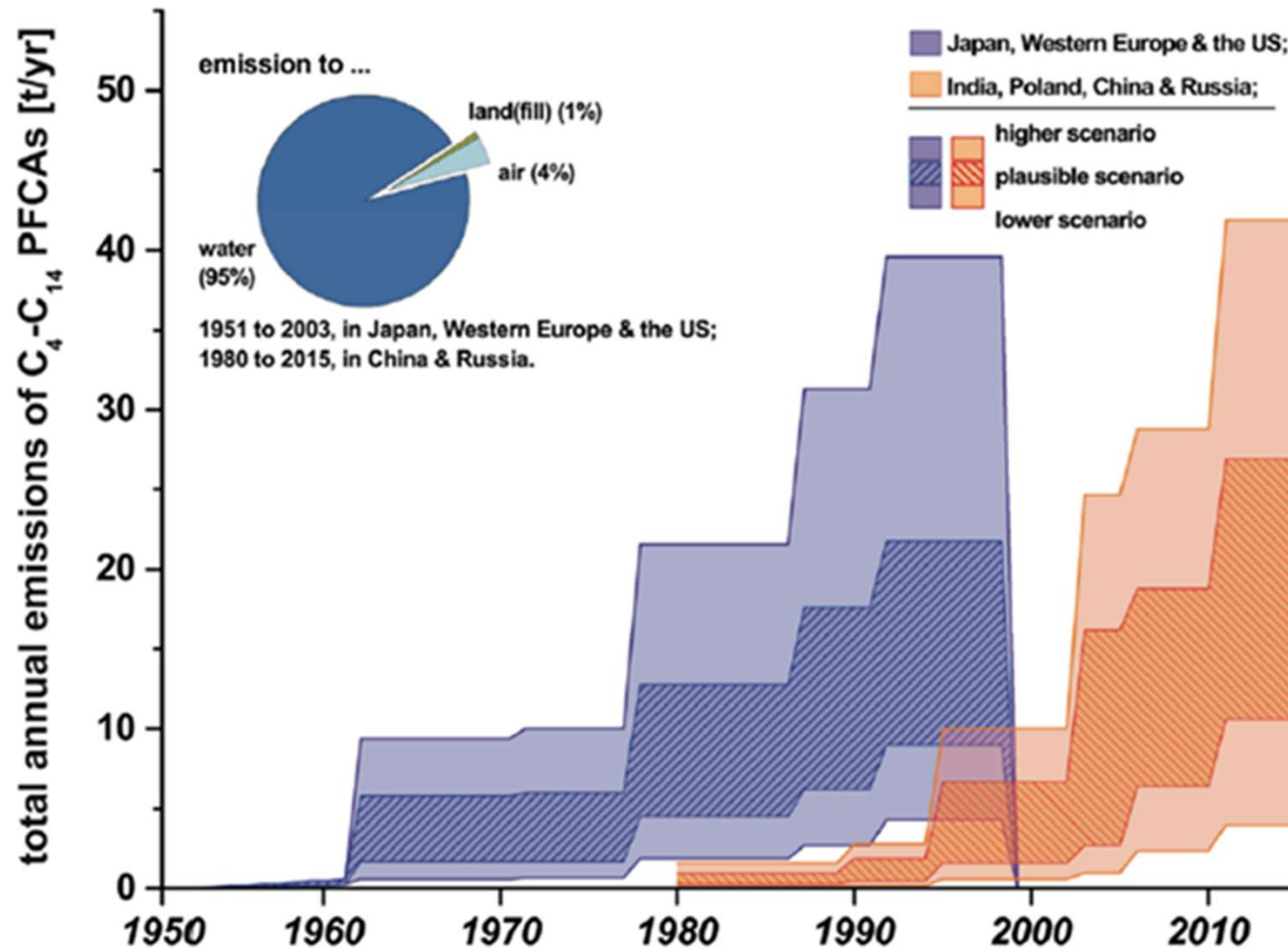


What's the problem with PFAS?

- Carbon-fluorine bond is incredibly strong
 - Fluorine atoms “shield” carbon from chemical reactions
 - PFAS do not undergo biotic or abiotic degradation
 - Precursor PFAS do transform into “terminal compound” PFAS
 - Thermally degrade only at high temperatures (>1800°F)

