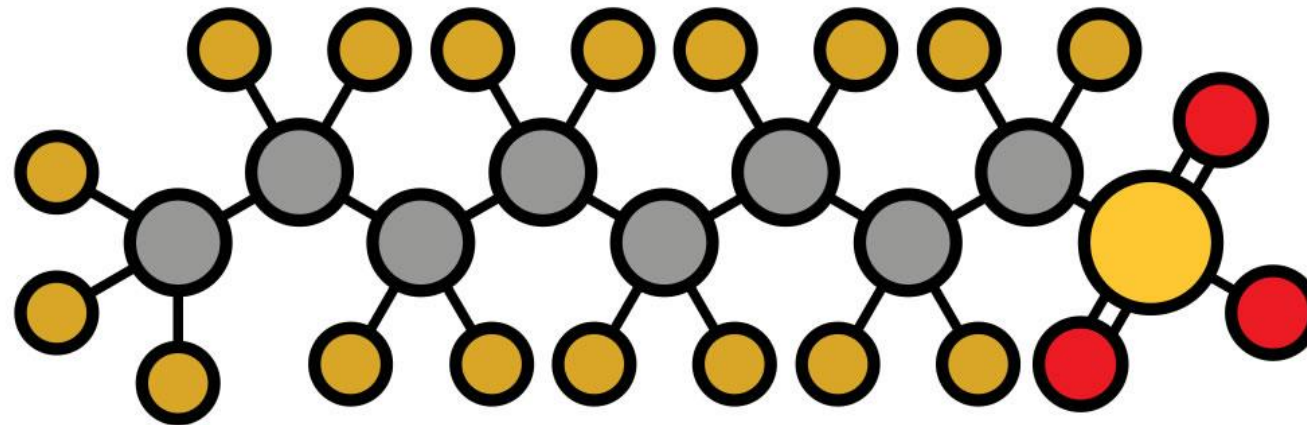


# Introduction to per- and polyfluoroalkyl substances (PFAS)

Meghan Williams  
Environmental Toxicologist  
Water Quality Bureau

# Today's presentation

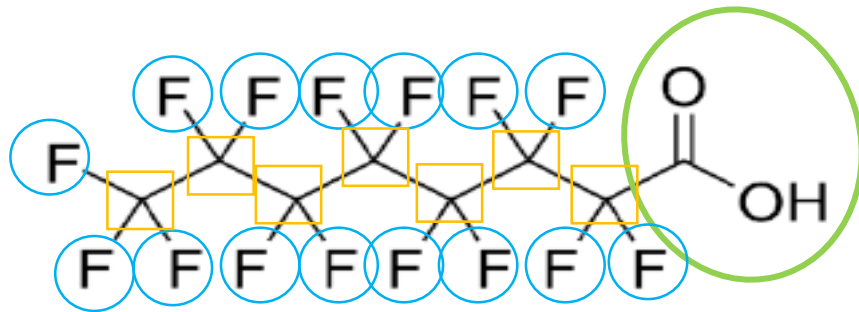
- What are PFAS and where did they come from?
- Why are PFAS a problem?



# What are PFAS?

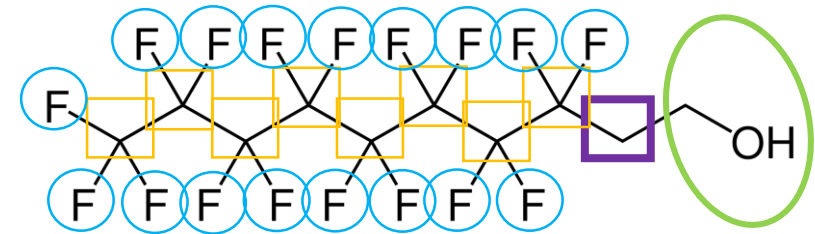
- General structure: **fluorinated carbon** chain (tail) attached to **functional group** (head)

**Perfluorinated** compounds:  
fully-fluorinated tail



PFOA (perfluorooctanoic acid)

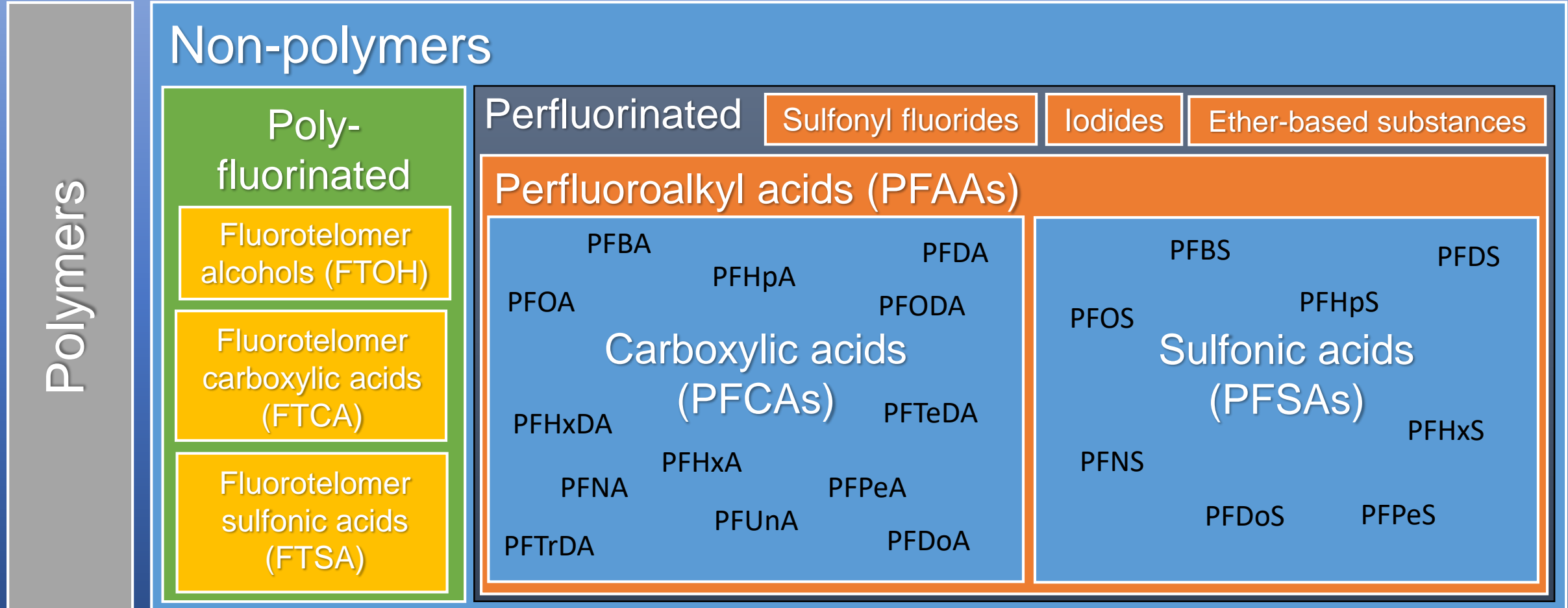
**Poly**fluorinated compounds: at least one carbon is **not attached** to a fluorine



8:2 FTOH (fluorotelomer alcohol)

