Per- and polyfluoroalkyl substances (PFAS) in Wisconsin waters

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Wisconsin Department of Natural Resources
Bureau of Water Quality

March 3, 2020

Today's presentation

Introduction: what are PFAS, where did they come from, why should I care?

Monitoring for PFAS: protocols and 2019 results

Surface water quality standards for PFOS and PFOA

Discussion/questions

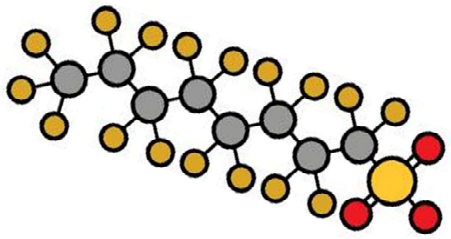

Image credit: http://www.biocycle.net/wp-content/uploads/2018/07/20b.jpg

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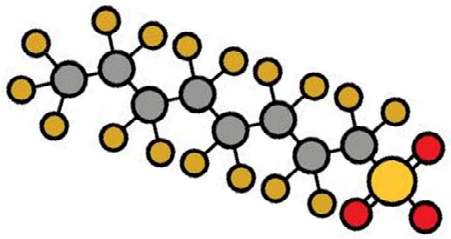

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What are PFAS?

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

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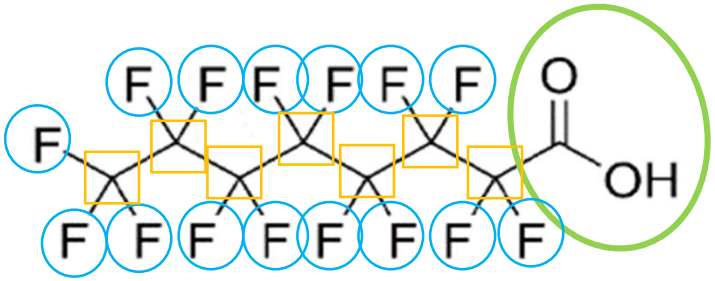
Perfluorinated compounds:
fully-fluorinated tail



PFOA
(perfluorooctanoic acid)

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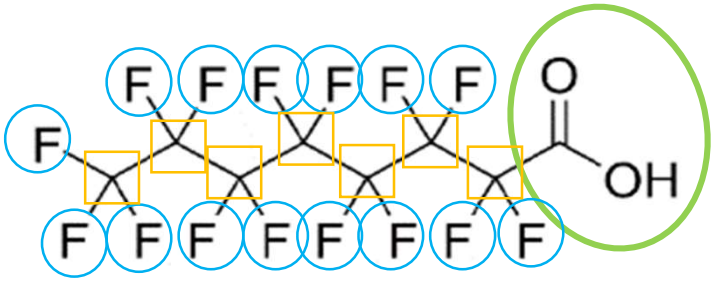
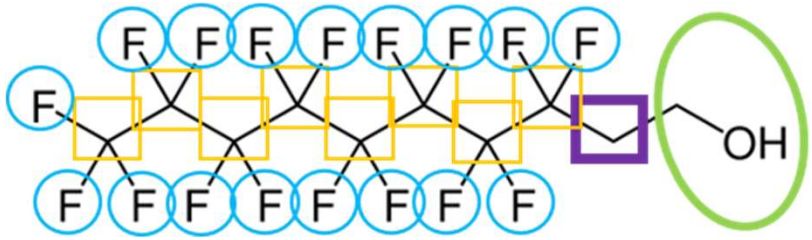


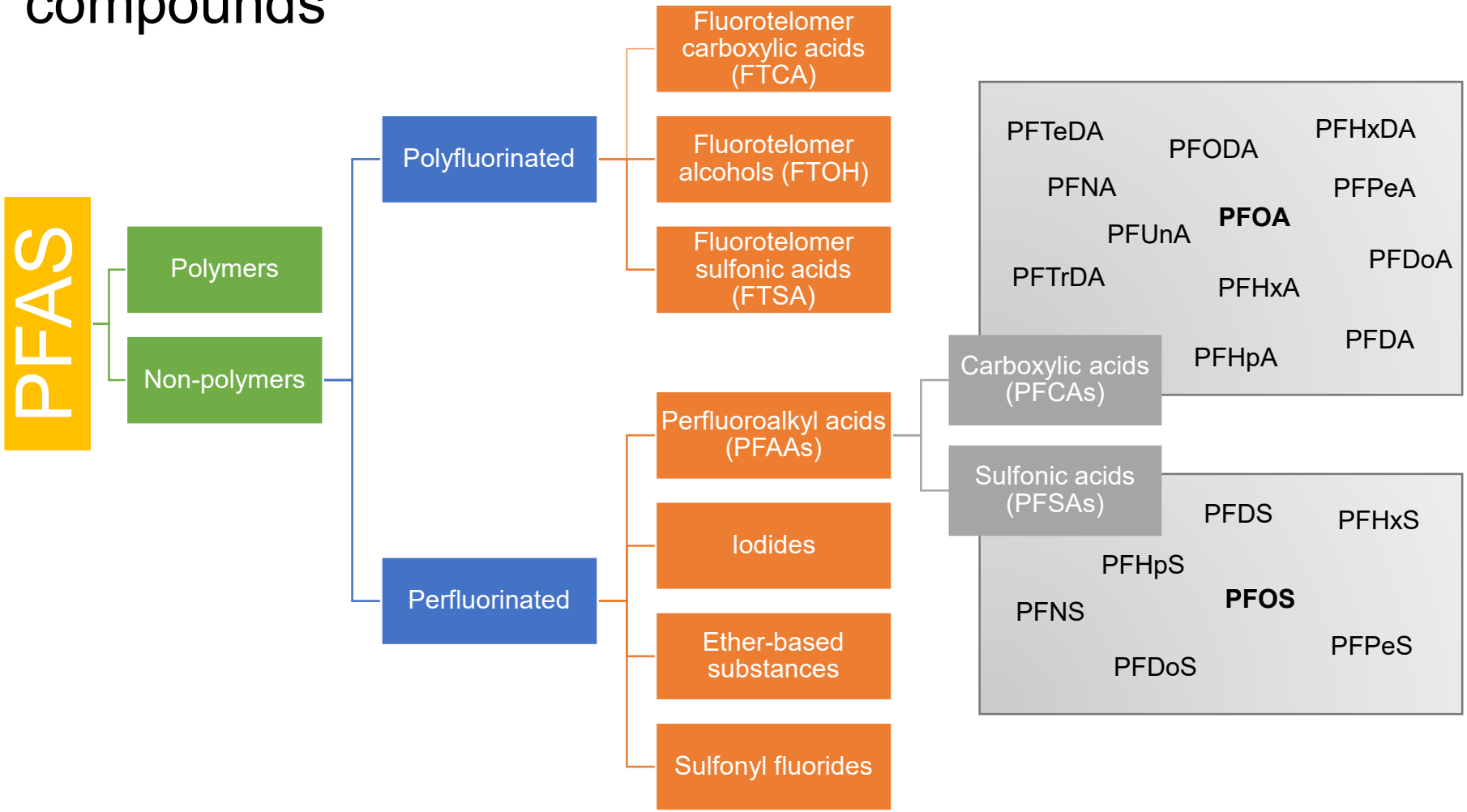
PFOA
(perfluorooctanoic acid)

Polyfluorinated compounds: at least one carbon is **not attached** to a fluorine



8:2 FTOH
(fluorotelomer alcohol)

4000+ human-made compounds

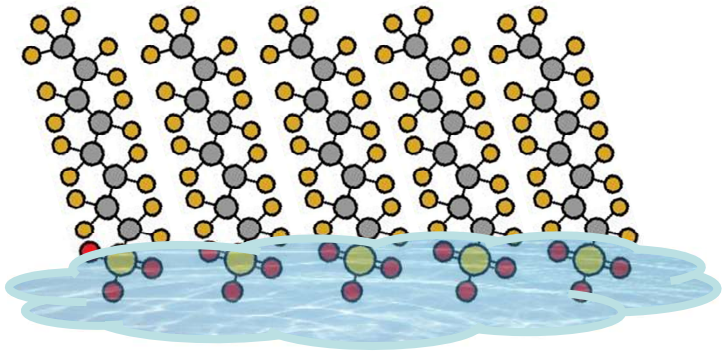


Structure of PFAS imparts useful properties

Excellent water- and oil-repelling properties

Tail is hydrophobic and lipophobic, head is polar and hydrophilic

Readily form films at air-water interface



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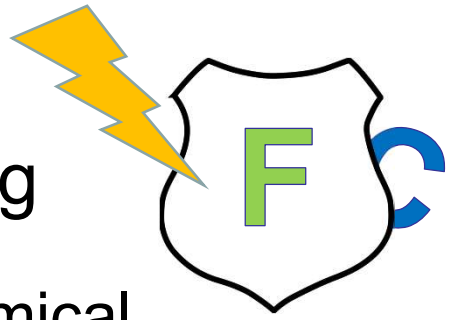
What are PFAS used for?

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		

https://pfas-1.itrcweb.org/wp-content/uploads/2017/11/pfas_fact_sheet_history_and_use__11_13_17.pdf
https://commons.wikimedia.org/wiki/File:US_Navy_021022-N-5362A-011_Fire_fighting_training_during_Diligent_Warrior_2003.jpg
https://upload.wikimedia.org/wikipedia/commons/6/6b/Imos_Pizza_in_the_box_1.jpg

https://cdn.pixabay.com/photo/2016/09/13/23/02/shampoo-1668525_960_720.jpg
https://www.fontesia.com/wp-content/uploads/2018/01/70-0714-9234-5-600x600.png
https://crdms.images.consumerreports.org/c_lfill,w_240,h_175/prod/products/cr/models/399723-frying-pans-nonstick-amazonbasics-nonstick-10008298

Why are PFAS a problem?



Carbon-fluorine bond is incredibly strong

- Fluorine atoms “shield” carbon from chemical reactions
- C-F does not undergo biotic or abiotic degradation
- C-F thermally degrades only at high temperatures

All PFAS are very persistent

Some PFAS are highly bioaccumulative

Why are PFAS a problem?