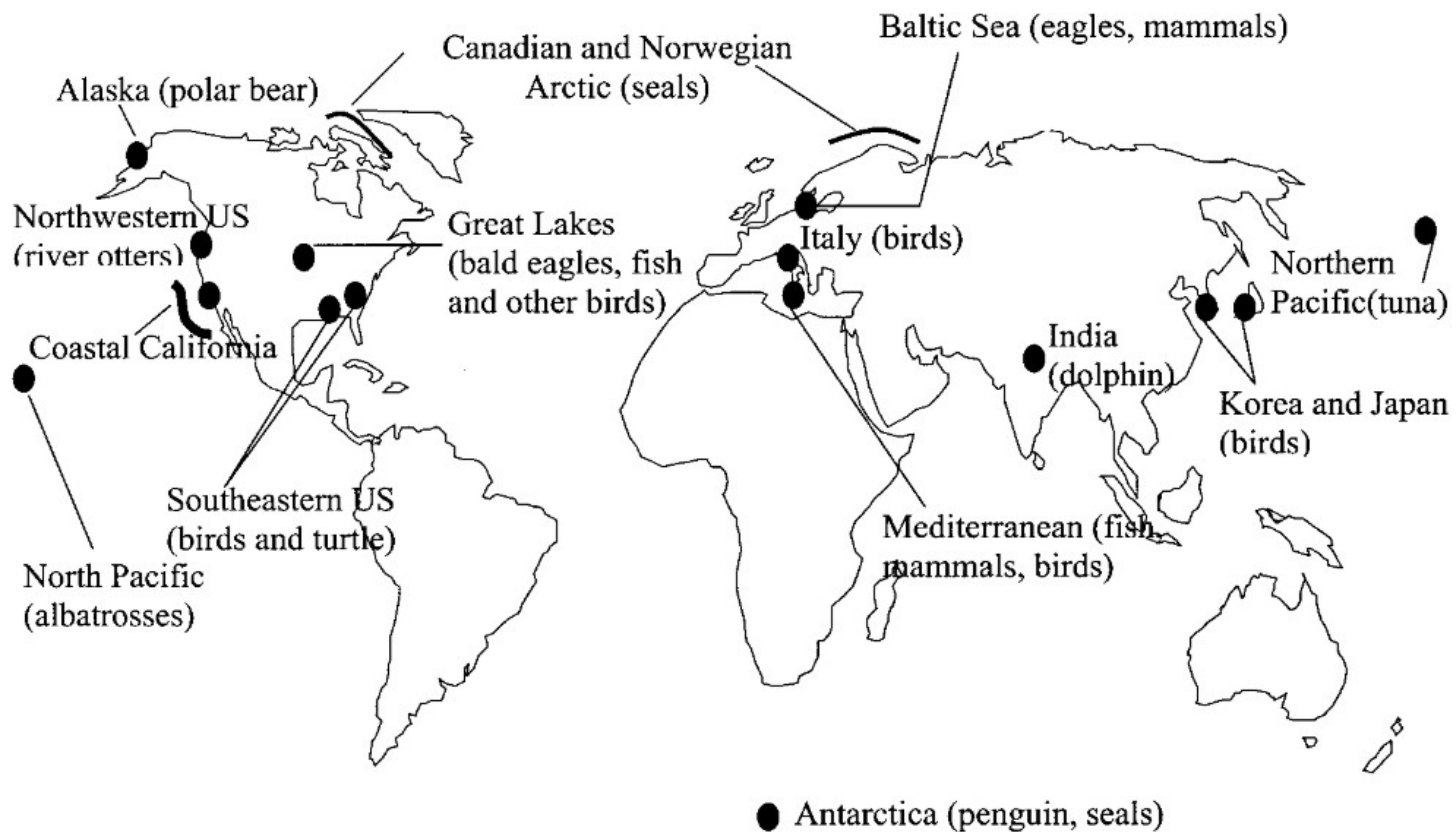


What's the problem with PFAS?



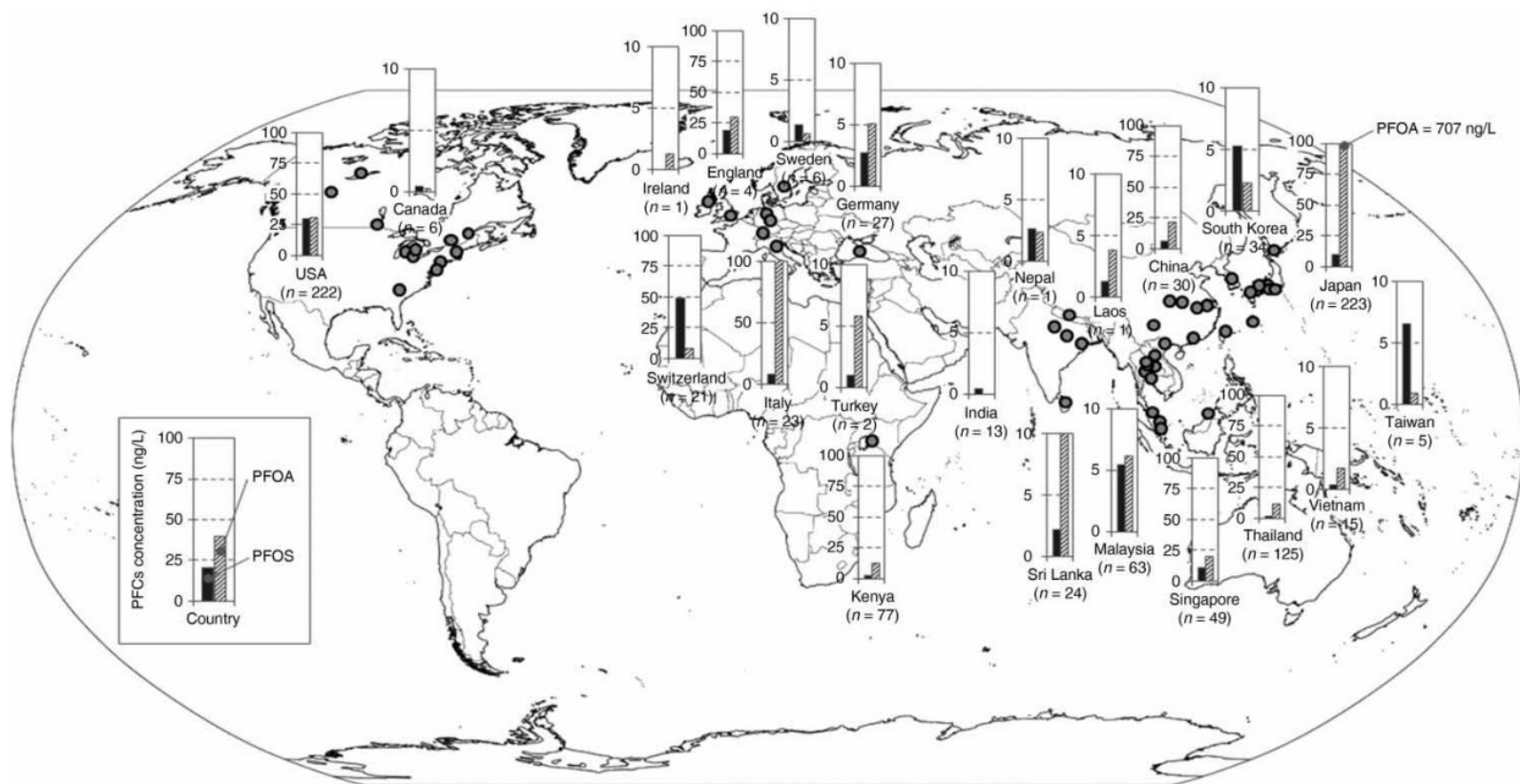
What's the problem with PFAS?

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



What's the problem with PFAS?