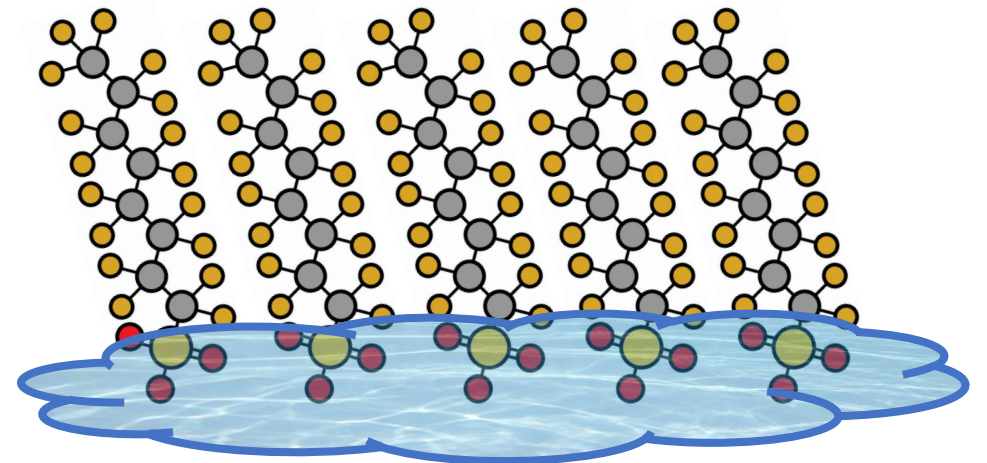
# PFOS and PFOA are only 2 of 4,000+ PFAS compounds

## PFAS









# Structure of PFAS imparts valuable properties

- Tail is hydrophobic and lipophobic, head is polar and hydrophilic
- Readily form films at air-water interface
- Unique structure means they have excellent water- and oil-repelling properties



# What are PFAS used for?

PFAS <sup>1</sup>	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 <sup>2</sup> )
PFOA		Initial Production	Protective Coatings 					
PFNA					Initial Production	Architectural Resins		
Fluoro-telomers					Initial Production	Firefighting Foams	Predominant form of firefighting foam	
Dominant Process <sup>3</sup>		Electrochemical Fluorination (ECF)						Fluoro-telomerization (shorter chain ECF)
Pre-Invention of Chemistry /			Initial Chemical Synthesis / Production			Commercial Products Introduced and Used		

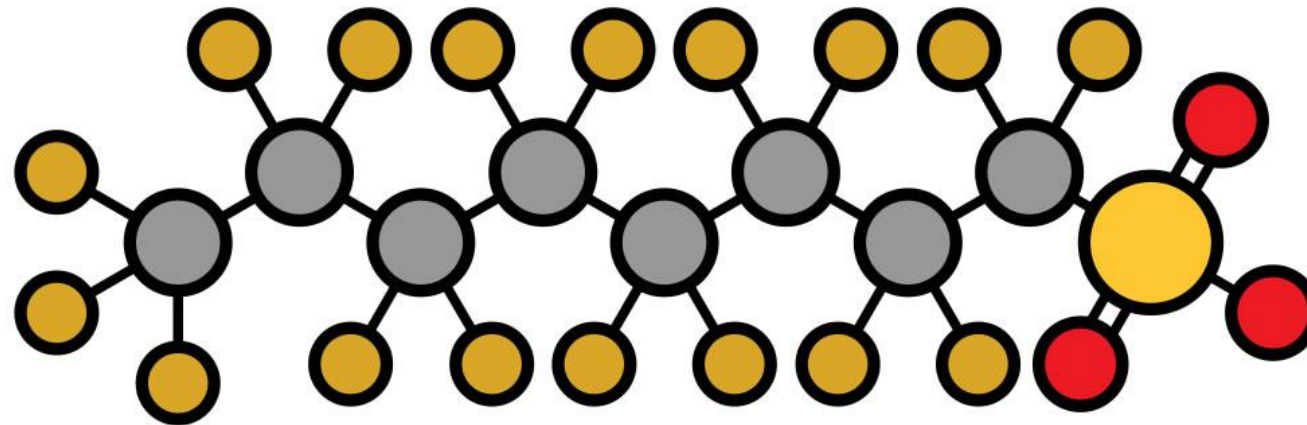
[https://pfas-1.itrcweb.org/wp-content/uploads/2017/11/pfas\\_fact\\_sheet\\_history\\_and\\_use\\_11\\_13\\_17.pdf](https://pfas-1.itrcweb.org/wp-content/uploads/2017/11/pfas_fact_sheet_history_and_use_11_13_17.pdf)  
[https://commons.wikimedia.org/wiki/File:US\\_Navy\\_021022-N-5362A-011\\_Fire\\_fighting\\_training\\_during\\_Diligent\\_Warrior\\_2003.jpg](https://commons.wikimedia.org/wiki/File:US_Navy_021022-N-5362A-011_Fire_fighting_training_during_Diligent_Warrior_2003.jpg)  
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<https://www.fontesia.com/wp-content/uploads/2018/01/70-0714-9234-5-600x600.png>  
[https://crdms.images.consumerreports.org/c\\_fill,w\\_240,h\\_175/prod/products/cr/models/399723-frying-pans-nonstick-amazonbasics-nonstick-10008298](https://crdms.images.consumerreports.org/c_fill,w_240,h_175/prod/products/cr/models/399723-frying-pans-nonstick-amazonbasics-nonstick-10008298)



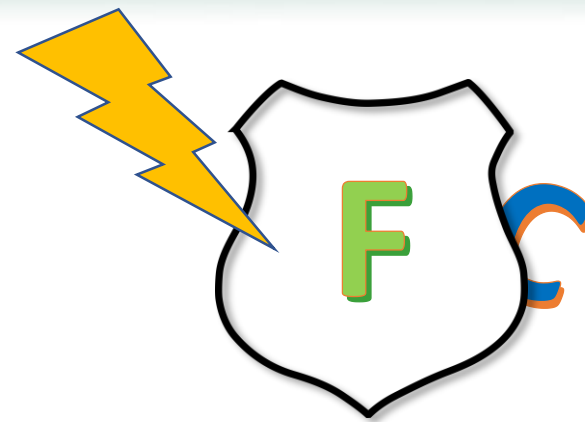
# Today's presentation

- What are PFAS and where did they come from?
- **Why are PFAS a problem?**



# Why are PFAS a problem?

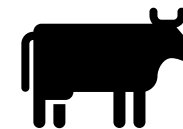
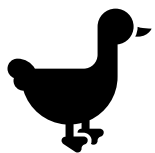
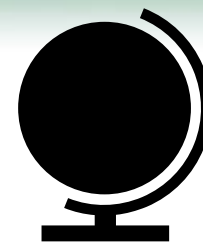
- Carbon-fluorine bond is incredibly strong
  - Fluorine atoms “shield” carbon from chemical reactions
- PFAS do not undergo biotic or abiotic degradation
- Thermally degrade only at high temperatures
- Very persistent
- Some PFAS are highly bioaccumulative





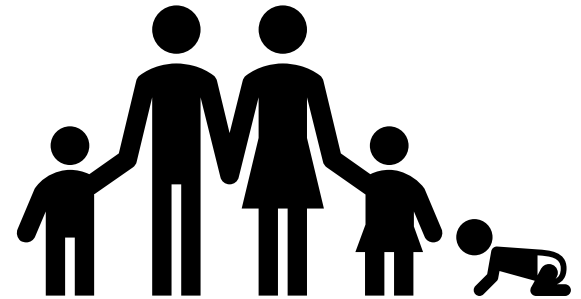
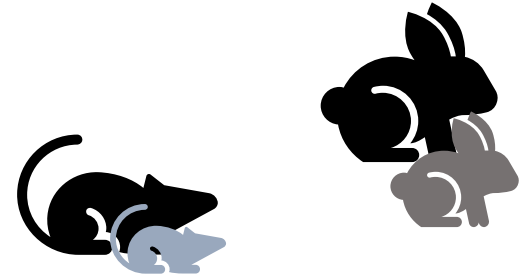
# Why are PFAS a problem?

- 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?