Persistence + bioaccumulation = global distribution

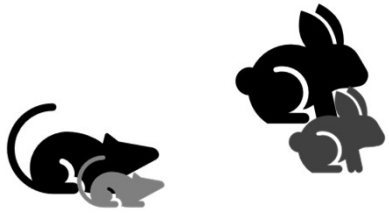
- PFAS have been found in wildlife on all continents
- PFAS have been found in surface waters globally

- PFAS have been found in blood samples from humans across the world

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



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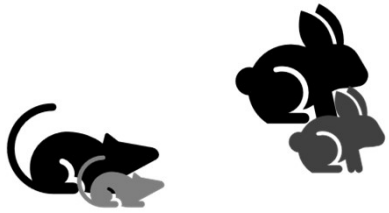
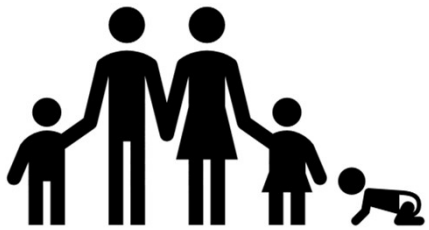


- Probable links to human health effects:
  - Childhood growth and development
  - Pregnancy-related hypertension
  - Hormone regulation
  - Increased cholesterol levels
  - Immune system effects
  - Cancer risk



Summary

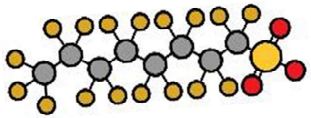
PFAS are a family of 4,000+ human-made compounds

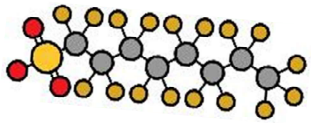
Their unique chemical structure gives them useful properties

They are extremely resistant to degradation and some are highly bioaccumulative

PFAS have been found almost everywhere

PFAS cause adverse health effects in animals and humans





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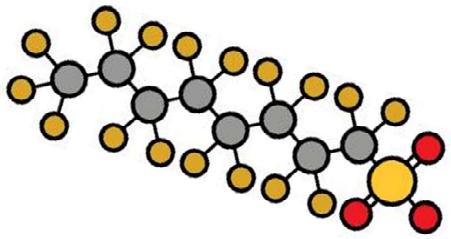

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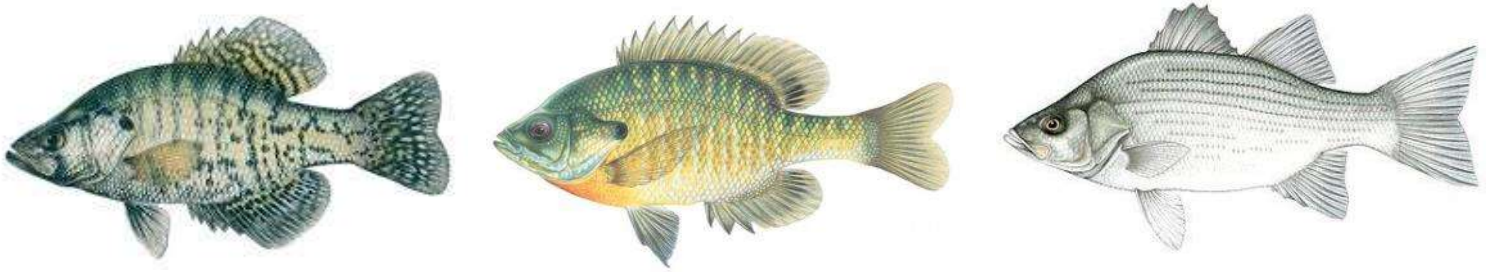
PFAS Detection at Low Levels

- Dissolved Oxygen – mg/l
  - ~7 mg/l Coldwater streams
  - 7,000,000 ng/l
- Total Phosphorus – mg or µg/l
  - 75 µg/l – streams
  - 75,000 ng/l
- PFOS– ng/l
  - 12 ng/l – Michigan's surface water standard

Previous WDNR Monitoring

- 2006-2012 fish sampled from large rivers & Great Lakes with high industrial use
- PFOS found in >99% of samples
- PFOS Variation:
  - Species: highest in fillets of white bass, crappie, and bluegill



WDNR PFAS Monitoring

- Wisconsin State Lab of Hygiene
  - Fish tissue and drinking water methods
  - Surface water method develop in 2019

- Surface water chemistry SOP
  - Adapting Michigan DEQ protocols
  - Approved materials & SOP

PFAS Alternatives
Silicone
Stainless Steel
High-density polyethylene (HDPE)
PVC or Neoprene