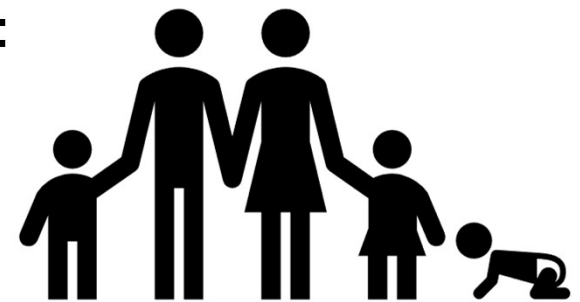
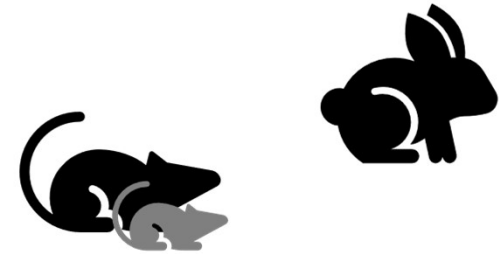
- Persistence = global distribution
 - PFAS have been found in surface waters globally





What's the problem with PFAS?

- Persistence = bioaccumulation = 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
 - Chance of becoming pregnant
 - Hormone regulation
 - Increased cholesterol levels
 - Immune system effects
 - Cancer risk



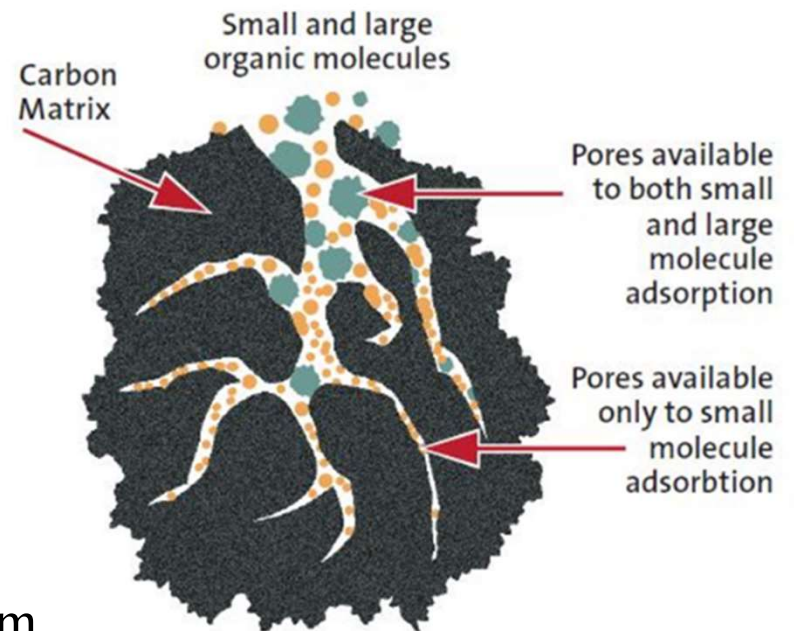
*It is important to note that human health effects were often found only in highly exposed populations (i.e., Dupont workers in Ohio River Valley)



Wastewater Treatment Technologies for PFAS

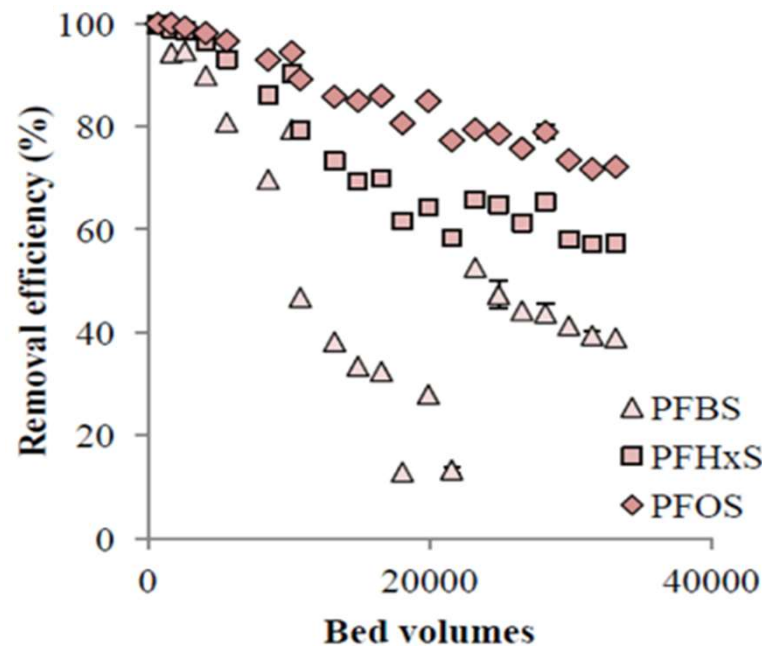
PFAS Wastewater Treatment

- 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 m²/gram
 - Once adsorption capacity reached, carbon is either regenerated or replaced



PFAS Wastewater Treatment

- GAC Column Experiment Example



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

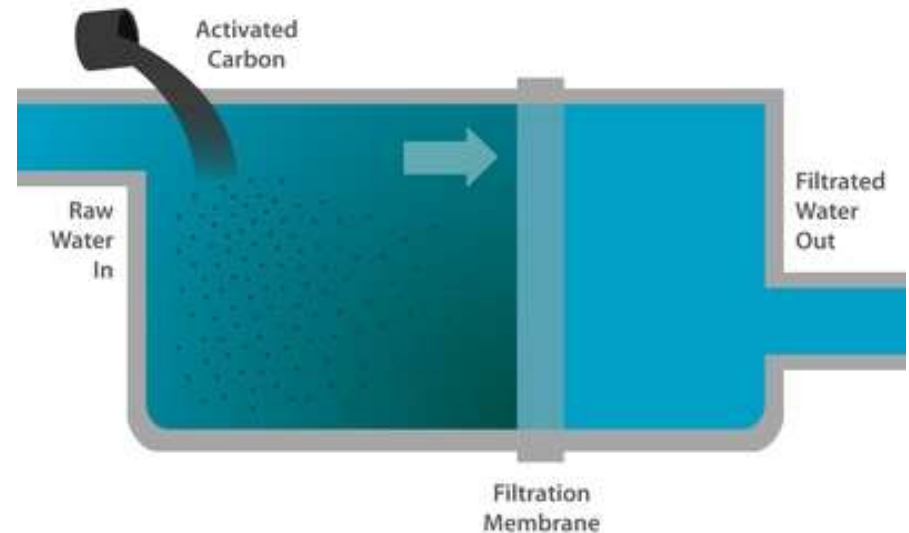


PFAS Wastewater Treatment

- GAC
 - Most widely-used/studied treatment for PFAS
 - High removal efficiency (89 - 99%) of long-chained PFAS ($\geq C8$; PFOA, PFOS)
 - **Poor removal of smaller-chained PFAS ($< C6$)**
 - Background organics negatively impact efficiency
 - What to do with spent carbon?
 - Landfills
 - Incineration
 - **Little information on created byproducts!**