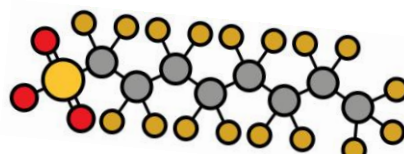
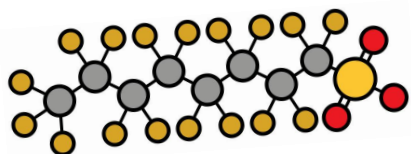
- PFAS have documented toxicity
  - Animal studies have shown negative effects on:
    - Liver
    - Immune system
    - Reproduction and development
    - Thyroid (endocrine system)
    - Cancers
  - Probable links to human health effects:
    - Childhood growth and development
    - Pregnancy-related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



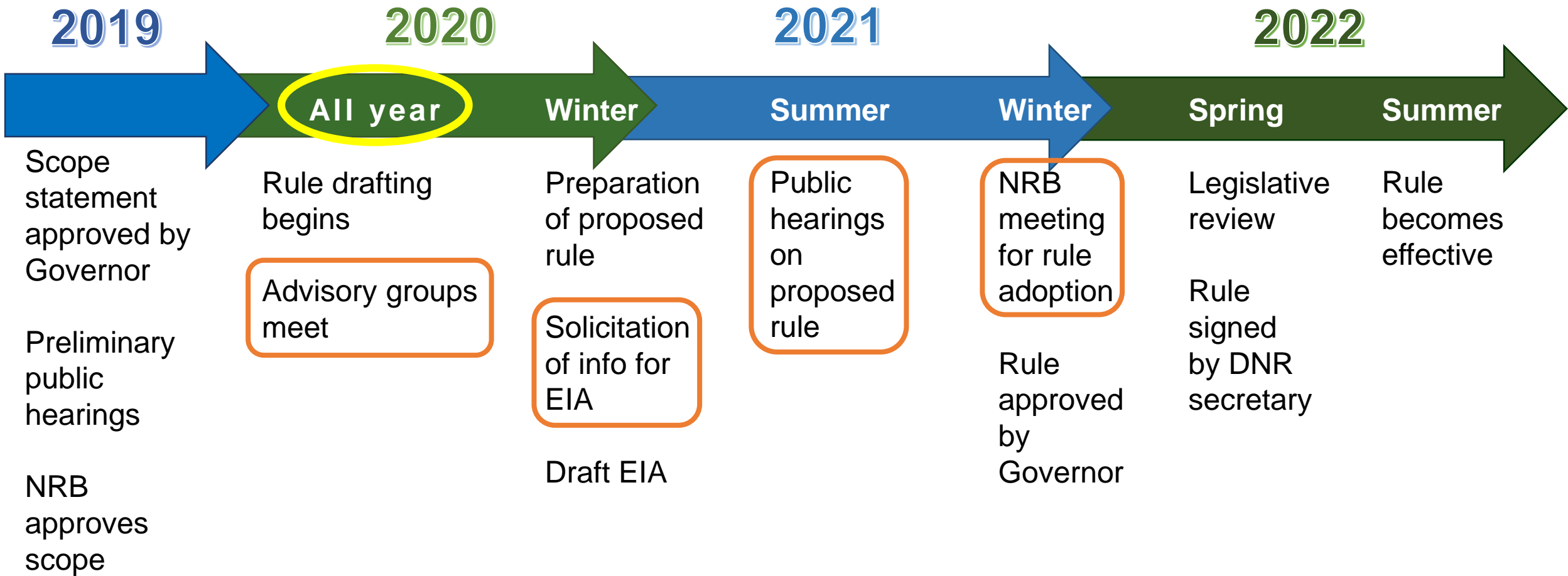


# Summary

- 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



# Rulemaking process and timeline







# Wisconsin Statute 280

280.11(1) The department shall, after a public hearing, prescribe, publish and enforce minimum reasonable standards and rules and regulations for methods to be pursued in the obtaining of pure drinking water for human consumption and the establishing of all safeguards deemed necessary in protecting the public health against the hazards of polluted sources of impure water supplies intended or used for human consumption, including minimum reasonable standards for the construction of well pits. It shall have general supervision and control of all methods of obtaining groundwater for human consumption including sanitary conditions surrounding the same, the construction or reconstruction of wells and generally to prescribe, amend, modify or repeal any rule or regulation theretofore prescribed and shall do and perform any act deemed necessary for the safeguarding of public health.



# Maximum Contaminant Level (MCL)



The maximum permissible level of a contaminant in water which is delivered to any user of a public water system.



# Synthetic Organics MCLs

**NR 809.20 Synthetic organic contaminant maximum contaminant levels and BATS. (1) APPLICABILITY.** The following maximum contaminant levels for synthetic organic contaminants apply to community water systems and non-transient non-community water systems.

<b>Contaminant</b>	<b>MCL (mg/L)</b>
Alachlor	0.002
Atrazine	0.003
Benzo[a]pyrene	0.0002
Carbofuran	0.04
Chlordane	0.002
2,4-D	0.07
Dalapon	0.2
Dibromochloropropane	0.0002
Di(2-ethylhexyl)adipate	0.4
Di(2-ethylhexyl)phthalate	0.006
Dinoseb	0.007
Diquat	0.02

<b>Contaminant</b>	<b>MCL (mg/L)</b>
Endothall	0.1
Endrin	0.002
Ethylene Dibromide	0.00005
Glyphosate	0.7
Heptachlor	0.0004
Heptachlor epoxide	0.0002
Hexachlorobenzene	0.001
Hexachlorocyclopentadiene	0.05
Lindane	0.0002
Methoxychlor	0.04
Oxamyl	0.2
Pentachlorophenol	0.001
Picloram	0.5
Polychlorinated biphenyls (PCBs)	0.0005
Simazine	0.004
2,3,7,8-TCDD (Dioxin)	$3 \times 10^{-8}$
Toxaphene	0.003
2,4,5-TP	0.05



# Analytical Methods

(2) ANALYTICAL METHODS. Analysis for the synthetic organic contaminants listed in s. [NR 809.20](#) shall be conducted using the methods prescribed in Table CM.

**Table CM**  
**SDWA Approved Methodology for Synthetic Organic Contaminants**

<b>Contaminant</b>	<b>EPA Methods<sup>1</sup></b>	<b>SM<sup>9</sup></b>	<b>SM Online<sup>10</sup></b>	<b>ASTM</b>	<b>Other</b>
<b>Regulated Parameters:</b>					
<b>Synthetic Organic Chemicals</b>					



# Reporting and Recording Keeping

## Subchapter V

- Reporting results to DNR
- Maintain record of results
- Consumer confidence reports



# Public Notification

## Subchapter VII

- Public notices
  - An MCL violation
  - Failure to monitor



# Who will be affected?

- Municipal water systems (cities, townships, sanitary districts)
- Mobile home parks, apartment buildings, condominium associations
- Small businesses that are public water systems
- Laboratories certified to perform PFAS analysis in drinking water
- Wisconsin Department of Natural Resources
- Wisconsin Department of Health Services
- Wisconsin Department of Safety and Professional Services
- Treatment installation businesses
- Public
  - Benefits to public health from reduction in PFAS exposure via drinking water





# Surface Water Quality PFAS Rules

## Revisions to NR 105, NR 106, and NR 219

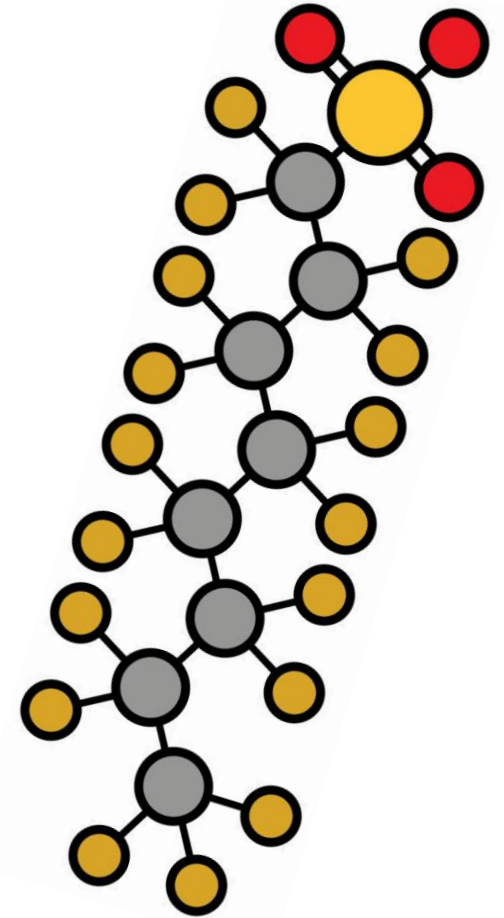
Marcia Willhite

Water Evaluation Section Chief

Water Quality Bureau

# Today's presentation

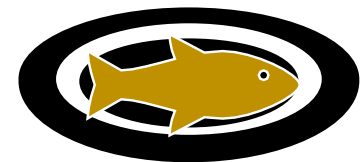
- Chapter revisions
- Authority for water quality standards
- What does NR 105 say about standard development?
- How will these new standards be used?





