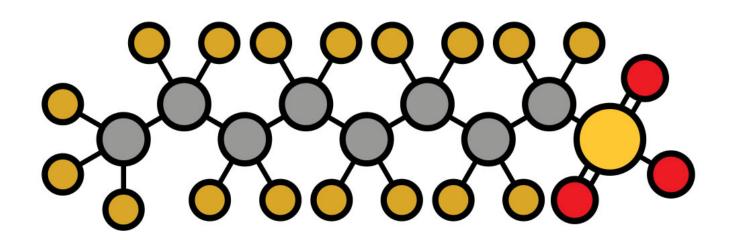
Introduction to per- and polyfluoroalkyl substances (PFAS)

Meghan Williams
Environmental Toxicologist
Water Quality Bureau

Today's presentation

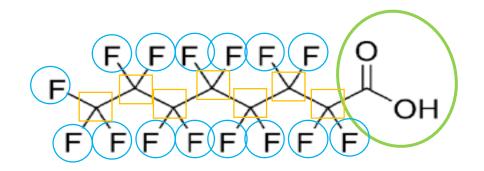
- What are PFAS and where did they come from?
- Why are PFAS a problem?



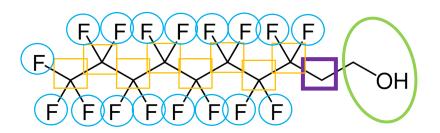
What are PFAS?

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

Perfluorinated compounds: fully-fluorinated tail



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



Sulfonyl fluorides

PFDoA

lodides

PFAS

Polymers

Non-polymers

Polyfluorinated

Fluorotelomer alcohols (FTOH)

Fluorotelomer carboxylic acids (FTCA)

Fluorotelomer sulfonic acids (FTSA) PETILUOTOAIKYI ACIDS (PFAAS)

PFBA PFDA
PFHPA PFODA

Carboxylic acids
(PFCAS) PFTEDA

PFHXDA
PFNA PFPEA
PFUNA

Perfluorinated

PFTrDA

PFBS PFDS

PFHpS
Sulfonic acids
(PFSAs)
PFHxS
PFNS
PFDoS PFPeS

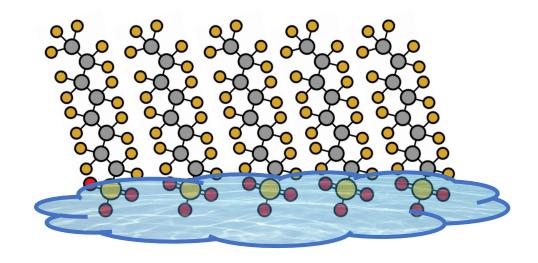
Ether-based substances

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

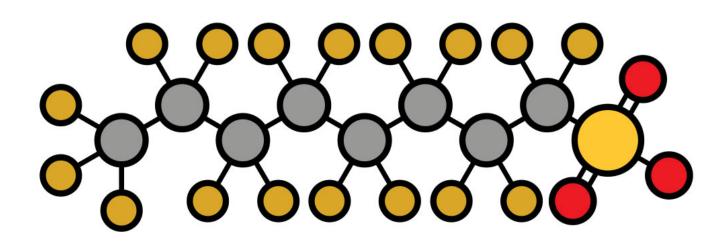


What are PFAS used for?

PFAS 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	NO.			U.S. Reduction of PFOS, PFOA, PFNA (and other select PFAS ²)		
PFOA				Protective Coatings						
PFNA					Initial Production	Architectural	Resins			
Fluoro- telomers					Initial Production	Firefighting Fo	oams	Predominant form of firefighting foam		
Dominant Process ³		Electrochem	Fluoro- telomerization (shorter chain ECF)							
Pre-Invention of Chemistry /			Initial Chemical Synthesis / Production			Commercial Products Introduced and Used				