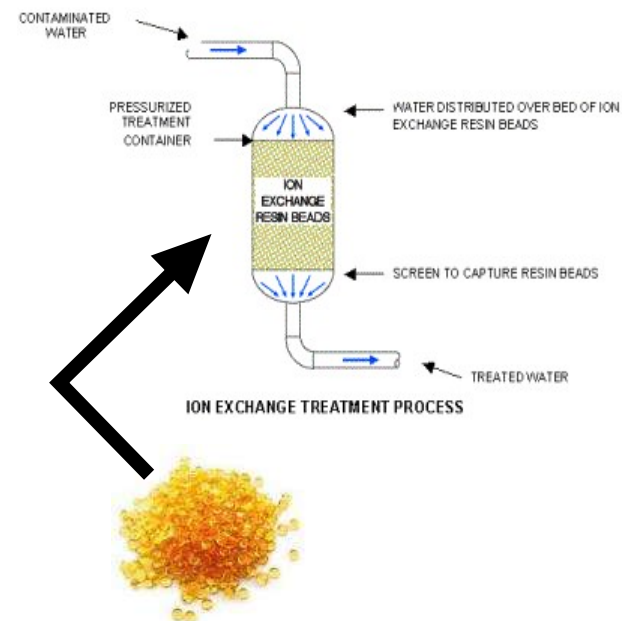
PFAS Wastewater Treatment

- PAC (Powdered Activated Carbon)
 - Same principle as with GAC, pollutants adsorb to carbon surface
 - Same issues with removal efficiencies affected by organics
 - Solids filtered out
 - Disposal of media
 - Landfill
 - Incineration



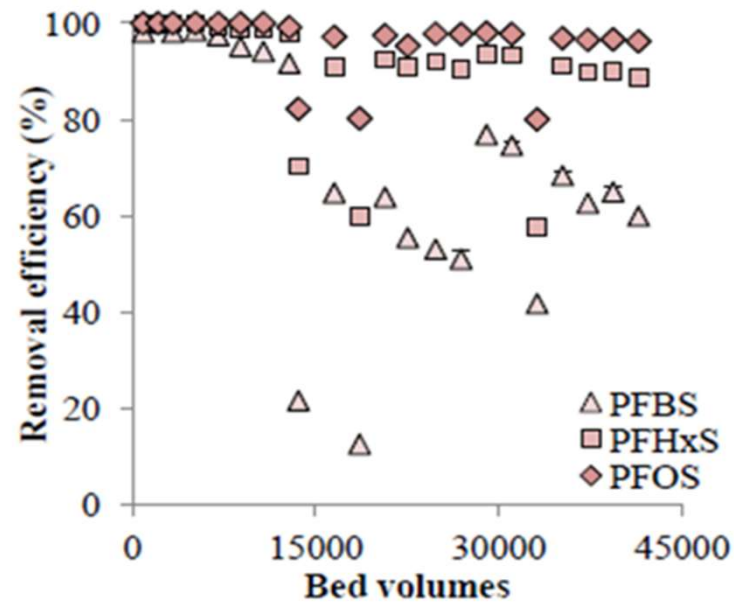
PFAS Wastewater Treatment

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



PFAS Wastewater Treatment

- Anion-Exchange Resin Column Experiment Example



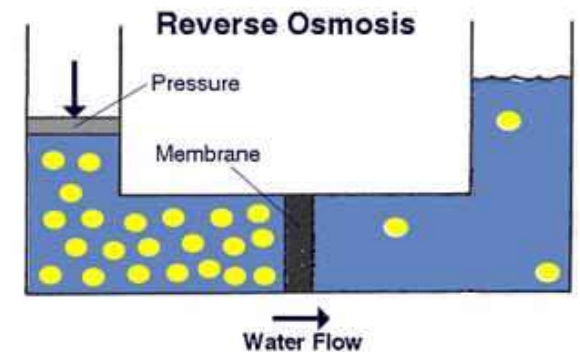
PFAS Wastewater Treatment

- Anion-Exchange Resin
 - Same issues as GAC:
 - Breakthrough of smaller-chained PFAS
 - Organic matter reduces efficiency
 - Disposal of spent resin
 - Landfills
 - Incineration

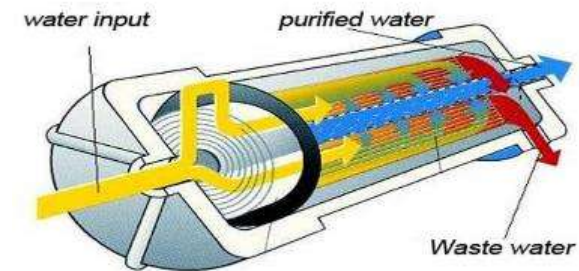


PFAS Wastewater Treatment

- 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**
 - Concentrated Volume: Typically 10-20% of original
 - More initial capital costs than GAC
 - Shown to be effective for treating landfill leachate, but not widely used