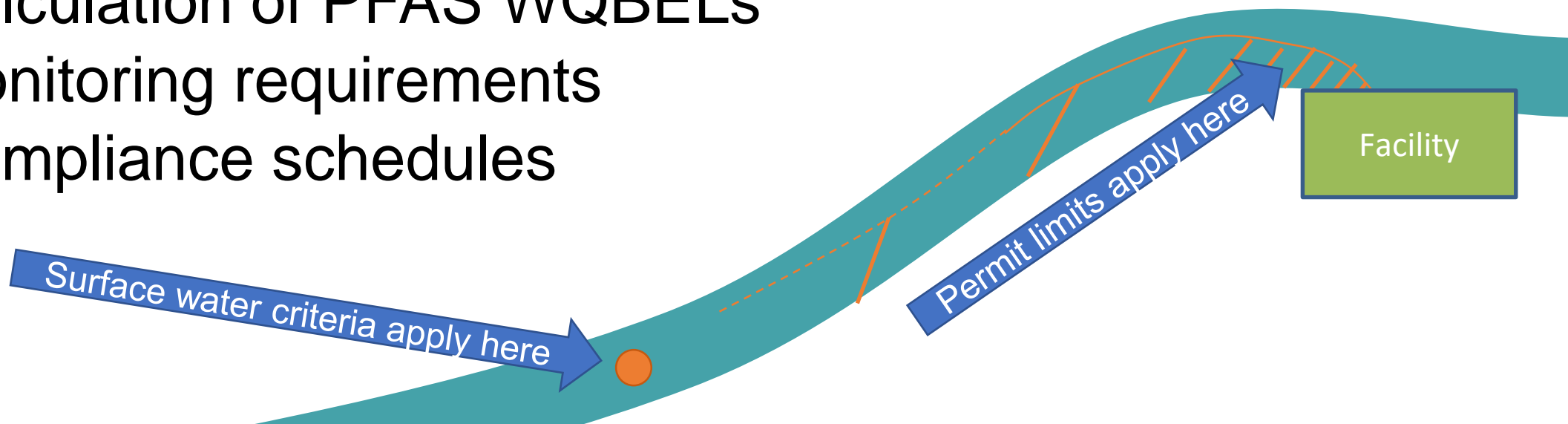
# Chapter NR 105: Surface Water Quality Criteria and Secondary Values for Toxic Substances

- Create surface water quality criteria for PFOS and PFOA
- Protect humans from adverse effects of PFOS and PFOA resulting from:
  - Contact with surface water
  - **Ingestion of fish from surface waters**



# Chapter 106: Procedures for Calculating WQBELs for Point Source Discharges to Surface Waters

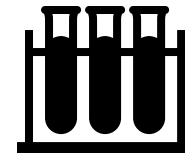
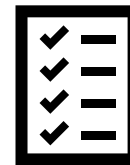
- Develop procedures to implement new criteria in WPDES permits
  - Calculation of PFAS WQBELs
  - Monitoring requirements
  - Compliance schedules





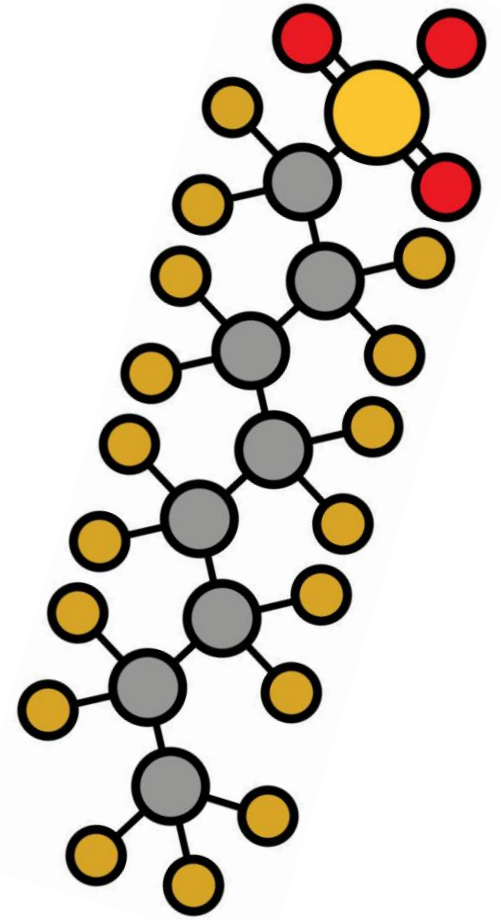
# Chapter NR 219: Analytical Test Methods and Procedures

- Additions to the list of approved test methods for detecting PFAS in:
  - Surface waters
  - Wastewater effluent
  - Biosolids



# Today's presentation

- Chapter revisions
- **Authority for water quality standards**
- What does NR 105 say about standard development?
- How will these new standards be used?





# Authority for WQS Development

- Federal Clean Water Act:

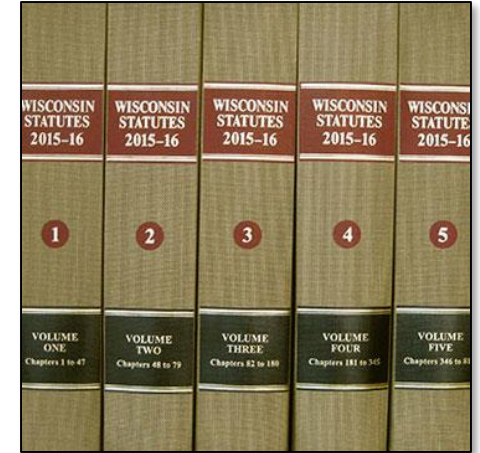
*“The objective of this Act is to restore and maintain the chemical, physical, and biological integrity of the nation’s waters.”*

- State must identify designated uses
- State must establish criteria to protect designated uses



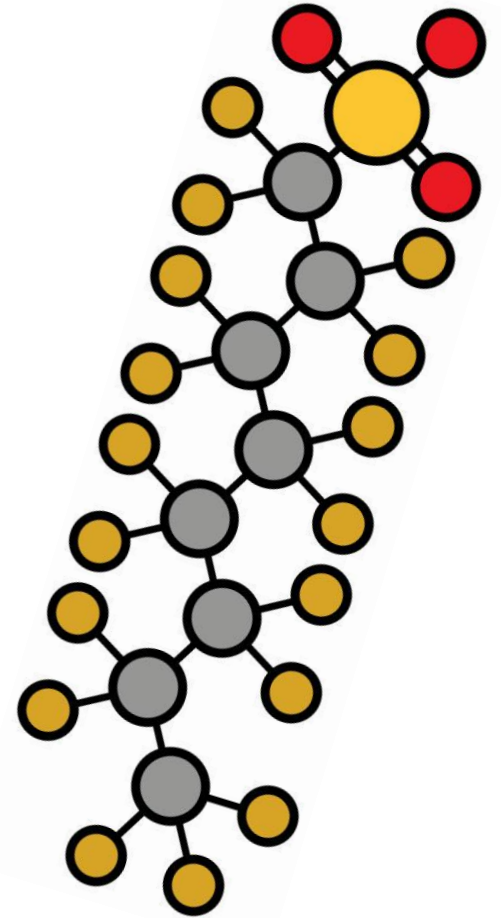
# Authority for WQS Development

- Wisconsin §281.15: water quality standards
  - The Department shall develop water quality standards to protect public health and welfare.
  - The Department must consider information on likely social, economic, energy usage, and environmental costs associated with attaining criteria.
  - The Department shall establish criteria which are no more stringent than reasonably necessary to assure attainment of the designated use for the waterbodies in question.