PFAS "Sites" Explored in 2019 Monitoring

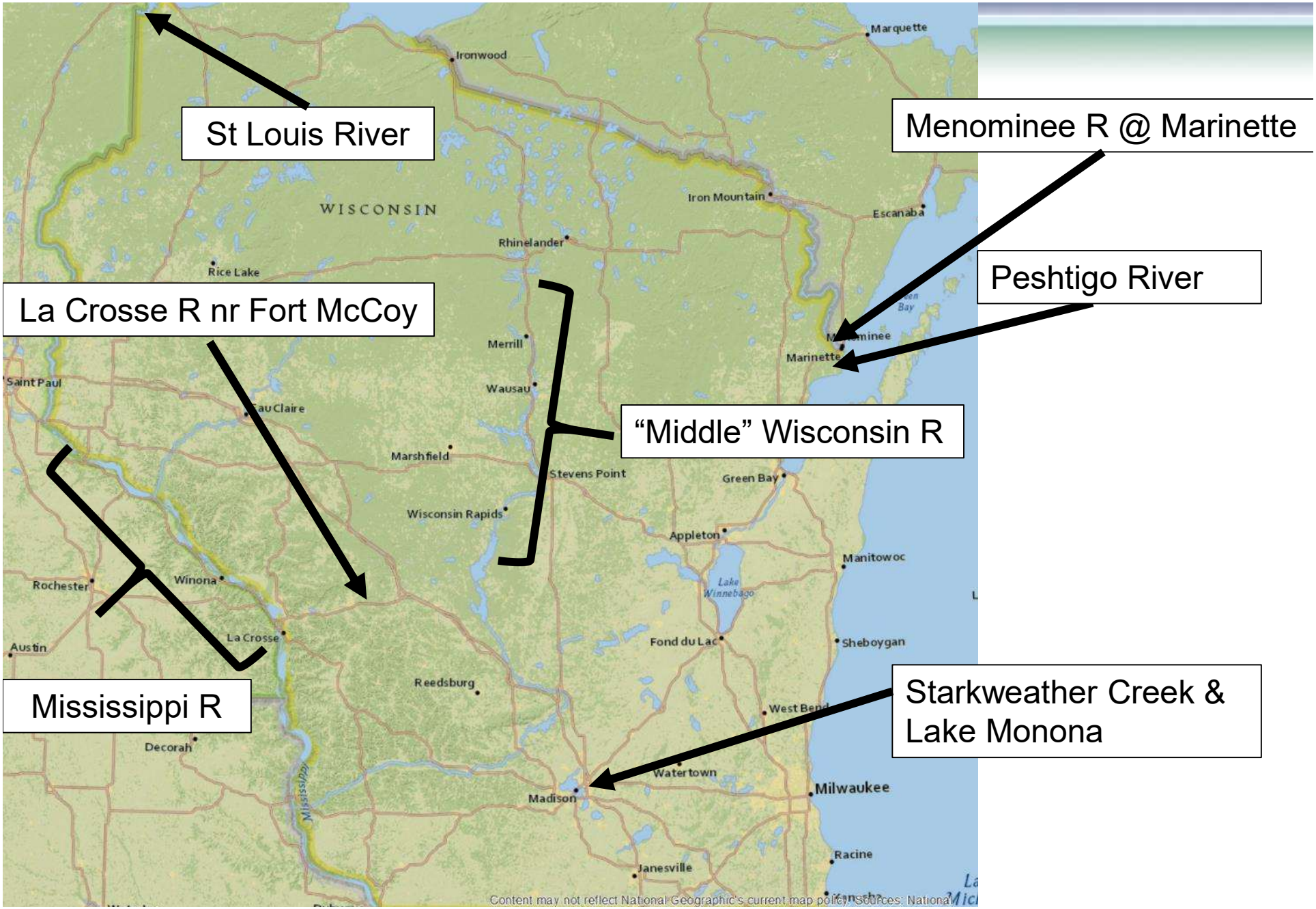
AFFF Training Grounds

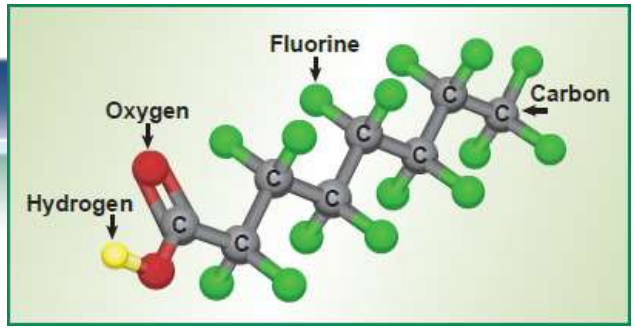
Municipal & Industrial Waste

Unknown/Multiple

Land Spreading Municipal Biosolids

2019 WR Surface Water and Fish Tissue Monitoring

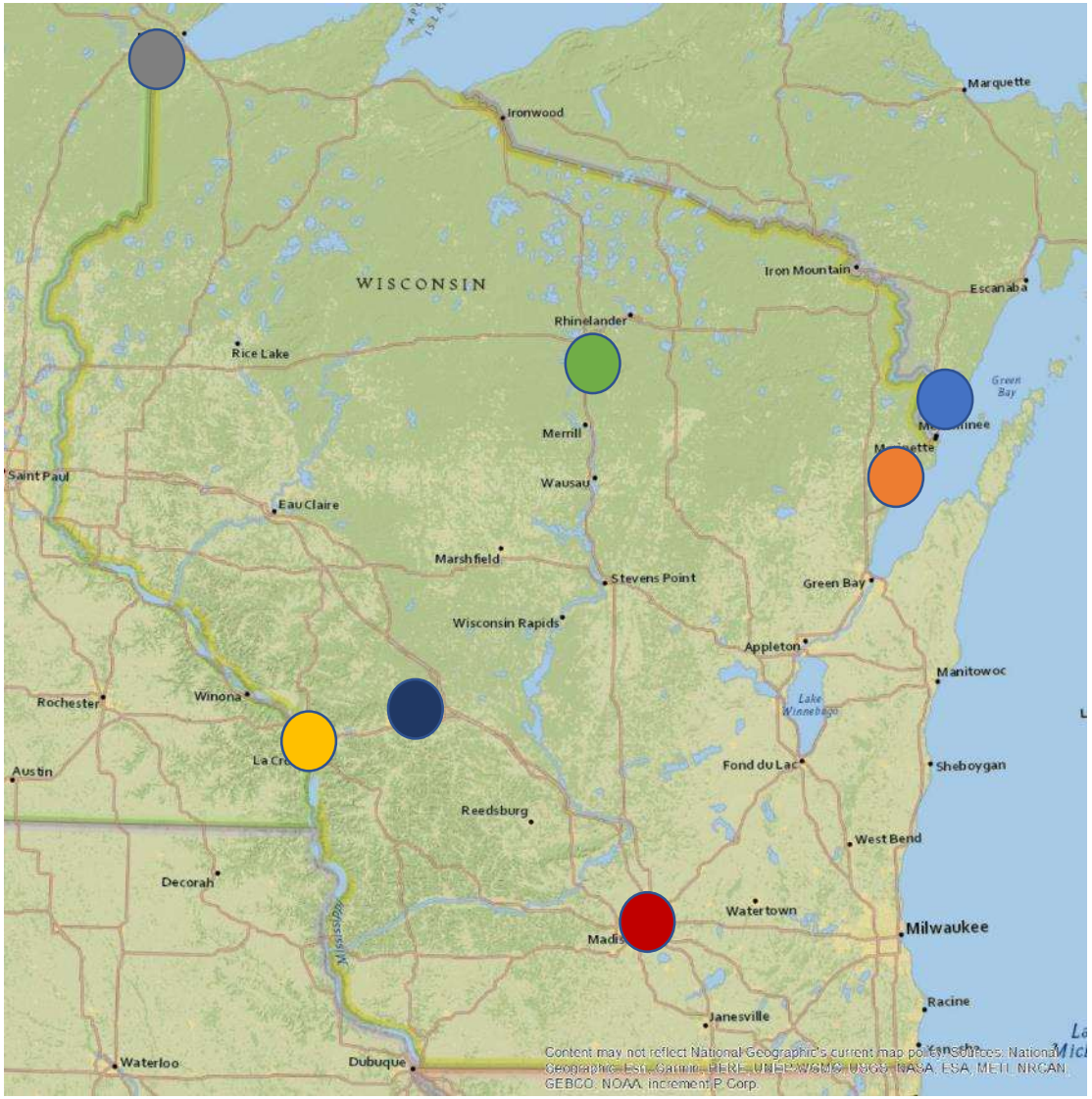


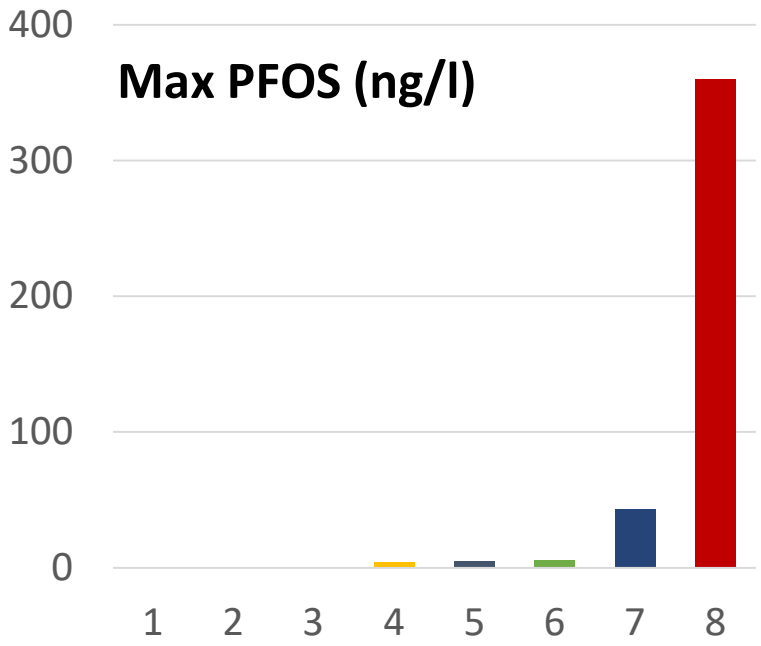


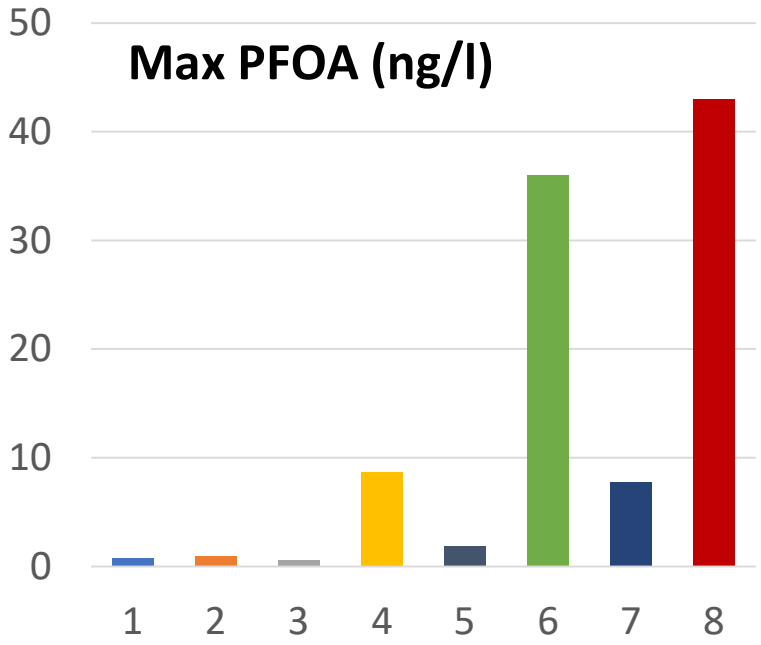
2019 Monitoring Results

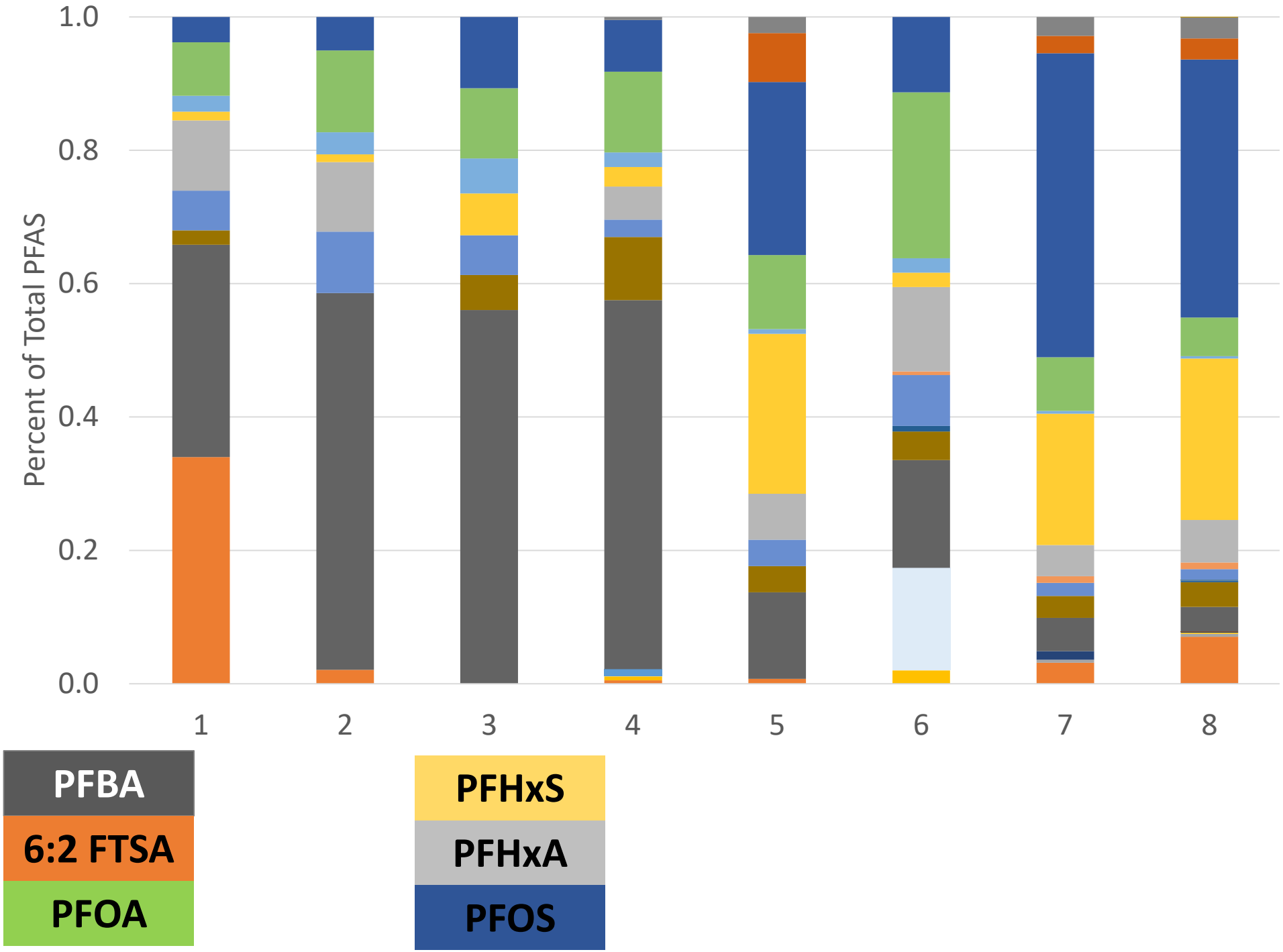
Surface Water:

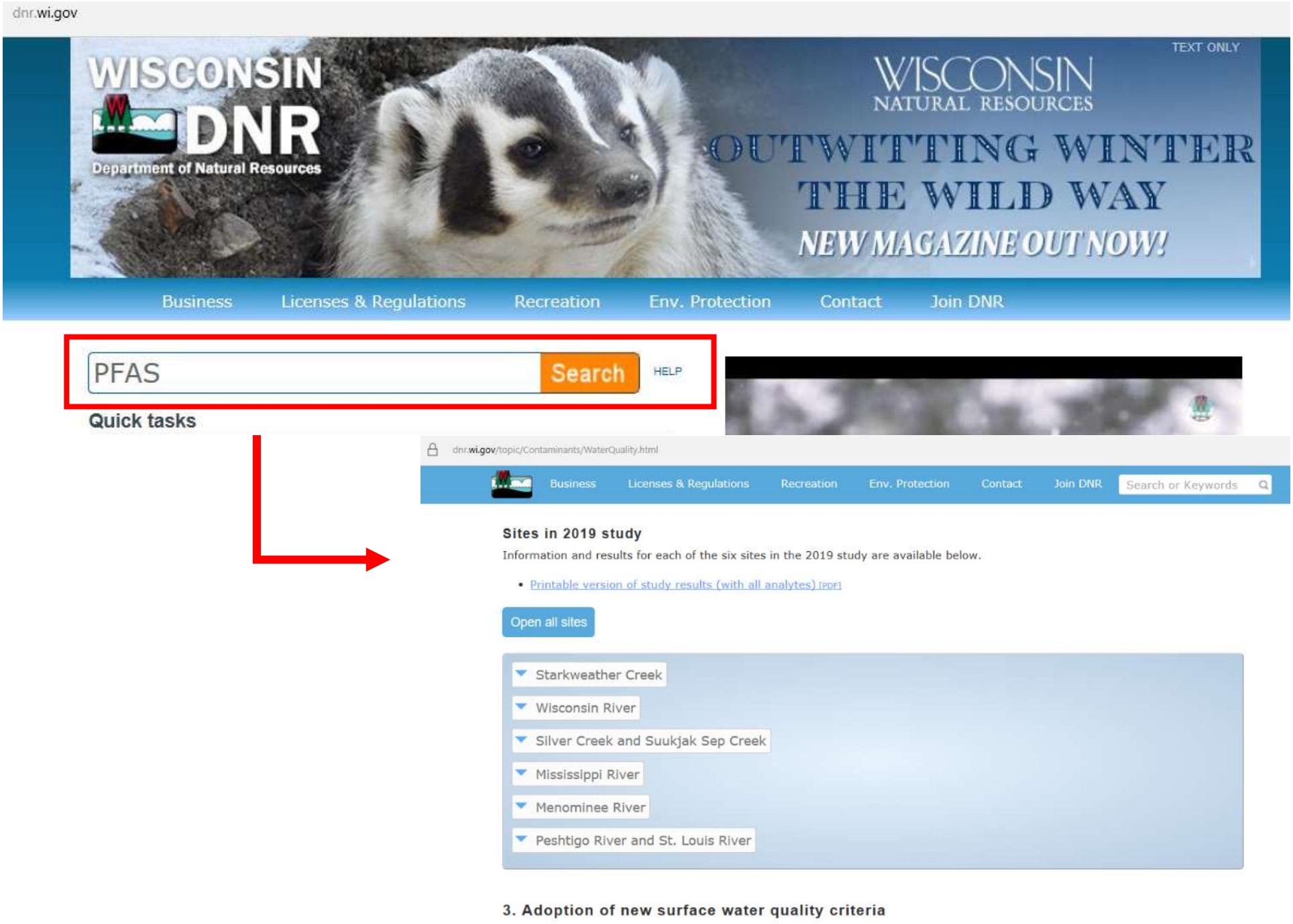
- PFAS compounds were detected at all locations
  - Including "control" sites
  - Found at varying concentrations & compounds
  - 3 to 17 (out of 36) compounds per site
- Highest concentrations of PFOS at Starkweather Creek (Dane County)
- 2nd – Silver Creek (Monroe County)
  - Each are small streams near known sources