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



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



Wisconsin Monitoring Efforts

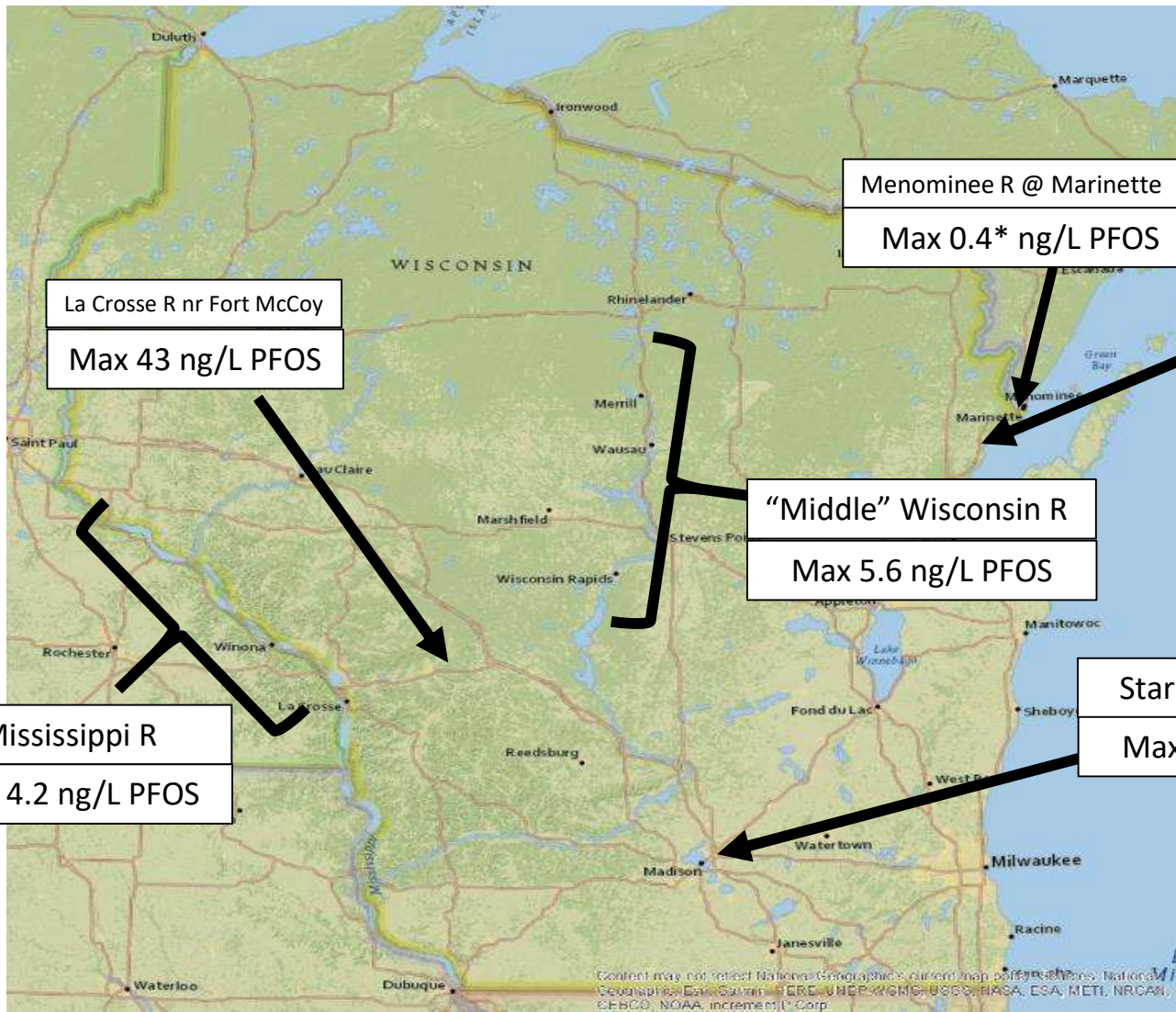


Surface Water Monitoring: 2019

- Fish Tissue Sampling
 - Target resident individuals
 - WSLH processes & analyzes
 - Initial results expected 1/2020
- Surface Water Chemistry
 - Adapted Michigan EGLE protocols
 - Approved materials & SOP
 - Analyzed at WSLH



2019 Surface Water and Fish Tissue Monitoring



Mississippi R
Max 4.2 ng/L PFOS

La Crosse R nr Fort McCoy
Max 43 ng/L PFOS

Menominee R @ Marinette
Max 0.4* ng/L PFOS

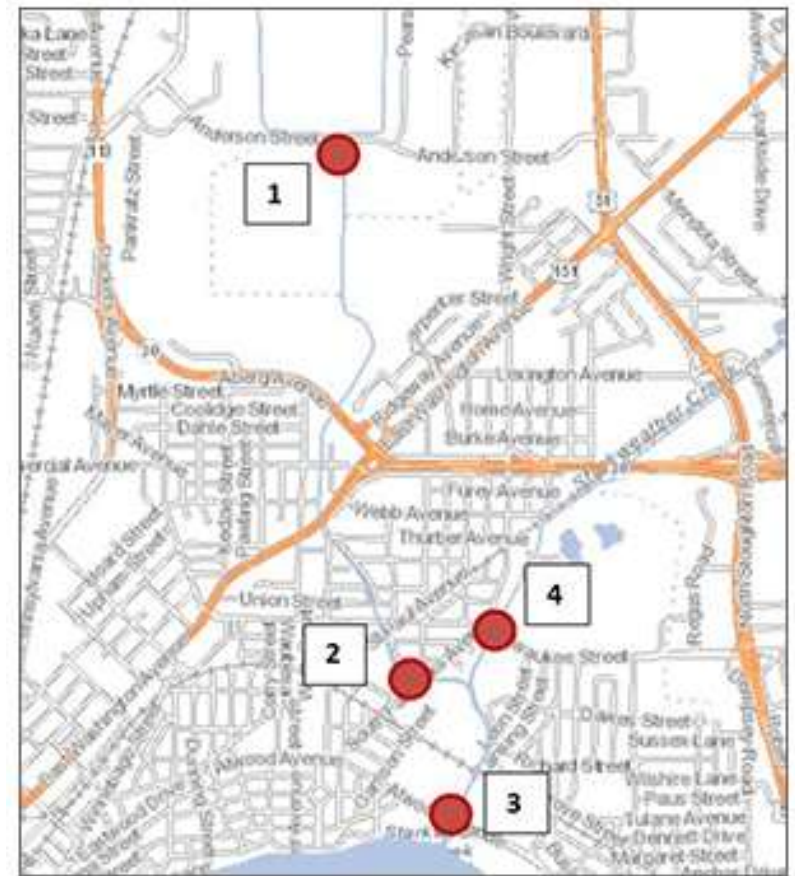
Peshtigo R & St. Louis R
Max 0.63 ng/L PFOS