# Today's presentation

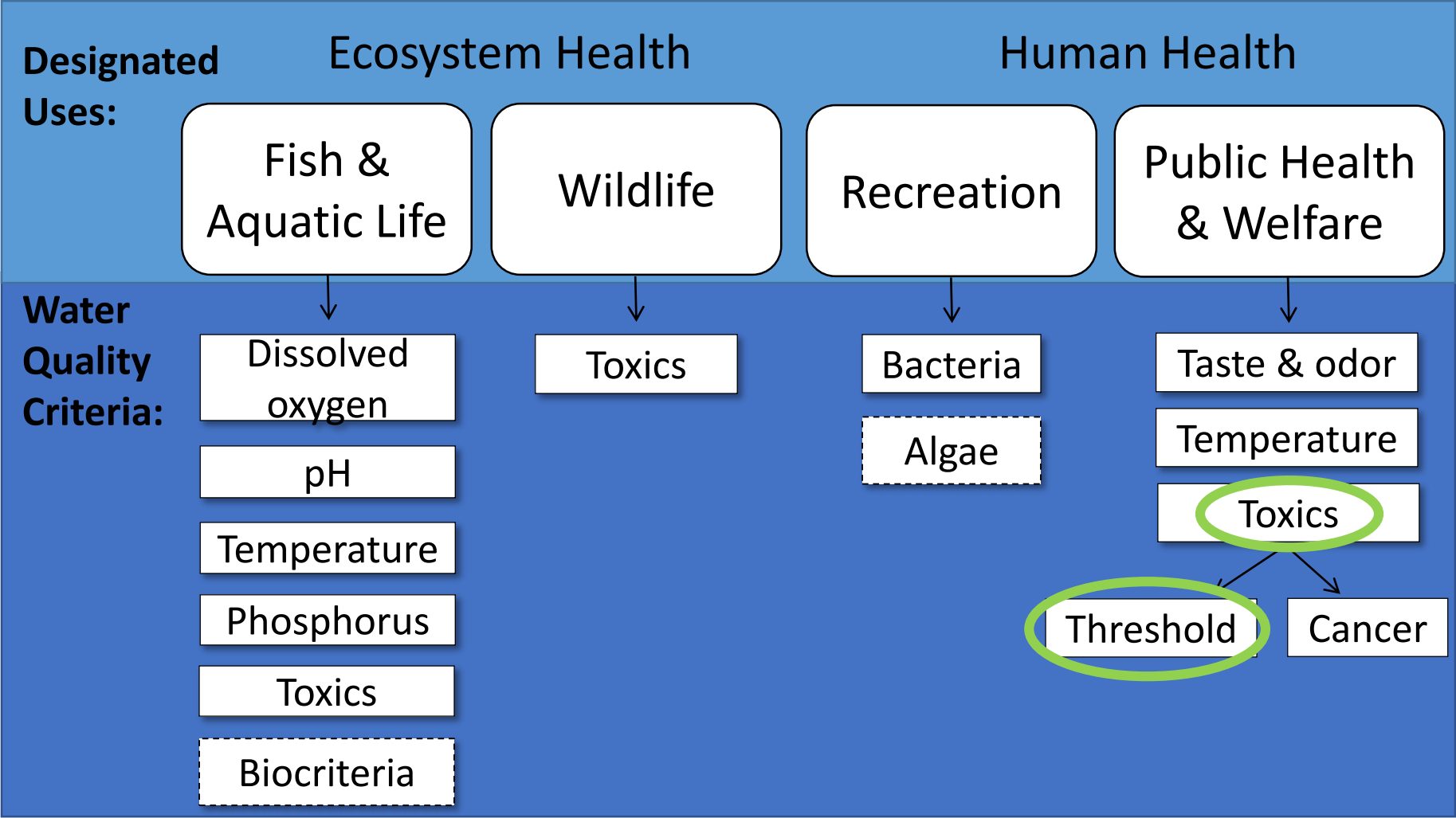
- Chapter revisions
- Authority for water quality standards
- **What does NR 105 say about standards development?**
- How will these new standards be used?





# NR 105: Surface Water Quality Criteria for Toxic Substances

- Contains current criteria for public health and aquatic life protection
- Contains methods for developing human health, aquatic life, and wildlife criteria
- Establishes how bioaccumulation factors shall be determined