WISCONSIN
Ironwood
Marquette
Iron Mountain
Escanaba
Rhinelander
Rice Lake
Merrill
Wausau
Saint Paul
Eau Claire
Marshfield
Stevens Point
Green Bay
Wisconsin Rapids
Appleton
Manitowoc
Rochester
Winona
Austin
Fond du Lac
Sheboygan
Reedsburg
West Bend
Decorah
Watertown
Milwaukee
Racine
Janesville
Waterloo
Dubuque
Content may not reflect National Geographic's current map policy. Sources: National Geographic, Esri, Garmin, FEMA, USGS, NASA, ESA, METI, NRCAN, GEBCO, NOAA, increment P Corp.

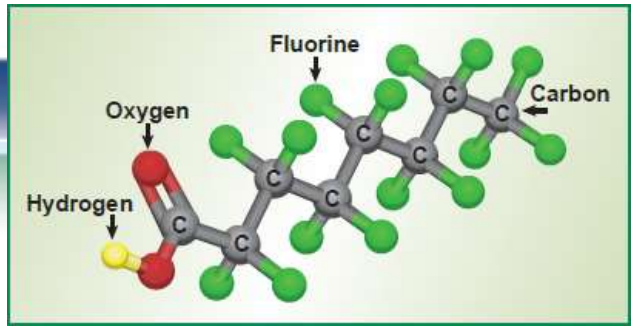

Max PFOS (ng/l)
400
300
200
100
0
1
2
3
4
5
6
7
8


Max PFOA (ng/l)
50
40
30
20
10
0
1
2
3
4
5
6
7
8


1.0
0.8
0.6
0.4
0.2
0.0
Percent of Total PFAS
1
2
3
4
5
6
7
8
PFBA
6:2 FTSA
PFOA
PFHxS
PFHxA
PFOS



https://dnr.wi.gov/topic/Contaminants/WaterQuality.html

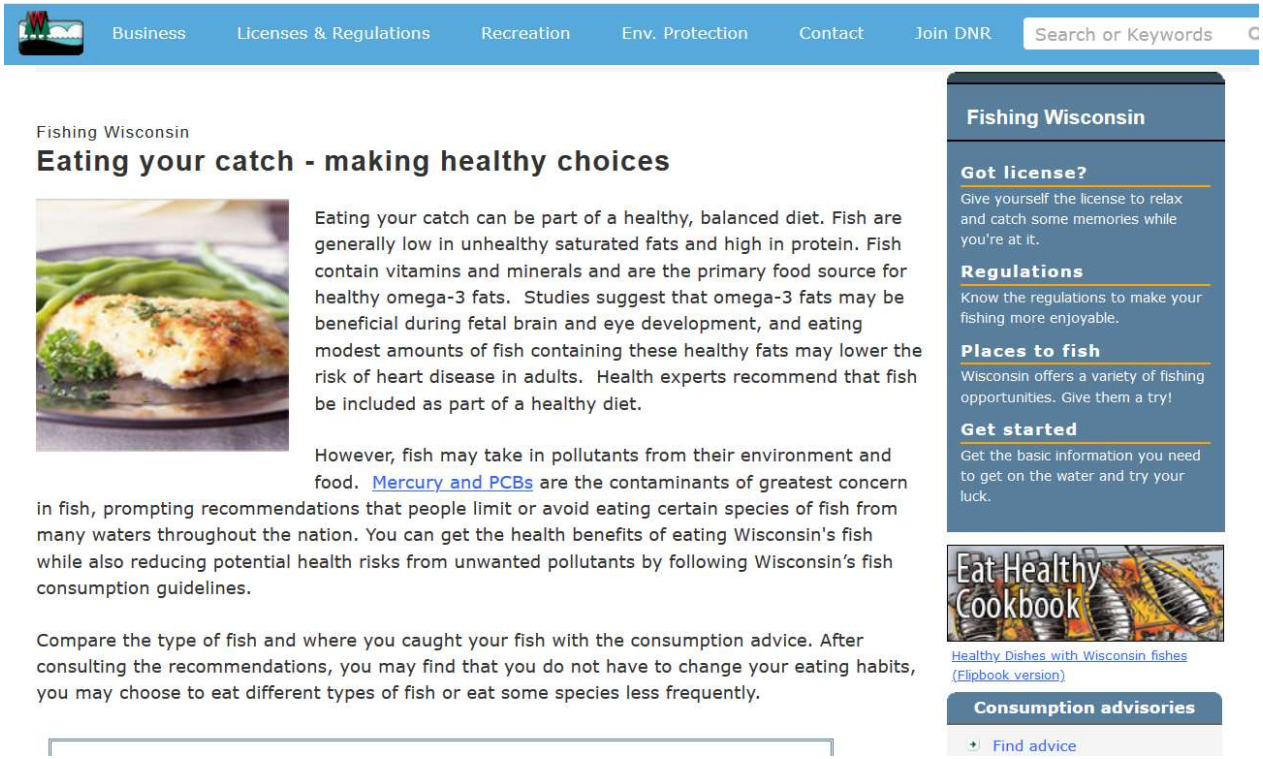


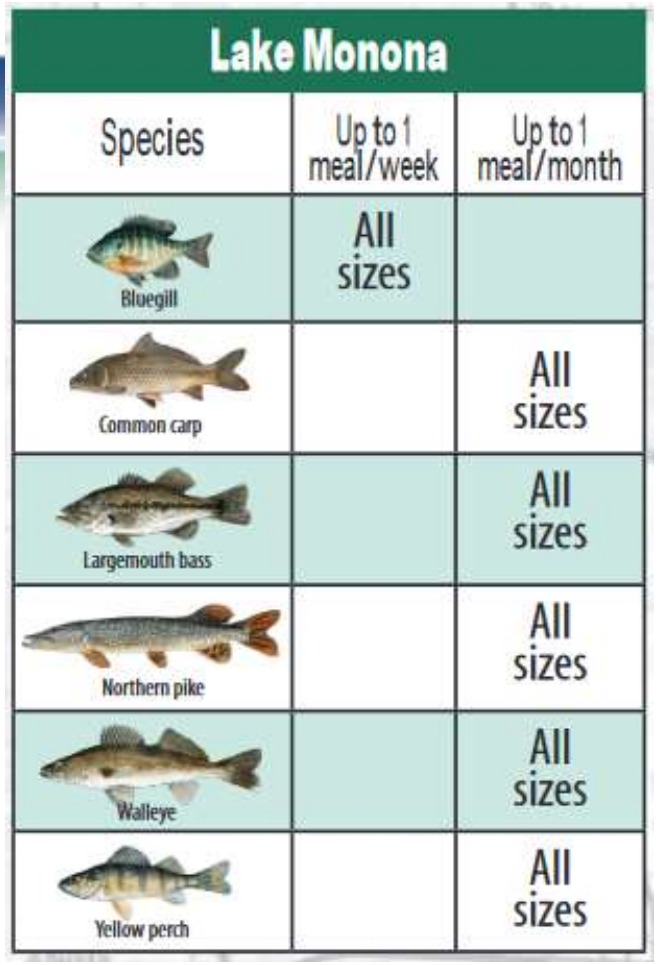
2019 Monitoring Results

Fish Tissue:

- Starkweather Creek and Lake Monona
  - Generally, comparable concentrations for top predators and panfish
  - 2006-2012 higher in panfish
  - A comprehensive contaminants survey is planned for spring 2020 on Lake Monona
- Waiting for lab results for remaining fish
  - Mississippi River
  - Wisconsin River
  - Marinette River

Updates to Fish Consumption Advice





Lake Monona

Species	Up to 1 meal/week	Up to 1 meal/month
Bluegill	All sizes	
Common carp		All sizes
Largemouth bass		All sizes
Northern pike		All sizes
Walleye		All sizes
Yellow perch		All sizes

https://dnr.wi.gov/topic/fishing/consumption/

Ways to reduce your PFAS exposure

Minimize ingestion of untreated surface water (skin contact is not a concern)