"Middle" Wisconsin R
Max 5.6 ng/L PFOS

Starkweather Creek
Max 360 ng/L PFOS

Starkweather Creek Results

- 4 locations, 3 samples
- Results (ng/L):
 - 1:
 - PFOA: 23, 30, 20
 - PFOS: 79, 180, 71
 - 2:
 - PFOA: 43, 40, 34
 - PFOS: 270, 360, 220
 - 3:
 - PFOA: 27, 24, 18
 - PFOS: 160, 180, 120
 - 4:
 - PFOA: 2.6, 2.1, 2.3
 - PFOS: 2.6, 1.8, 1.5





Letter Sent to 125 POTWs

- PFAS Background
- Known Industrial Sources
- Statement that POTWs are not original sources of PFAS, but PFAS pass through them
- Requested Actions
- Invitation to participate in the State Lab of Hygiene Study
- Statement of Department's Intent in sending letter
- Additional Resources



Recipients

- 125 POTWs
 - 27 Authorized Pretreatment Programs
 - 91 Other POTWs with SIUs
 - 6 found by query of permit fact sheets
 - 1 community with PFAS in water supply



Requested Actions

- Voluntary sampling of influent and effluent
 - 36 PFAS compounds
 - Please use isotope dilution method
 - Within 90 days of receipt of letter
- Source Identification and Reduction
 - If PFOA+PFOS > 20 ng/L
 - Invitation to work with DNR to develop plan to sample potential sources
 - Invitation to work with DNR and sources to eliminate PFAS
 - Product substitution
 - Operational Controls
 - Cleanup of historical contamination
 - Pretreatment





Intended Outcomes

- Primary Goal: Avoid effluent limitations at POTWs
 - Address sources before standards take affect
 - Avoid back-end treatment at POTWs
- Parallel Michigan's demonstrated approach
- Scope extent of PFAS contamination in Wisconsin
- Inform Economic Impact Analysis for standards rulemaking
 - Make informed decisions based upon data



Actual Outcomes

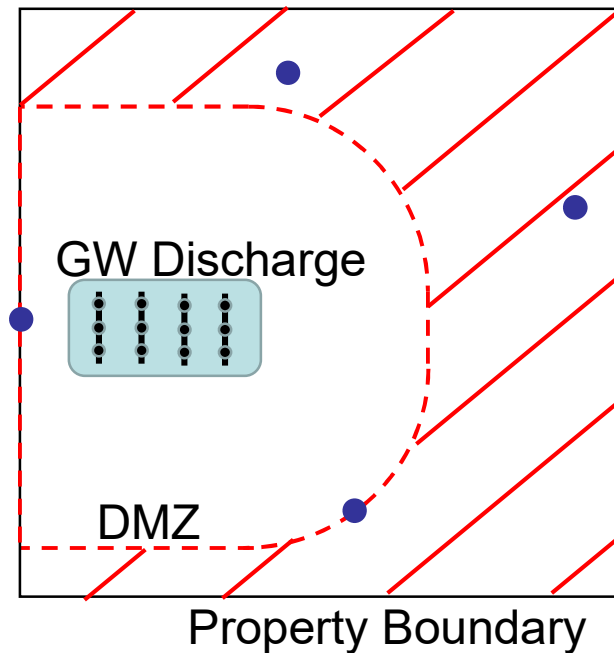
- 2 POTWs completed sampling
- Several POTWs have indicated they may sample once labs have been certified
 - Labs can be certified for PFAS testing of wastewater as of 10/29/2019 (up to 36 compounds)
- POTWs have indicated they will look to work with pretreatment industries to reduce PFAS in effluent



Wisconsin Rulemaking Efforts

Groundwater Standards

- DHS 6/21/19 Recommendation
 - 20 ng/L PFOA + PFOS Enforcement Standard
 - 2 ng/L PFOA+PFOS Preventive Action Limit
- Standards apply to all state programs
- When adopted, will apply outside DMZs





Groundwater Standards: Process

- DNR
 - Request DHS review of pollutants
 - DNR requested 2 PFAS compounds and 25 others on 3/2/2018 (“Cycle 10”)
 - DNR requested 34 more PFAS compounds and 6 agricultural chemicals (“Cycle 11”)
- DHS
 - 1. Review Literature and Available Scientific Information
 - 2. Select Appropriate Science-based Standards
 - 3. Write Documents Explaining Findings/Recommendations (DHS completed review of PFOA and PFOS on 6/21/2019. Expect Cycle 11 in Fall 2020.)
- DNR
 - 1. Review Existing Rules
 - 2. Revise Rules to Achieve Compliance with Standards (Public Input)
 - 3. Enforce Standards



Cycle 10 Recommendations

Substance	New or Existing	Enforcement Standard Recommended Value	Enforcement Standard Recommended Value	Preventive Action Limit Recommended Value	Preventive Action Limit Recommended Value
1,1-Dichloroethane	Existing	No Change	850 µg/L	No Change	85 µg/L
1,2,3-Trichloropropane	Existing	↓	0.3 ng/L	↓	0.03 ng/L
1,4-Dioxane	Existing	↓	0.35 µg/L	↓	0.035 µg/L
Aluminum	Existing	No Change	200 µg/L	No Change	20 µg/L
Bacteria (Total coliform)	Existing	No Change	0	No Change	0
Bacteria (<i>E. coli</i>)	New	n/a	0	n/a	0
Barium	Existing	No Change	2 mg/L	No Change	0.4 mg/L
Boron	Existing	↑	2,000 µg/L	↑	400 µg/L
Clothianidin	New	n/a	1,000 µg/L	n/a	200 µg/L
Cobalt	Existing	No Change	40 µg/L	↓	4 µg/L*
Dacthal MTP and TPA degradates	New	Combine with dacthal	70 µg/L	↓	7 µg/L*
Glyphosate	New	n/a	10 mg/L	n/a	1 mg/L
Glyphosate AMPA degradate	New	n/a	10 mg/L	n/a	2 mg/L
Hexavalent chromium	New	n/a	70 ng/L	n/a	7 ng/L
Imidacloprid	New	n/a	0.2 µg/L	n/a	0.02 µg/L
Isoxaflutole & Isoxaflutole Diketonitrile (DKN)	New	n/a	3 µg/L	n/a	0.3 µg/L
Isoxaflutole Benzoic Acid (BA)	New	n/a	800 µg/L	n/a	160 µg/L
Molybdenum	Existing	No Change	40 µg/L	↓	4 µg/L*
PFOA & PFOS	New	n/a	20 ng/L	n/a	2 ng/L
Strontium	New	n/a	1,500 µg/L	n/a	150 µg/L
Sulfentrazone	New	n/a	1,000 µg/L	n/a	100 µg/L
Tetrachloroethylene (PCE)	Existing	↑	20 µg/L	↑	2 µg/L
Thiamethoxam	New	n/a	100 µg/L	n/a	10 µg/L
Thiencarbazone-methyl	New	n/a	10 mg/L	n/a	2 mg/L
Trichloroethylene (TCE)	Existing	↓	0.5 µg/L	↓	0.05 µg/L