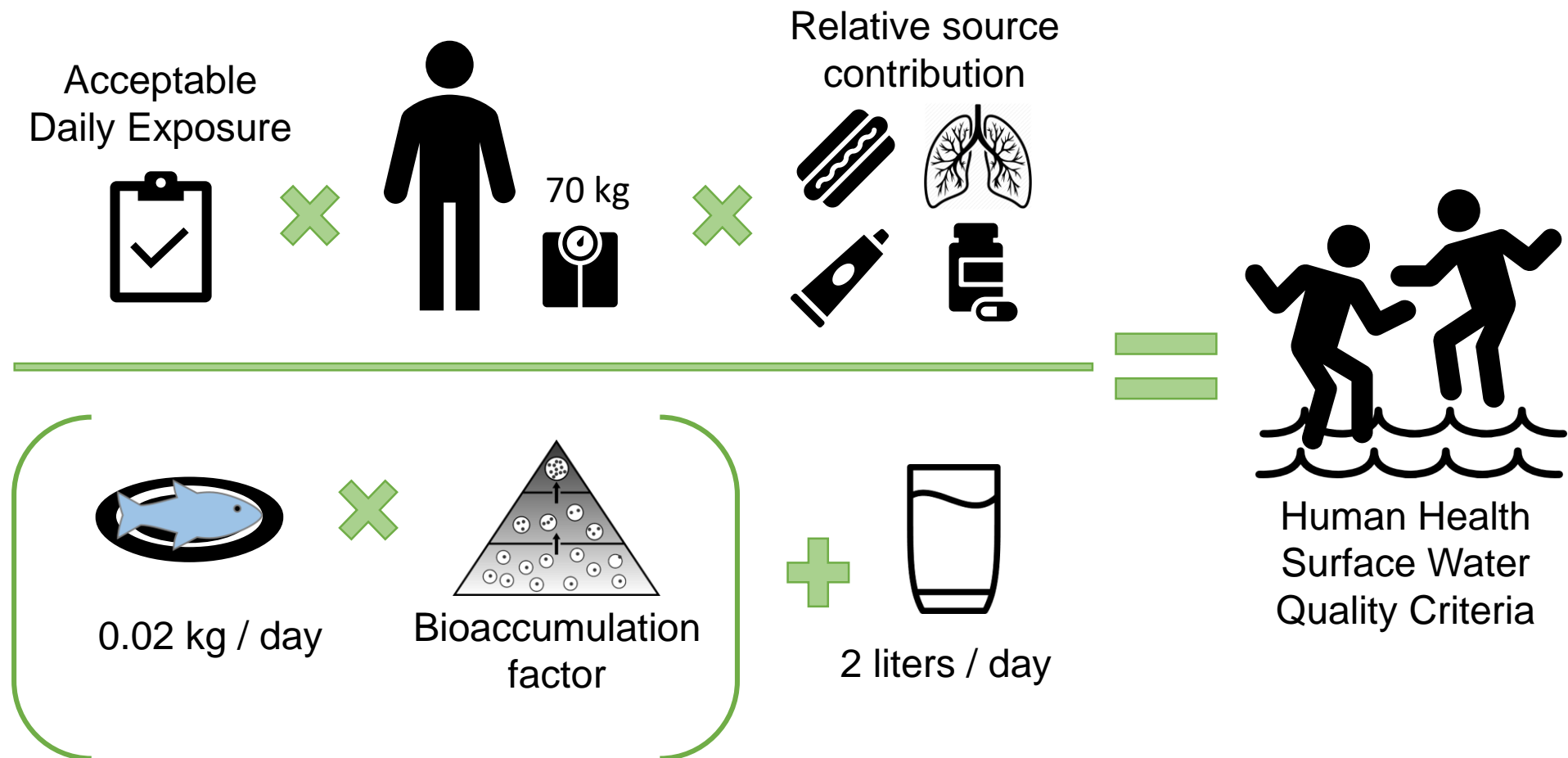


# NR 105.08: Human Threshold criteria

- Maximum concentration of a substance that will protect humans from adverse effects of:
  - Contact with or ingestion of surface water
  - Ingestion of aquatic organisms taken from those waters
- Science indicates a threshold below which no adverse effect is likely

# NR 105.08: Human Threshold criteria

How are criteria calculated?







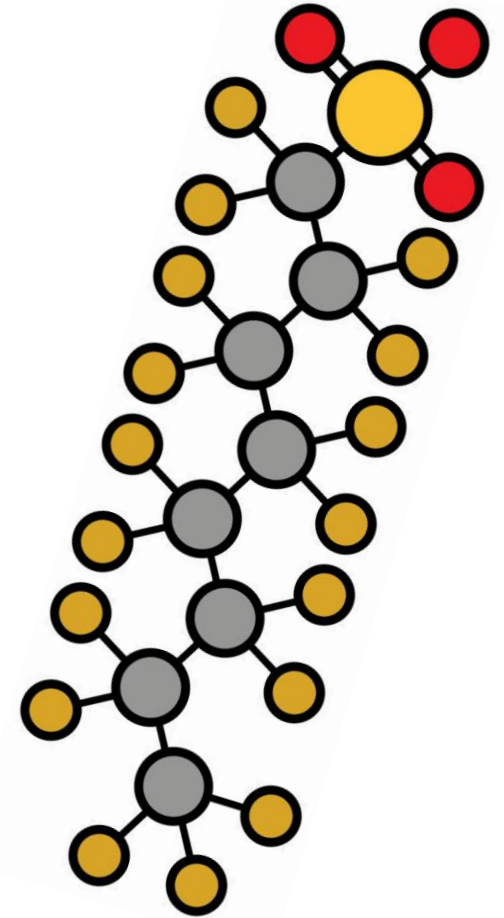
# NR 105.08: Human Threshold criteria

## Acceptable daily exposure

- Very prescriptive about how to determine ADE
  - What weight to give toxicity studies
  - How to translate animal studies to human exposure
  - How to apply uncertainty factors
- Specifies that the Department shall select an ADE based on sound scientific judgment

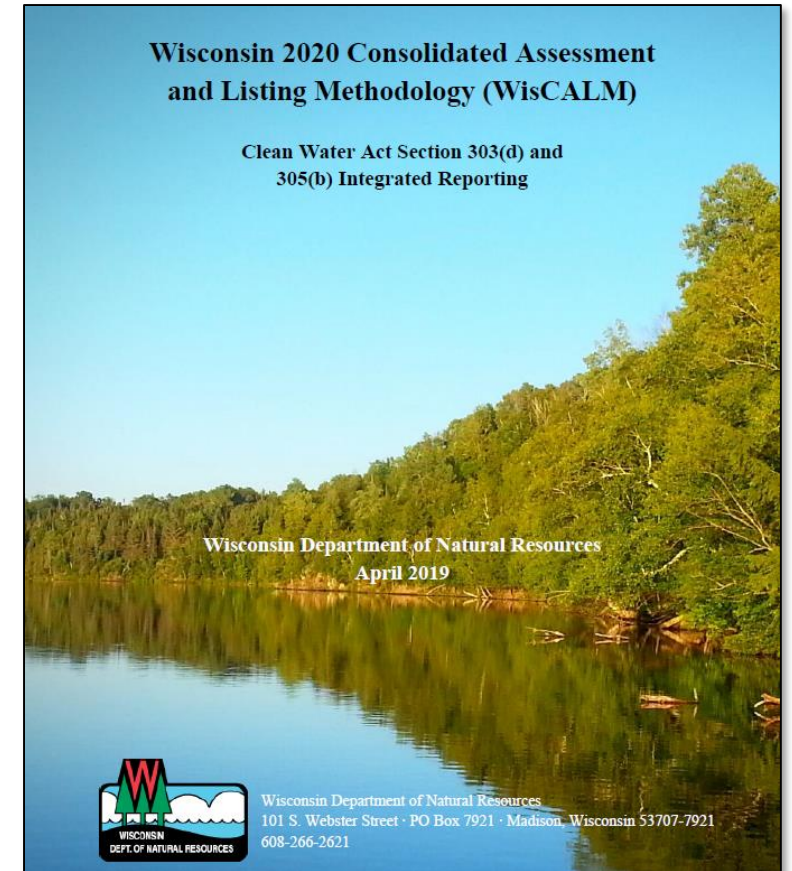
# Today's presentation

- Chapter revisions
- Authority for water quality standards
- What do these rules say about standard development?
- **How will these new standards be used?**



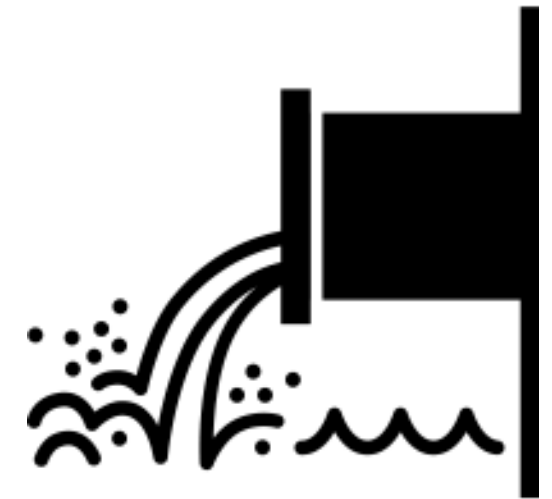
# Assessing attainment of designated use

- Designated Use: Public Health and Welfare
- Impairment: exceedance of WQS in rivers, lakes, or streams
  - Waterbodies with exceedances appear on Wisconsin's list of impaired waters as required by the Clean Water Act