Do not touch foams or allow pets/children to play in foams

Wash your hands after wading or playing in surface waters

Follow fish consumption advisories

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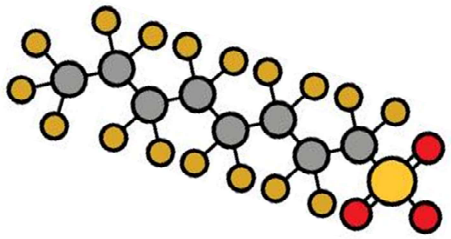
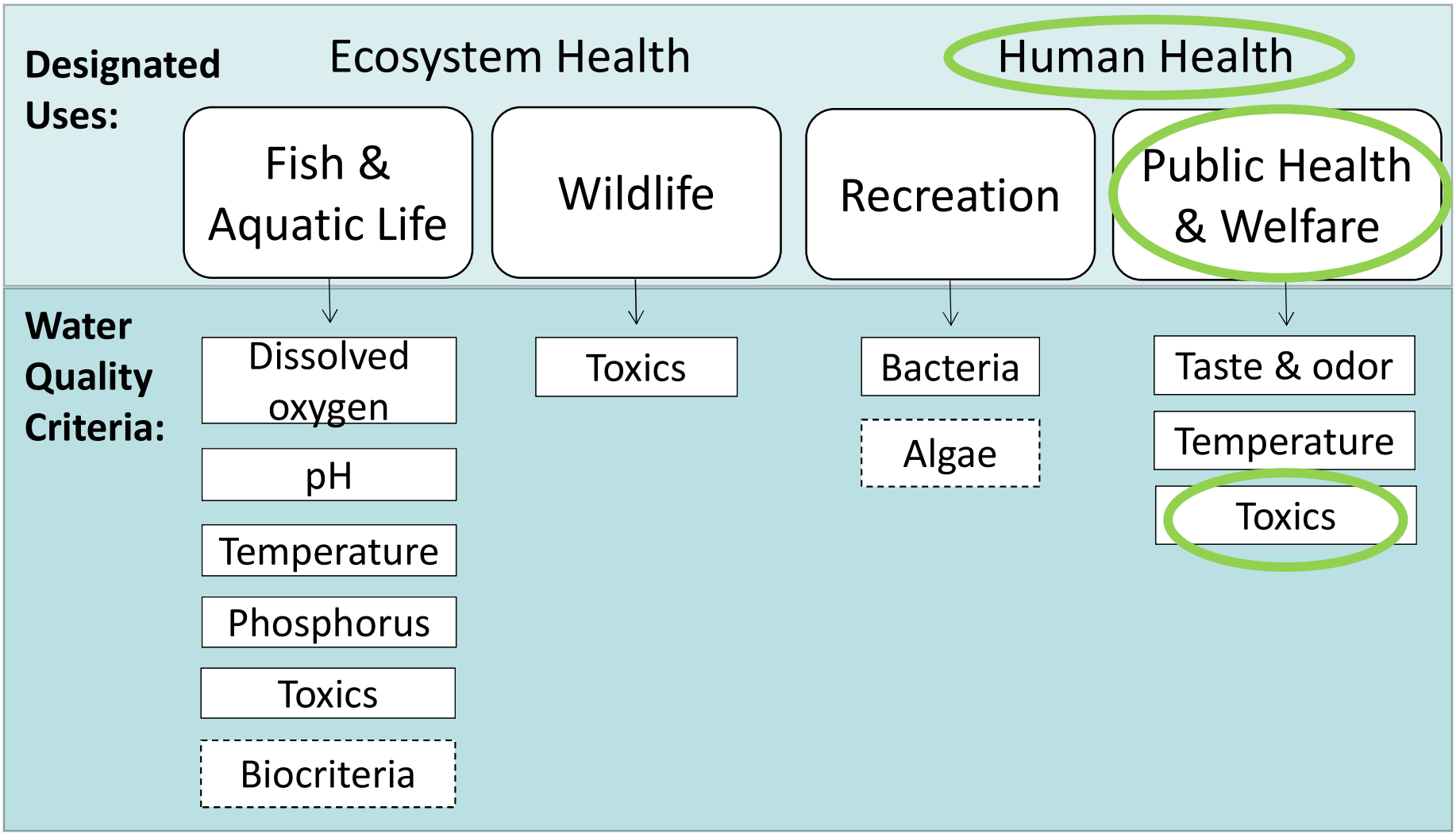


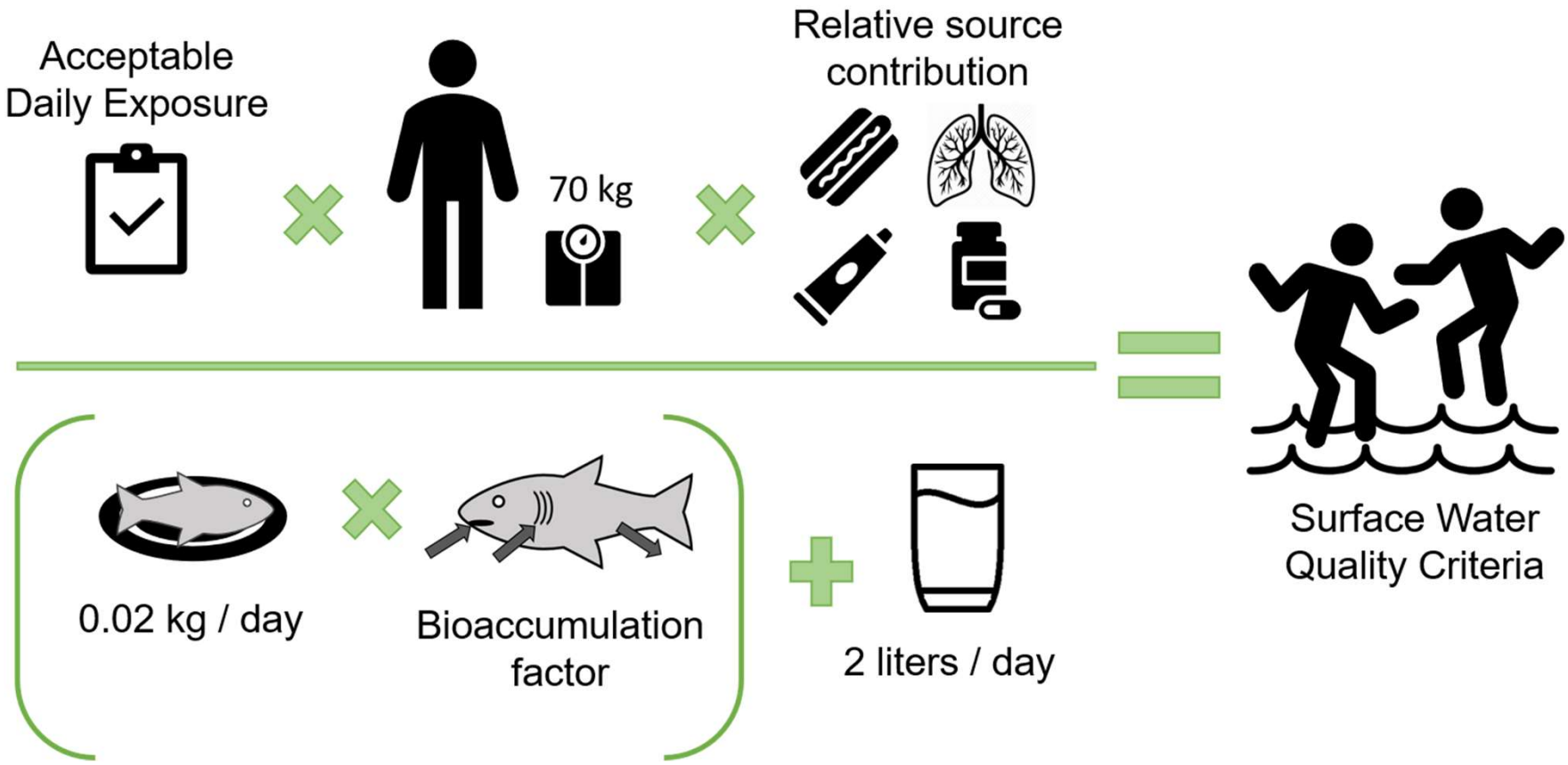
Image credit: http://www.biocycle.net/wp-content/uploads/2018/07/20b.jpg

Water Quality Standards
"The Three Legged Stool"

Water Quality Standards



Human Health Threshold Criteria



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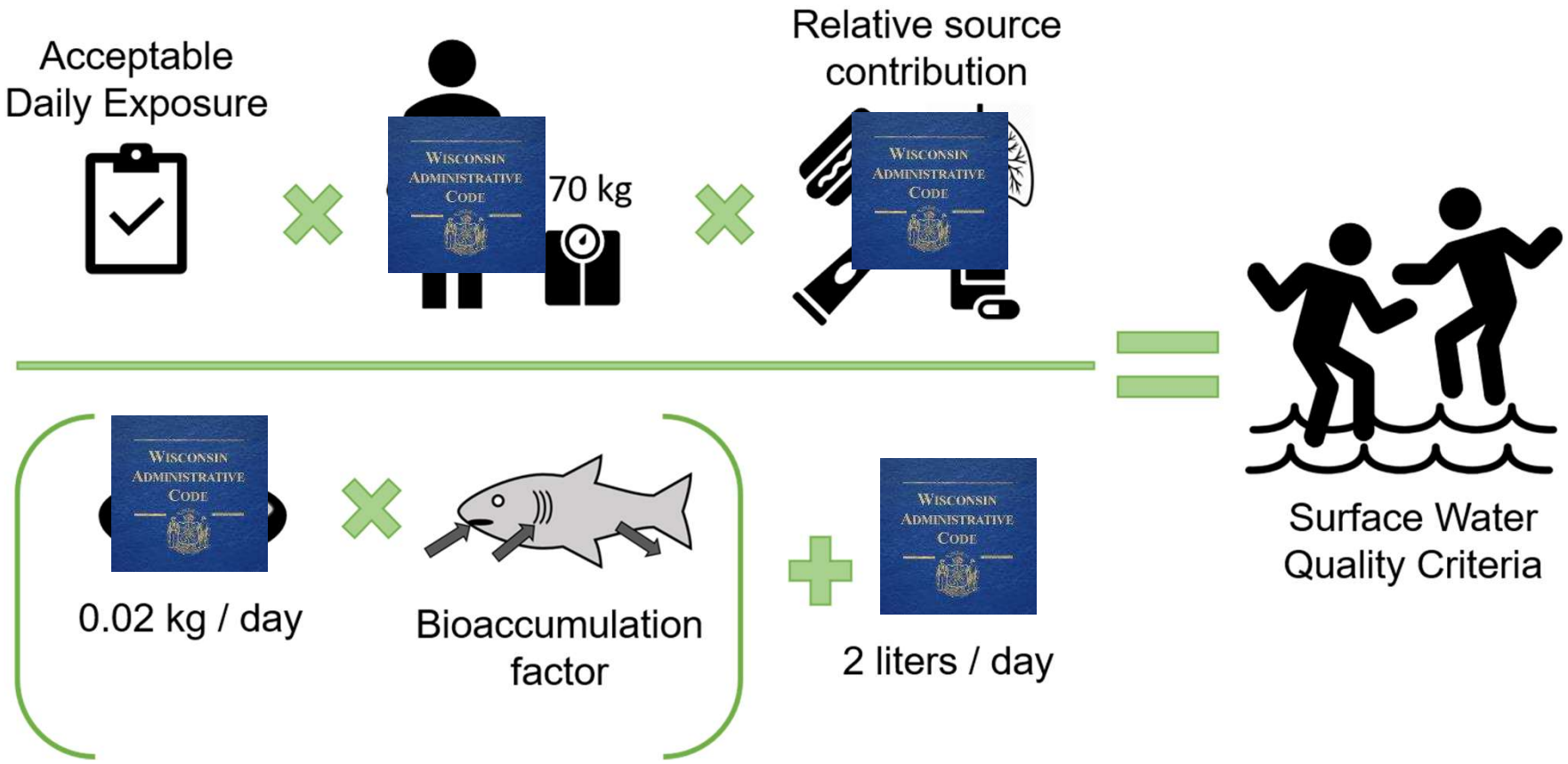