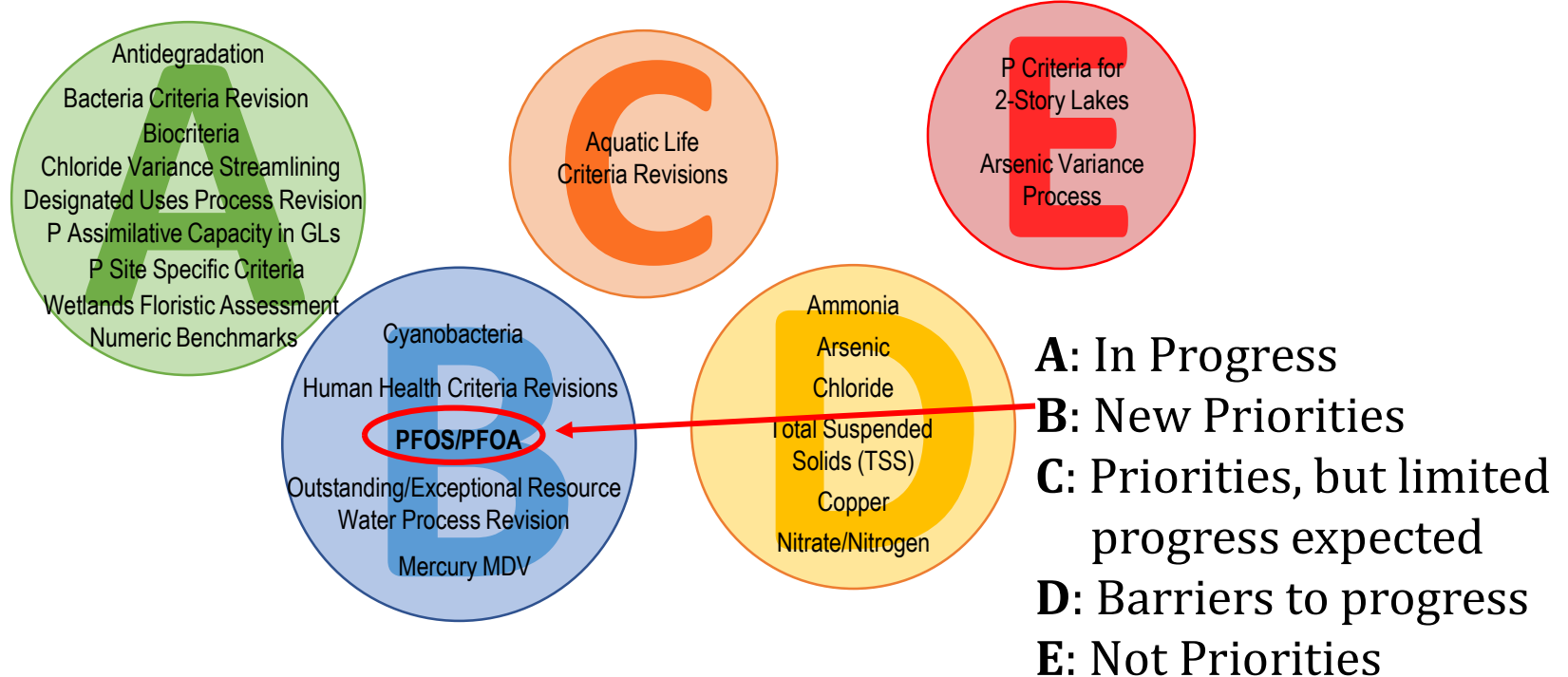
* Although DHS is not recommending a change in the enforcement standard for this substance, we are recommending a change in the preventive action limit. Please refer to the specific science support documents for each of the substances for more detail.