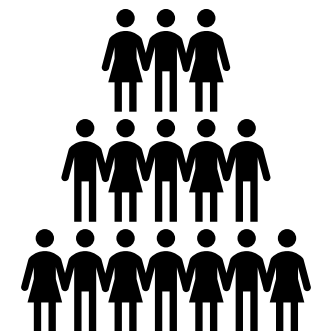
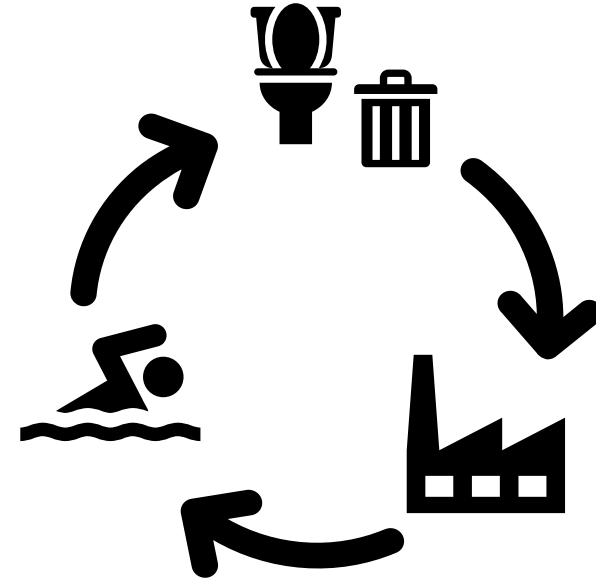
# Calculating WQBELs for point source discharges to surface waters (NR 106)


- 106.05: Determination of the necessity for WQBELs for toxics
- 106.06: Calculation of WQBEL for toxics
  - Bioaccumulative chemicals of concern
  - Limits based on chronic toxicity
- 106.07: Application and compliance with WQBEL in permits



# Affected entities

- Business/industry and municipalities
  - Facilities that discharge PFAS to surface waters
  - May be required to conduct monitoring
  - May receive PFAS WQBELs
- Public
  - Benefits to public health from reduction in PFAS exposure via surface waters





# Groundwater Quality Rules

## Revisions to NR 140

Bruce Rheineck

Groundwater Section Chief

Drinking Water & Groundwater Bureau



# NR 140 presentation

- Authority for groundwater quality standards
- What guides groundwater standard development?
- Chapter revisions
- How will these standards be used?





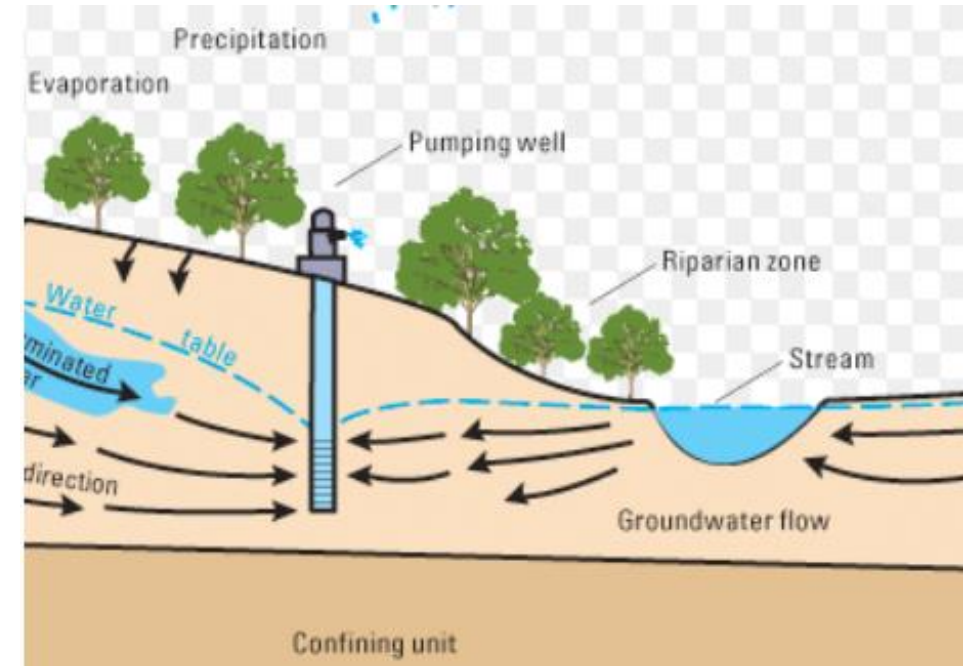


# Authority for Groundwater Quality Standards

- Wisconsin §160: Groundwater Protection Standards
  - Set numerical standards for use by all groundwater regulatory programs
  - Minimize concentration of polluting substances in groundwater
  - Protect public health, welfare and the environment

# NR 140 presentation

- Authority for groundwater quality standards
- **What guides groundwater standard development?**
- Chapter revisions
- How will these standards be used?





# Groundwater Quality Standard Development

- Wisconsin §160.05:
  - DNR compiles list of substances related to regulated activities detected in or which have a reasonable probability of entering groundwater
- Wisconsin §160.07:
  - DNR requests Department of Health Services (DHS) to review and recommend public health based standards
  - DNR sets or revises standards based on DHS recommendations



# Groundwater Quality Standard Development

- §160.07 – §160.13: DHS reviews literature & scientific information
  - Gather all available data, which can mean hundreds of scientific journal articles
  - Review specific concentrations set by the U.S. Environmental Protection Agency and other health-based guidelines
  - Follows process to select appropriate standard, scientific process is specified if a federal number or state drinking water standard is not available
  - Uses the most recent federal number unless there is significant technical and scientifically valid information that was not considered
  - Writes documents explaining findings and recommendations for each recommended standard and makes available to public

# NR 140 presentation

- Authority for groundwater quality standards
- What guides groundwater standard development?
- **Chapter revisions**
- How will these standards be used?



# “Cycle 10” Revisions

- Standards in NR 140.10 Table 1- Public health groundwater quality standards
  - Enforcement Standard (ES)
  - Preventive Action Limit (PAL)
  - Currently 138
- Standards in NR 140.12 Table 2- Public welfare groundwater quality standards
  - Set by DNR
  - Currently 8

NR 140.05 Published under s. 35.03, Wis. Stats., by the Legislative Reference Bureau. WISCONSIN ADMINISTRATIVE CODE

Subchapter II — Groundwater Quality Standards

NR 140.10 Public health related groundwater standards. The groundwater quality standards for substances of public health concern are listed in Table 1.

Notes: For all substances that have carcinogenic, mutagenic or teratogenic properties or substances that are otherwise listed in 105A of the natural resources code, the preventive action limit is 20% of the enforcement standard for all other substances that are of public health concern. Enforcement standards and preventive action limits for additional substances will be added to Table 1 as recommendations are developed pursuant to ss. 160.07, 160.13 and 160.15, Stats.

(22) "Wastewater and sludge storage or treatment lagoon" means a natural or man-made containment structure, constructed primarily of earthen materials for the treatment or storage of wastewater or sludge, which is not a land disposal system.

History: CS Register, September 1988, No. 315, eff. 10-1-85, or (1st) use of (17) and (18), Register, October 1988, No. 324, eff. 11-1-85, or (2nd) use of (17) and (18), March 1990, No. 429, eff. 4-1-94, or (19), (18), (19), (20) and (21), Register, August 1990, No. 475, eff. 9-1-95, or (22), Register, October 1990, No. 484, eff. 11-1-96, or (22), Register, December 1990, No. 516, eff. 1-1-99, or (22), Register, January 1991, No. 525, eff. 2-1-95, or (22), Register, February 1991, No. 534, eff. 3-1-95, or (22), Register, March 1991, No. 543, eff. 4-1-95, or (22), Register, April 1991, No. 552, eff. 5-1-95, or (22), Register, May 1991, No. 561, eff. 6-1-95, or (22), Register, June 1991, No. 570, eff. 7-1-95, or (22), Register, July 1991, No. 579, eff. 8-1-95, or (22), Register, August 1991, No. 588, eff. 9-1-95, or (22), Register, September 1991, No. 597, eff. 10-1-95, or (22), Register, October 1991, No. 606, eff. 11-1-95, or (22), Register, November 1991, No. 615, eff. 12-1-95, or 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# “Cycle 10” Revisions

- “Cycle 10” list: 27 proposed public health standards in NR 140 Table 1
- 16 new standards:
  - 11 pesticides, 2 metals, 1 bacteria, 2 PFAS (PFOA & PFOS)
- 11 existing standards reviewed for possible revision:
  - 5 metals, 5 solvents, 1 bacteria

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DEPARTMENT OF NATURAL RESOURCES

NR 140.03

Chapter NR 140  
GROUNDWATER QUALITY

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NR 140.02 Regulatory framework.  
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NR 140.04 Definitions.