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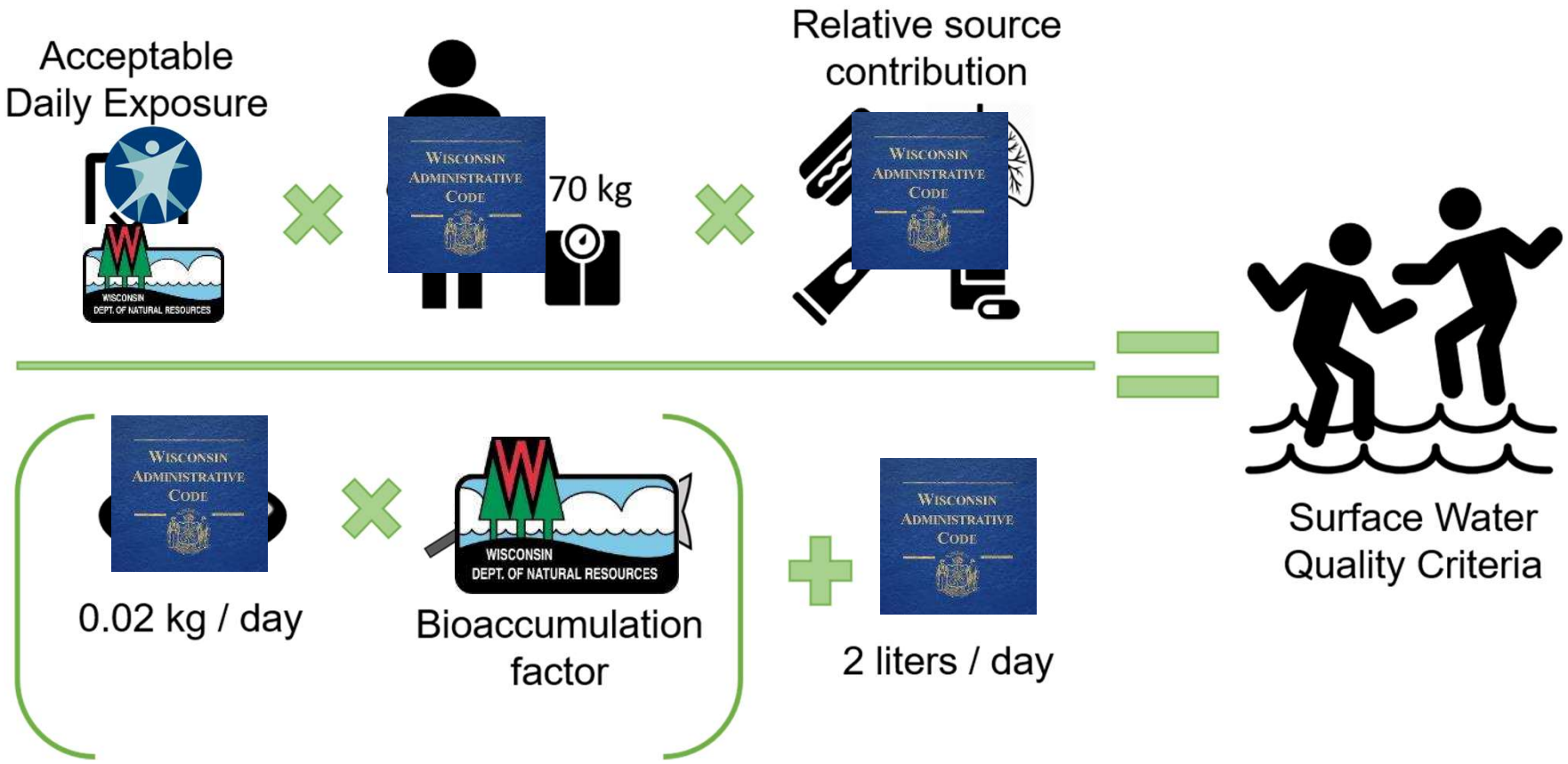

Acceptable Daily Exposure

- Maximum amount of a substance which, if ingested daily for a lifetime, results in no adverse human health effects

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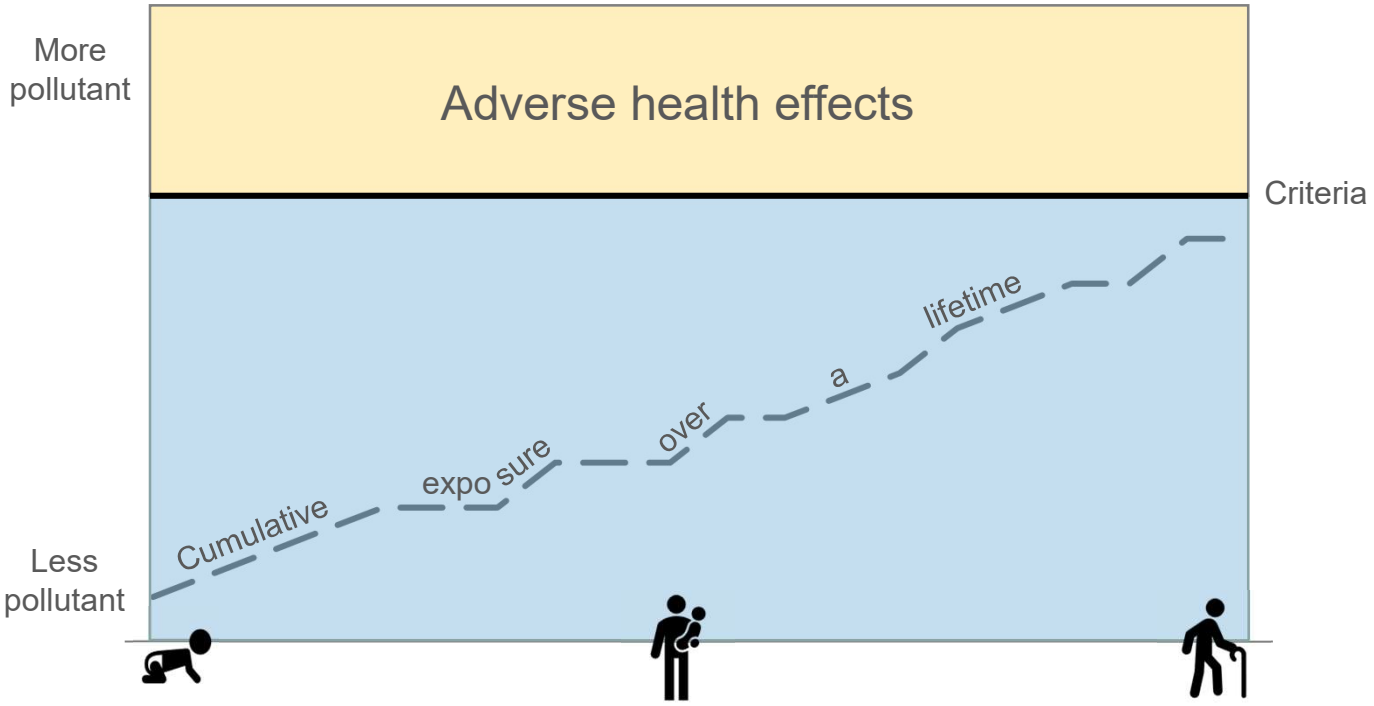
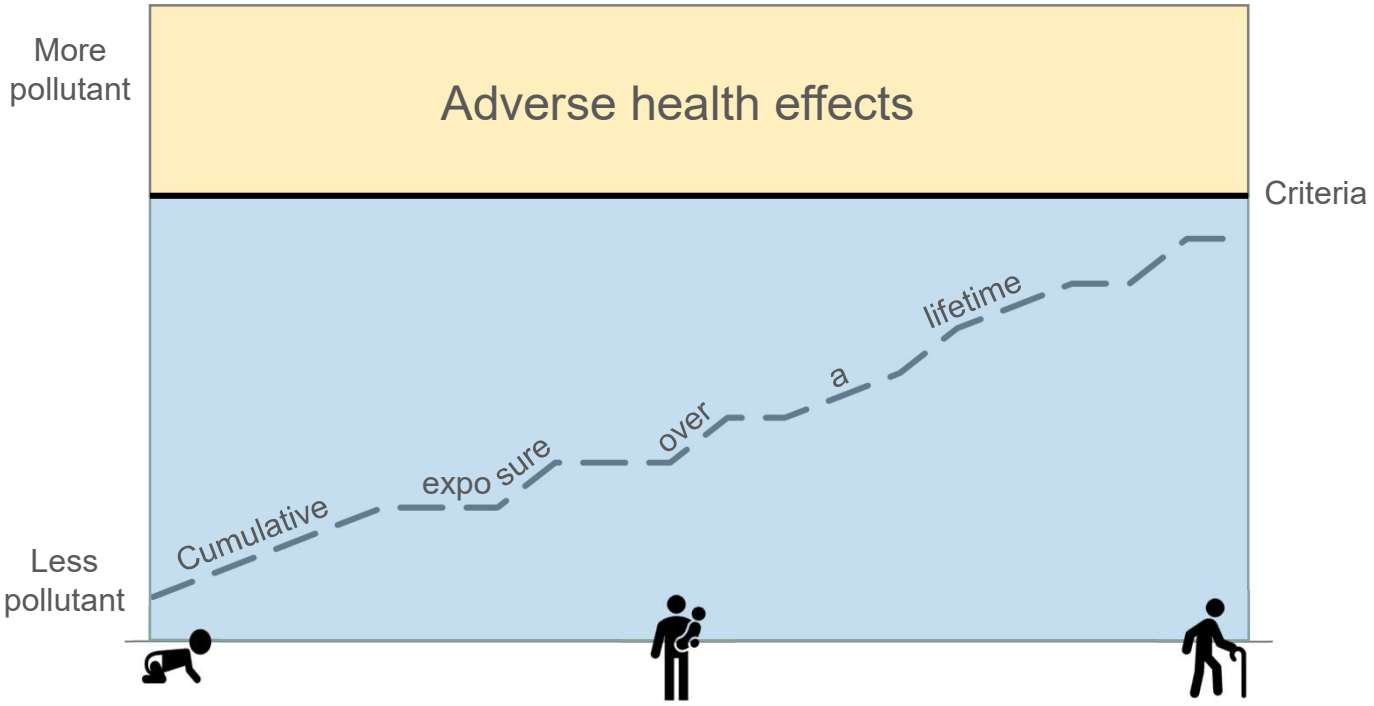