How WI's Recommended GW Standard Compares to Other States' Standards

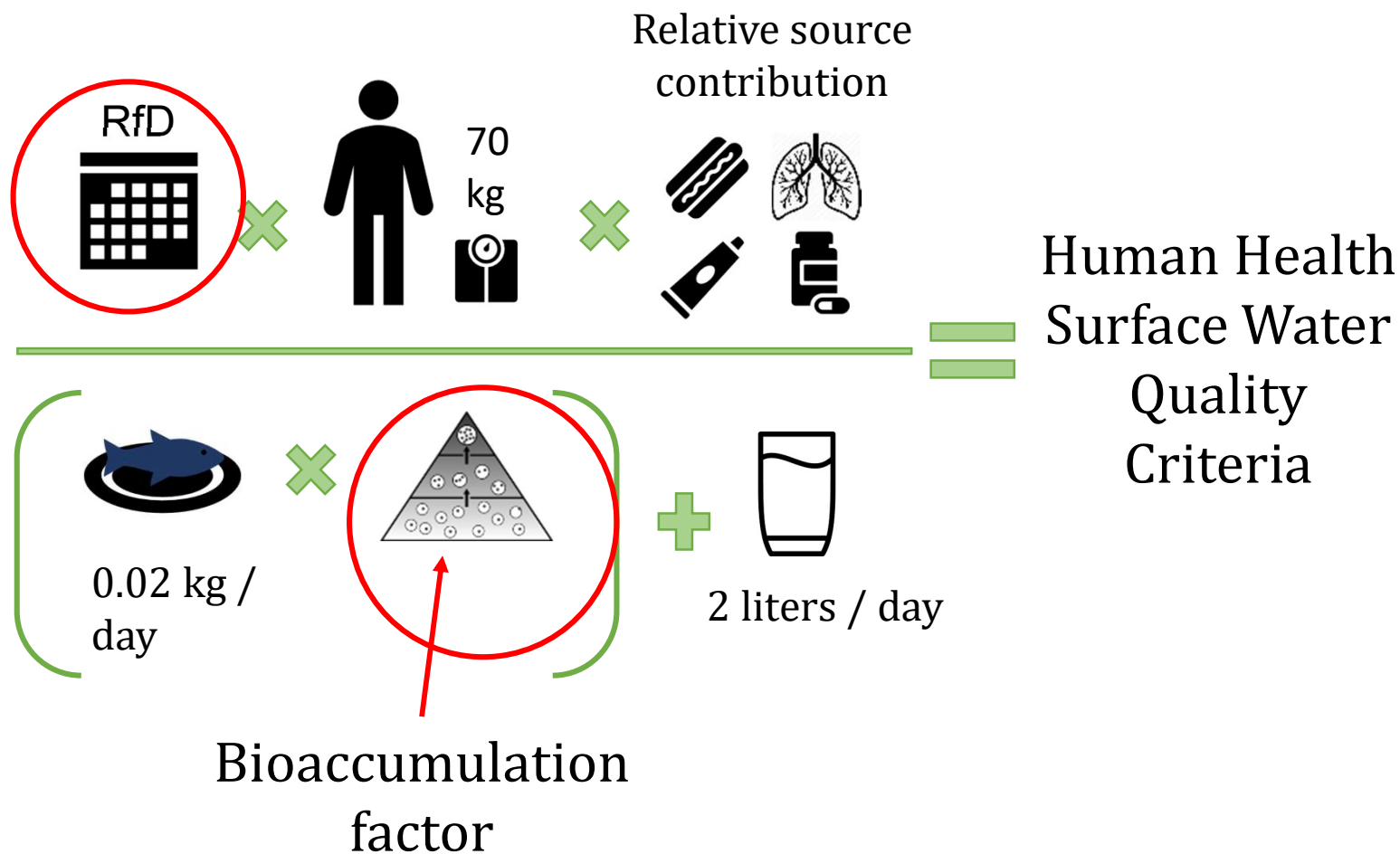
		Groundwater (all values in ppt)				Groundwater Standard/Guideline Policy Type
		PFOA	PFOS	PFHxS	PFNA	
Colorado	<i>Singular or combined</i>	70	70			<i>Site-specific Groundwater Quality Standard (proposed)</i>
Delaware	<i>Singular or combined</i>	70	70			<i>Reporting Level (not promulgated)</i>
Massachusetts		20	20	20	20	<i>Groundwater Standard (proposed)</i>
Michigan	<i>Singular or combined</i>	8	16			<i>Clean-up Standard (proposed)</i>
Minnesota		35	15	47		<i>Guidance Level</i>
New Hampshire		12	15	18	11	<i>Ambient Groundwater Quality Standard (proposed)</i>
New Jersey		10	10		10	<i>Groundwater Quality Standard</i>
Vermont	<i>Singular or combined</i>	20	20	20	20	<i>Cleanup Level (enforceable)</i>
Wisconsin	<i>Singular or combined</i>	20	20			<i>Groundwater Standard (proposed)</i>

Surface Water Quality Standards

- Triennial Standards Review



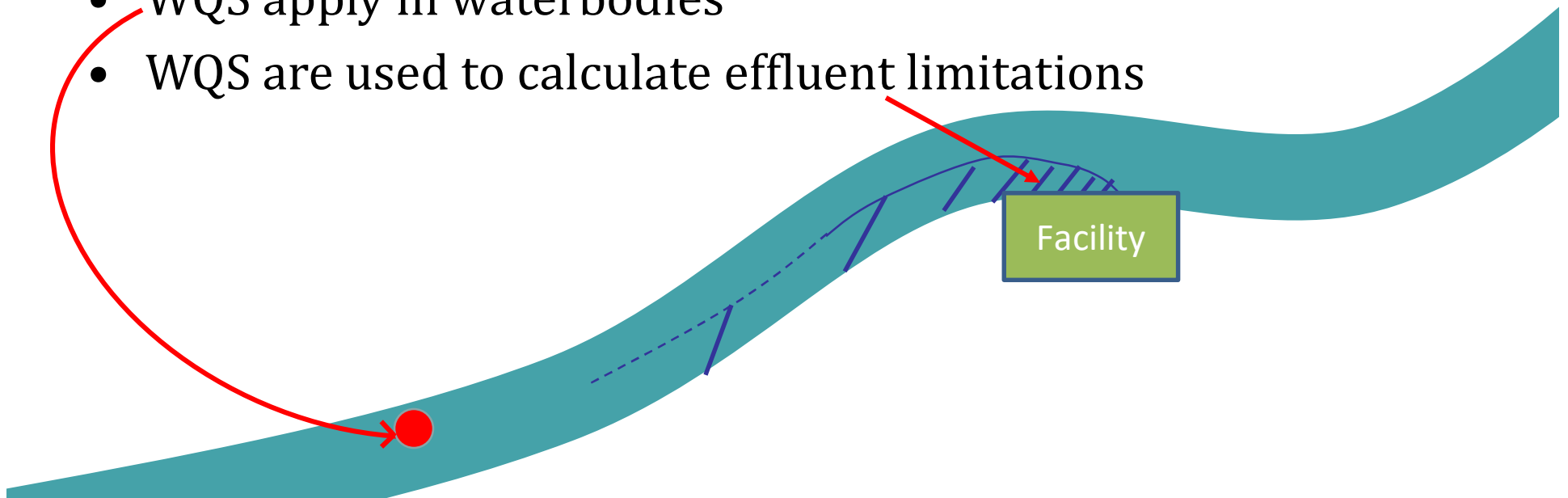
Water Quality Standards Development Process





Water Quality Standards

- WI currently does not have surface water quality standards (WQS) for PFAS
- Scope Statement approved by Governor for development of WQS
- WQS apply in waterbodies
- WQS are used to calculate effluent limitations





Summary

- PFAS are persistent
- Treatment technologies exist
- Best accepted strategy for contamination is to reduce PFAS at the source
- Scope Statements for groundwater and surface water standards go to the Natural Resources Board for approval (~2.5 year process if approved)



Questions?

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