Subchapter II — Groundwater Quality Standards  
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NR 140.26 Responses when an enforcement standard is attained or exceeded at a location other than a point of standard application.

Subchapter I — General  
NR 140.01 Purpose. The purpose of this chapter is to establish groundwater quality standards for substances detected in or having a reasonable probability of entering the groundwater resources of the state; to specify scientifically valid procedures for determining if a numerical standard has been attained or exceeded; to specify procedures for establishing points of standard application, and for evaluating groundwater monitoring data; to establish ranges of responses the department may require for exceedances for facilities, practices and activities regulated by this chapter; and to provide for the department's monitoring and enforcement programs, consistent with the rules, and does not create independent regulatory authority.

History: Cr. Register, September, 1983, No. 337, eff. 10-1-83.

NR 140.02 Regulatory framework. (1) This chapter supplements the regulatory authority elsewhere in the statutes and administrative rules. The department will continue to exercise its powers and duties in those regulatory programs, consistent with the enforcement standards and preventive action limits for substances in groundwater under this chapter. This chapter provides guidelines and procedures for the exercise of regulatory authority which is established elsewhere in the statutes and administrative rules, and does not create independent regulatory authority.

(2) The department may adopt regulations which establish specific design and management criteria for regulated facilities or activities, if the regulations will ensure that the regulated facilities or activities will not cause the concentration of a substance in groundwater affected by the facilities or activities to exceed the enforcement standards and preventive action limits under this chapter as a point of standard application. The department may adopt more stringent regulations under authority elsewhere in the statutes based on the best currently available technology for regulated activities and practices which ensure a greater degree of groundwater protection or when necessary to comply with state or federal laws.

(3) Preventive action limits serve to inform the department of potential groundwater contamination problems, establish the level of groundwater contamination at which the department is required to commence efforts to control the contamination and to controlling new releases of contamination as well as to restore groundwater quality contaminated by past releases of contaminants. Although a preventive action limit is not intended to always require remedial action, activities affecting groundwater must be regulated to minimize the level of substances to the extent technically and economically feasible, and to maintain compliance with the preventive action limits unless compliance is not technically and economically feasible.

(4) The department may take any actions within the context of regulatory programs established in statutes or rules outside of this chapter.

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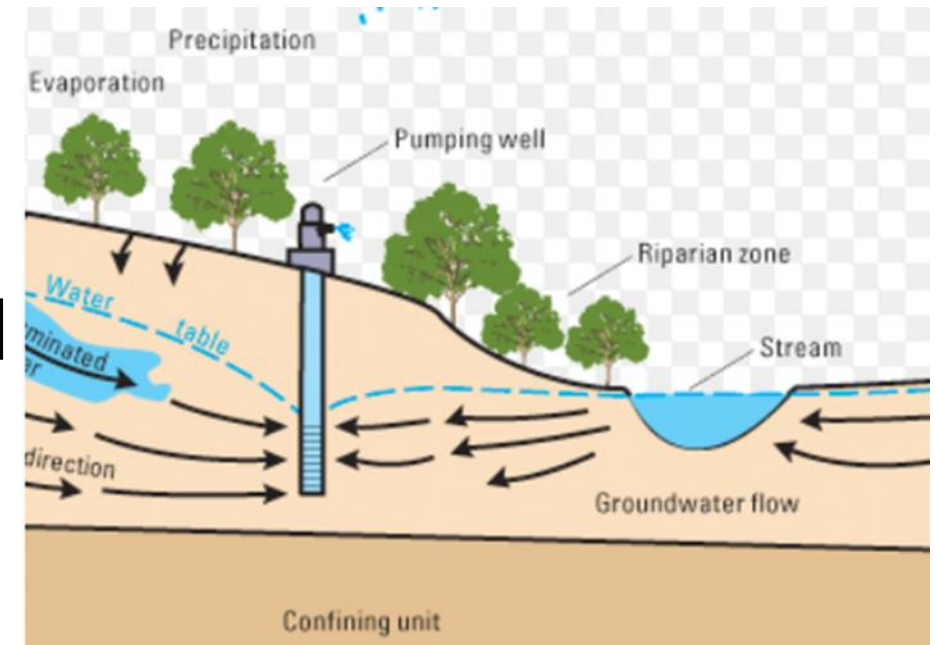
Register January 2020 No. 709



Substance	New or existing	Enforcement Standard Recommended Value	Preventive Action Limit Recommended Value
1,1-Dichloroethane	Existing	No change 850 µg/L	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	20 µg/L
Bacteria (Total coliform)	Existing	No change 0	0
Bacteria ( <i>E. coli</i> )	New	n/a 0	0
Barium	Existing	No change 2 mg/L	0.4 mg/L
Boron	Existing	↑ 2,000 µg/L	400 µg/L
Clothiandin	New	n/a 1,000 µg/L	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	1 mg/L
Glyphosate AMPA degradate	New	n/a 10 mg/L	2 mg/L
Hexavalent chromium	New	n/a 70 ng/L	7 ng/L
Imidacloprid	New	n/a 0.2 µg/L	0.02 µg/L
Isoxaflutole & Isoxaflutole Diketonitrile (DKN)	New	n/a 3 µg/L	0.3 µg/L
Isoxaflutole Benzoic Acid (BA)	New	n/a 800 µg/L	160 µg/L
Molybdenum	Existing	No change 40 µg/L	4 µg/L*
PFOA & PFOS	New	n/a 20 ng/L	2 ng/L
Strontium	New	n/a 1,500 µg/L	150 µg/L
Sulfentrazone	New	n/a 1,000 µg/L	100 µg/L
Tetrachloroethylene (PCE)	Existing	↑ 20 µg/L	2 µg/L
Thiamethoxam	New	n/a 100 µg/L	10 µg/L
Thiencarbazone-methyl	New	n/a 10 mg/L	2 mg/L
Trichloroethylene (TCE)	Existing	↓ 0.5 µg/L	0.05 µg/L

# NR 140 presentation

- Authority for groundwater quality standards
- What guides groundwater standard development?
- Chapter revisions
- **How will these standards be used?**



# How are standards used?

- Used by all state agencies regulating facilities and activities that may affect groundwater quality
- Each agency uses existing rules or revises/adopts rules following Wisconsin §160.21
- Used as standards for bottled water and well compensation grant program



# Examples of Facilities and Activities

- Spills and remediation sites
- Solid and hazardous waste management
- Land application of wastewater
- Mining operations
- Pesticide applications





# How are standards used?

- If PAL exceeded, agencies must take site specific action(s) from responses listed in NR 140.24
  - No action (if certain conditions met)
  - Require installation of wells and groundwater sampling/ site investigation
  - Require a change or increase in monitoring
  - Require change in design, construction or operational procedures
  - Prohibit an activity or close a facility
  - Require remedial action/ natural attenuation
  - Revise rules



# How are standards used?

- If ES exceeded, agencies must take site specific action(s) from responses listed in NR 140.26
  - Change in design, construction or management practice
  - Prohibit an activity or close a facility
  - Require remedial action / natural attenuation
  - Revise rules
- And may also
  - Require installation of wells and groundwater sampling/ site investigation
  - Require a change or increase in monitoring
- But cannot take no action





# Wrap up and Next Steps

- Next stakeholder meeting will be announced shortly. It should be in March.
- We plan to hold separate meetings for each of the rules after that.
- Information on upcoming meetings will be on the websites.
  - [NR809 rule webpage](#)
  - [NR105 rule webpage](#)
  - [NR140 rule webpage](#)



# Questions