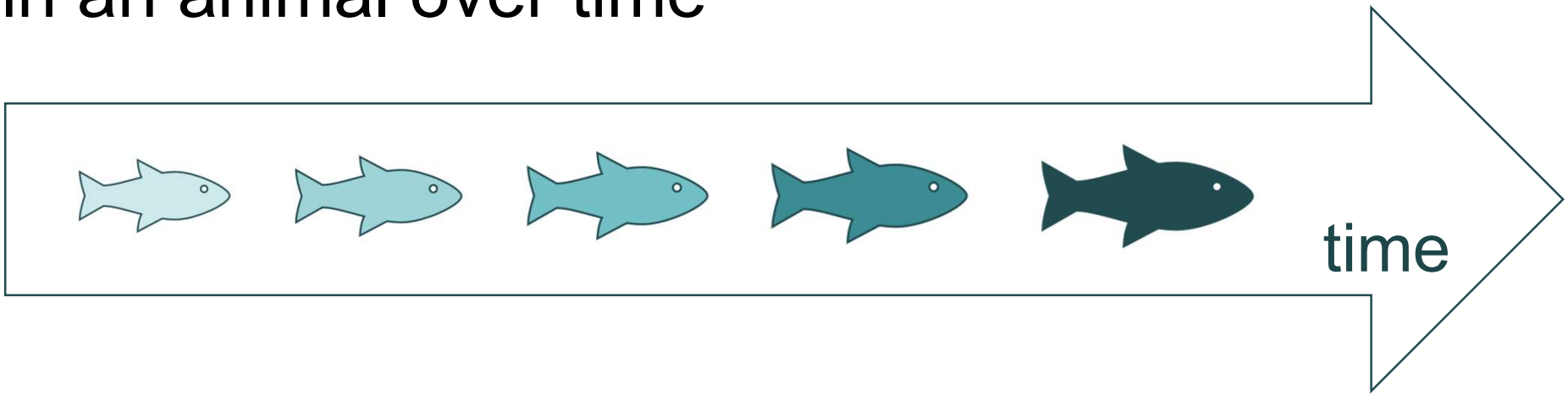
Acceptable Daily Exposure

- **DHS and DNR recommend an ADE of 2 ng/kg-day for both PFOS and PFOA**

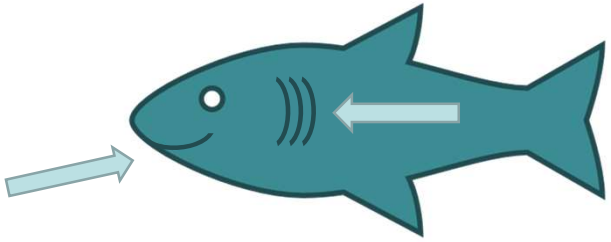


What is bioaccumulation?

Increase in the concentration of a contaminant in an animal over time



Incorporates uptake from diet and through gills



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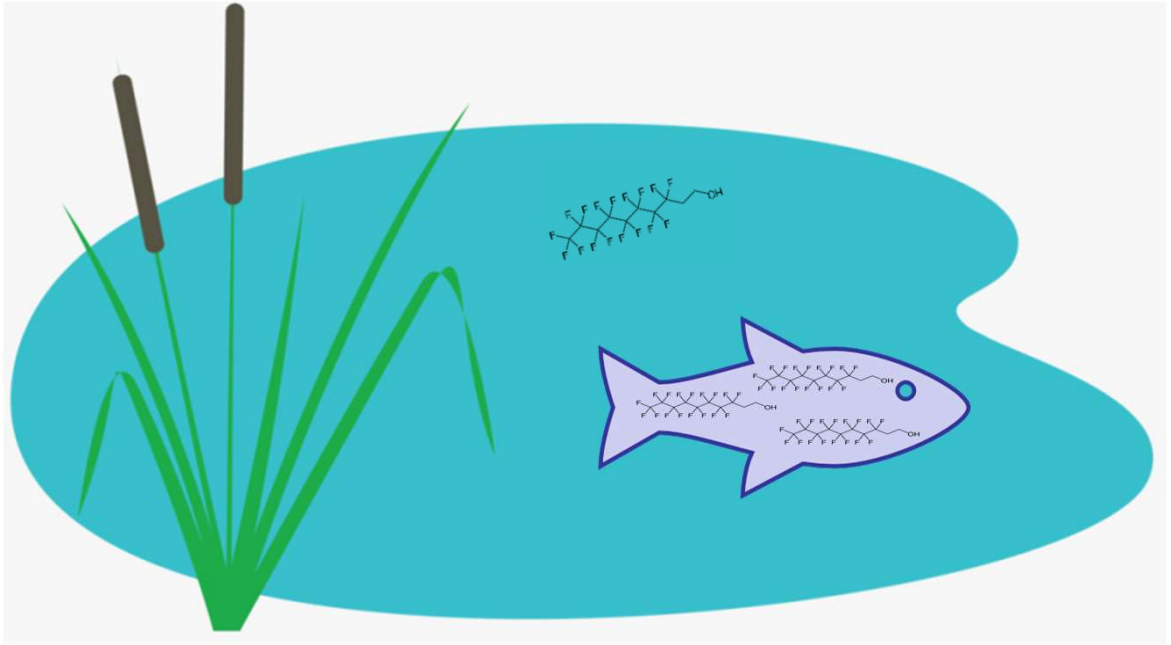
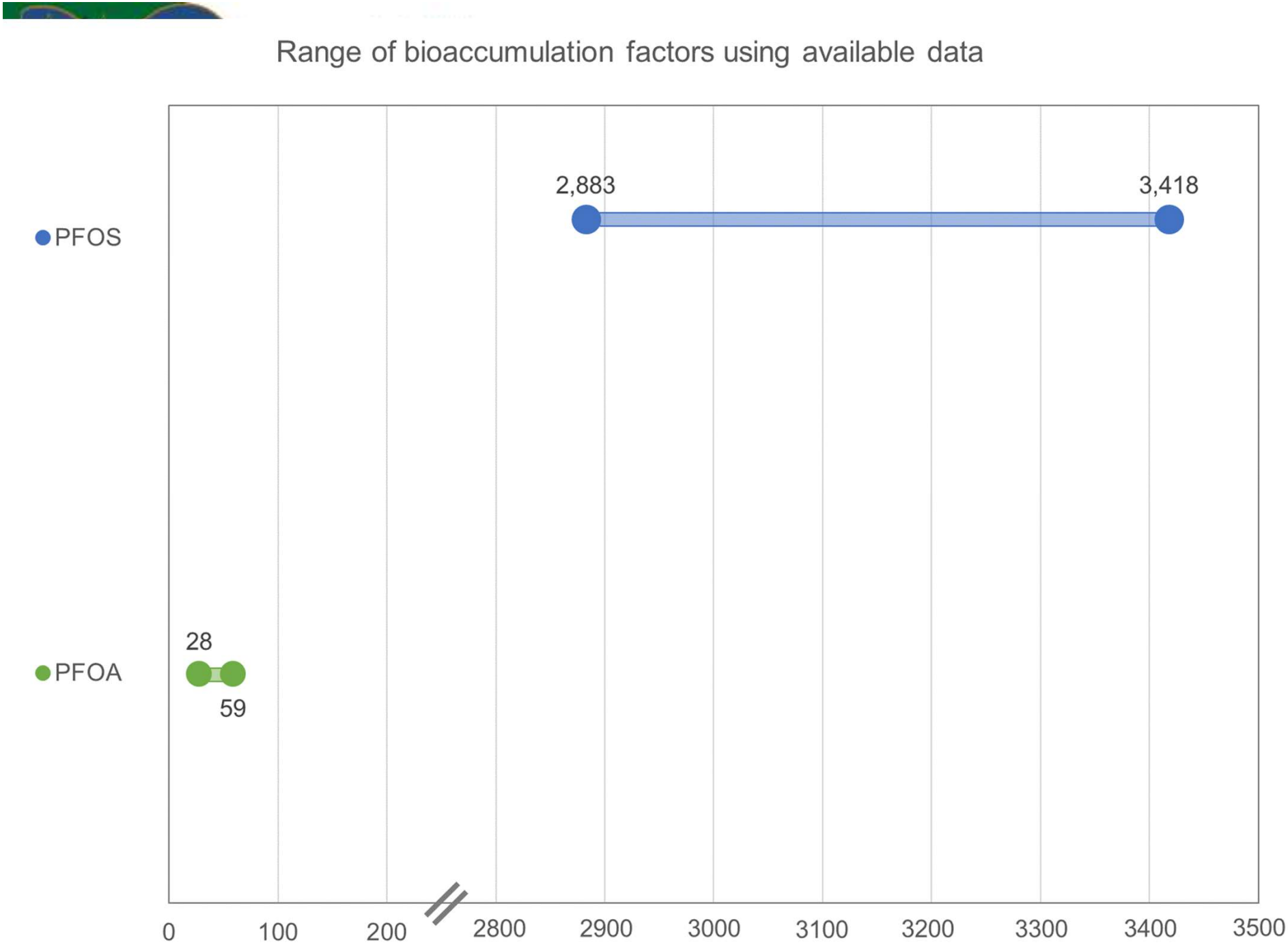
Bioaccumulation Factor

- The ratio of the concentration of a substance in fish tissue to its concentration in the ambient water



https://www.clipartwiki.com/clipimg/detail/25-253290_pond-clipart-pond-water-clipart.png


Range of bioaccumulation factors using available data
PFOS
PFOA
2,883
3,418
28
59
0
100
200
2800
2900
3000
3100
3200
3300
3400
3500

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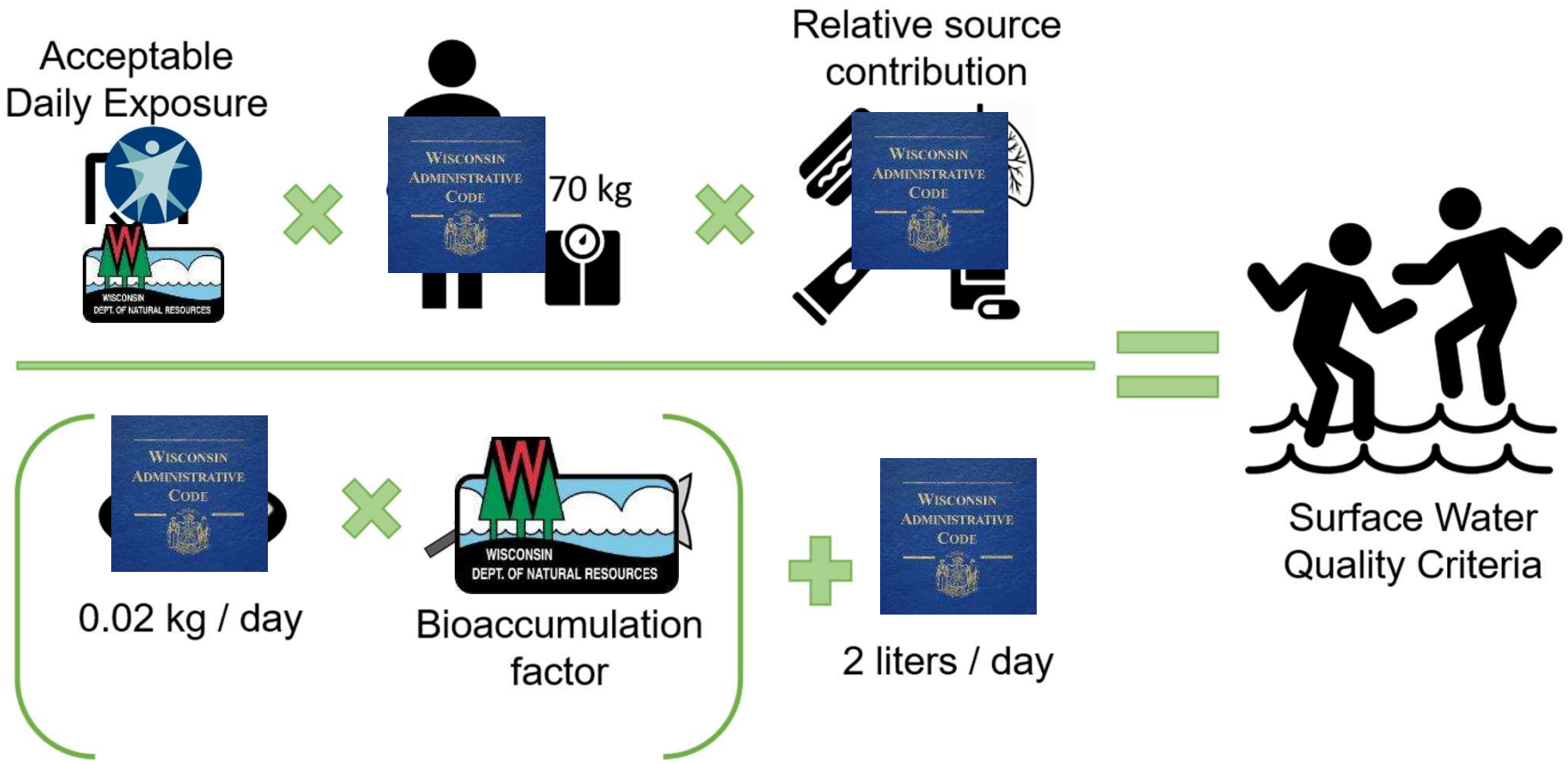


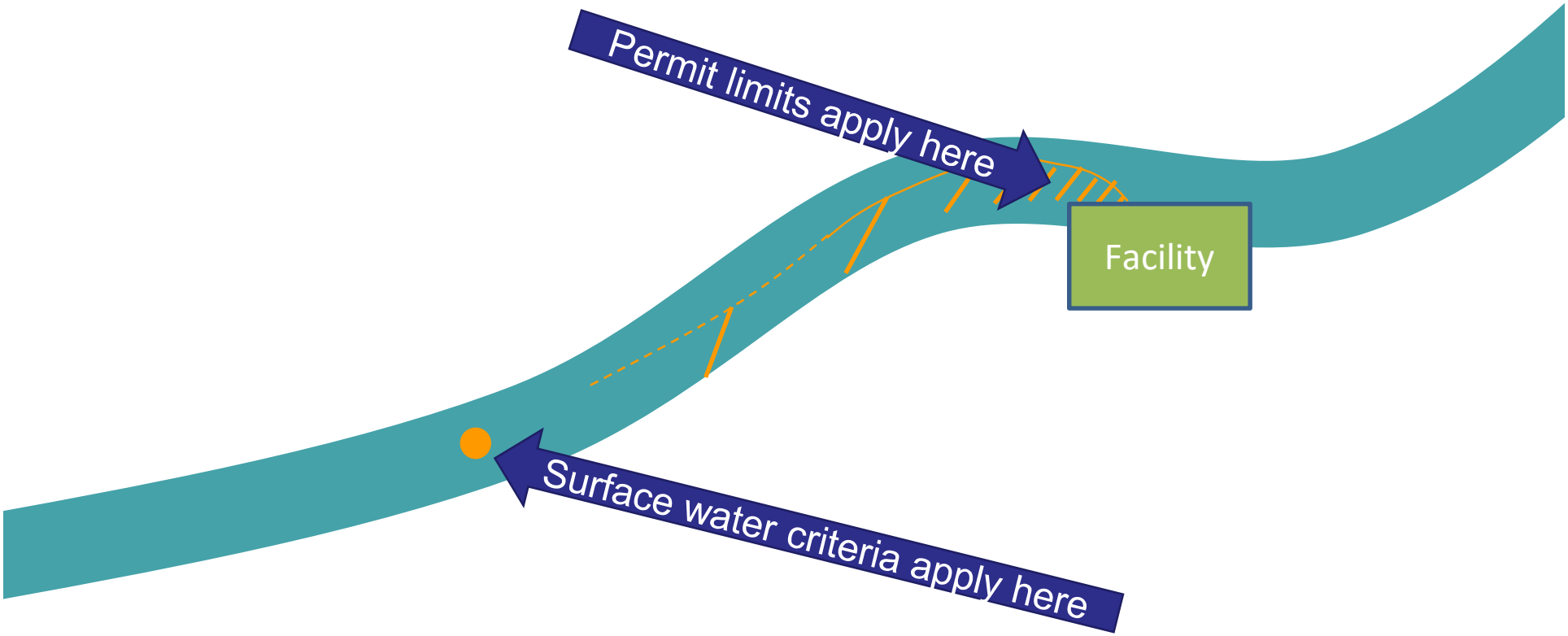
Likely range of surface WQC to protect Human Health

PFOS: ≤ 2 ng/L

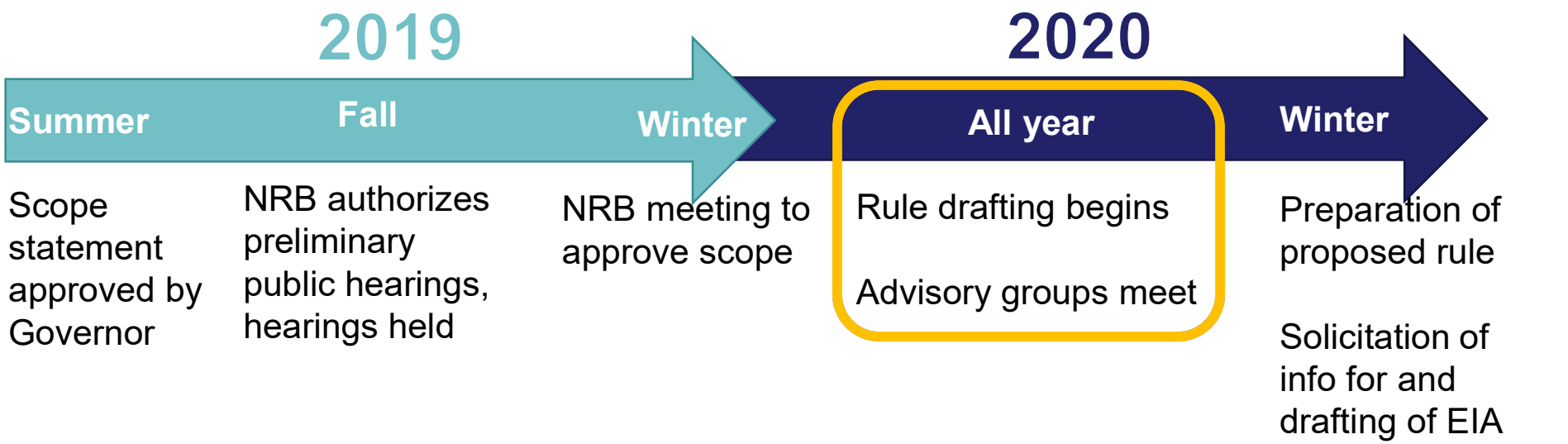
PFOA: 35 – 45 ng/L

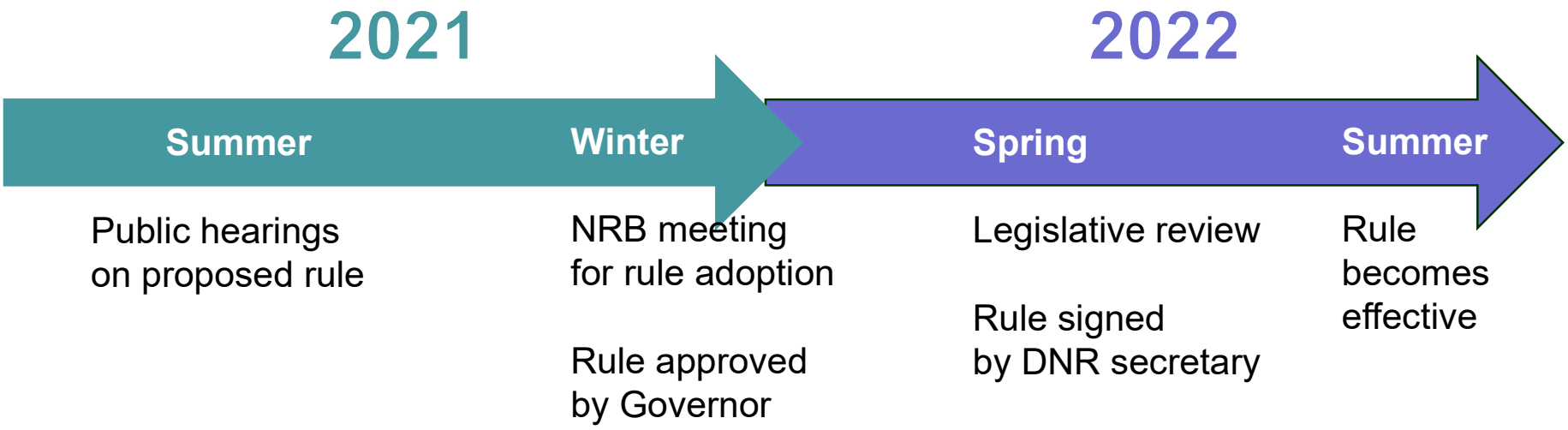
Photo credits: Flickr users ktgeek, lesterpubliclibrary; https://www.kitchenfrau.com/wp-content/uploads/2015/03/IMG_1394a-fish-sticks-682x1024.jpg

Relationship between surface water criteria and wastewater permits



Rulemaking timeline





Today's presentation

Introduction: what are PFAS, where did they come from, why should I care?

Monitoring for PFAS: protocols and 2019 results

Surface water quality standards for PFOS and PFOA

Discussion/questions

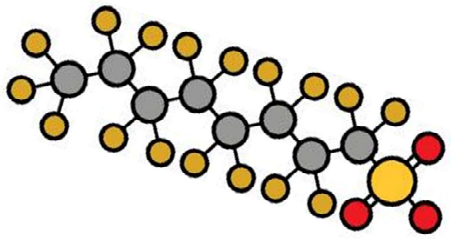


Image credit: http://www.biocycle.net/wp-content/uploads/2018/07/20b.jpg

Thank you!

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WISCONSIN
DEPT. OF NATURAL RESOURCES

Current advice

Lake Monona		
Species	Up to 1 meal/week	Up to 1 meal/month
 Bluegill	All sizes	
 Common carp		All sizes
 Largemouth bass		All sizes
 Northern pike		All sizes
 Walleye		All sizes
 Yellow perch		All sizes

Previous advice

Species	Sensitive populations	General population
Bluegill	1 meal/week	unrestricted
Common carp	1 meal/month	
Largemouth bass	1 meal/month	1 meal/week
Northern pike	1 meal/month	1 meal/week
Walleye	1 meal/month	1 meal/week
Yellow perch	1 meal/week	unrestricted