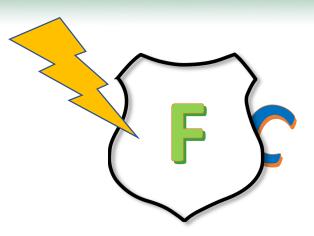
Today's presentation

- 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

























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

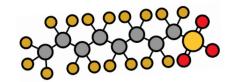


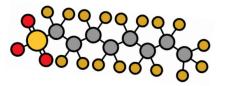




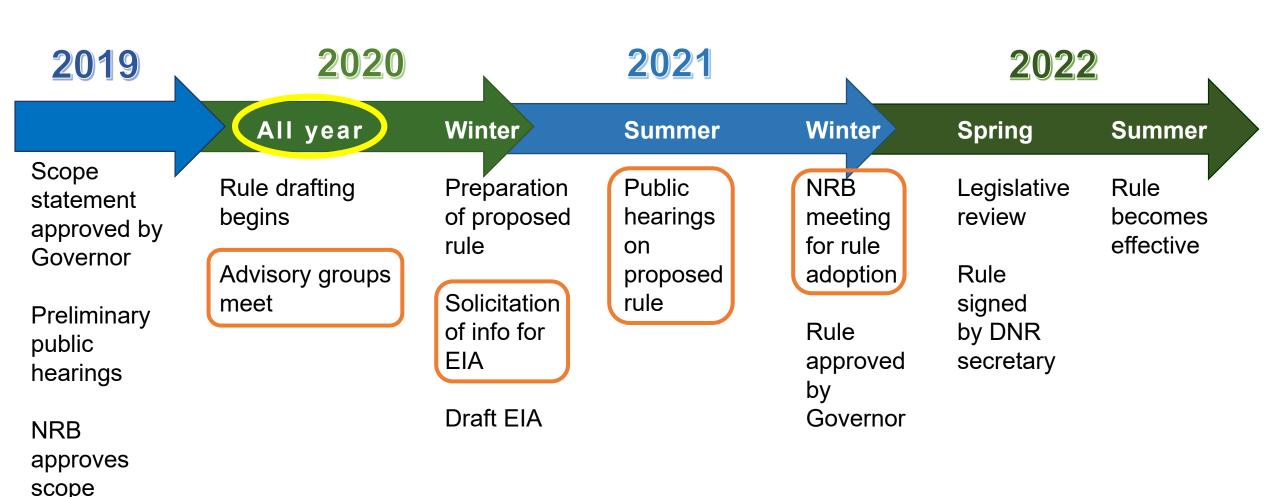
Summary

- 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



NR 809 – Safe Drinking Water

Subchapter I — Maximum Contaminant Levels, Monitoring and Analytical Requirements for Primary Drinking Water Contaminants

Subchapter V — Reporting, Consumer Confidence Reports and Record Keeping

Subchapter VII — Public Notification of Drinking Water Violations

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.

Contaminant	MCL (mg/L)		
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		

MCL (mg/L)		
0.1		
0.002		
0.00005		
0.7		
0.0004		
0.0002		
0.001		
0.05		
0.0002		
0.04		
0.2		
0.001		
0.5		
0.0005		
0.004		
$3x10^{-8}$		
0.003		
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

Contaminant	EPA Methods ¹	SM ⁹	SM Online ¹⁰	ASTM	Other	
Regulated Parameters:						
Synthetic Organic Chemicals						

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?

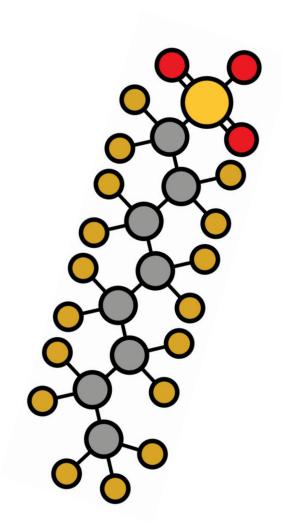
- Municipal water systems (cities, townships, sanitary districts)
- Mobile home parks, apartment buildings, condominium associations
- Small businesses that are public water systems
- Laboratories certified to perform PFAS analysis in drinking water
- Wisconsin Department of Natural Resources
- Wisconsin 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:

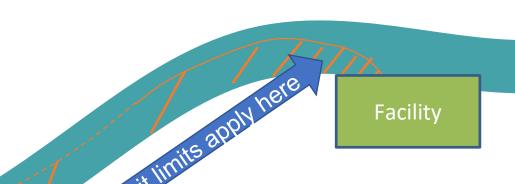


- Contact with surface water
- Ingestion of fish from surface waters



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



Surface water criteria apply here

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

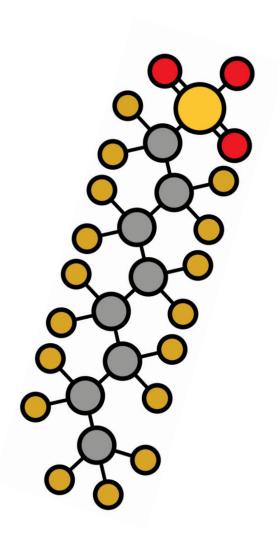






Today's presentation

- 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:

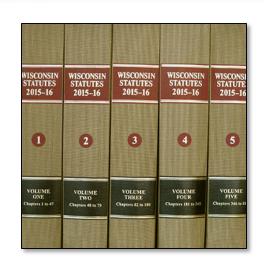
"The objective of this Act is to restore and maintain the chemical, physical, and biological integrity of the nation's waters."

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



Authority for WQS Development

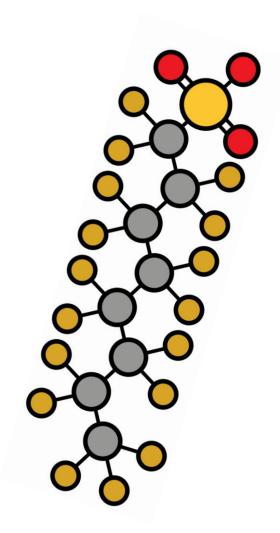
- Wisconsin §281.15: water quality standards
 - The Department shall develop water quality standards to protect public health and welfare.



- 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.

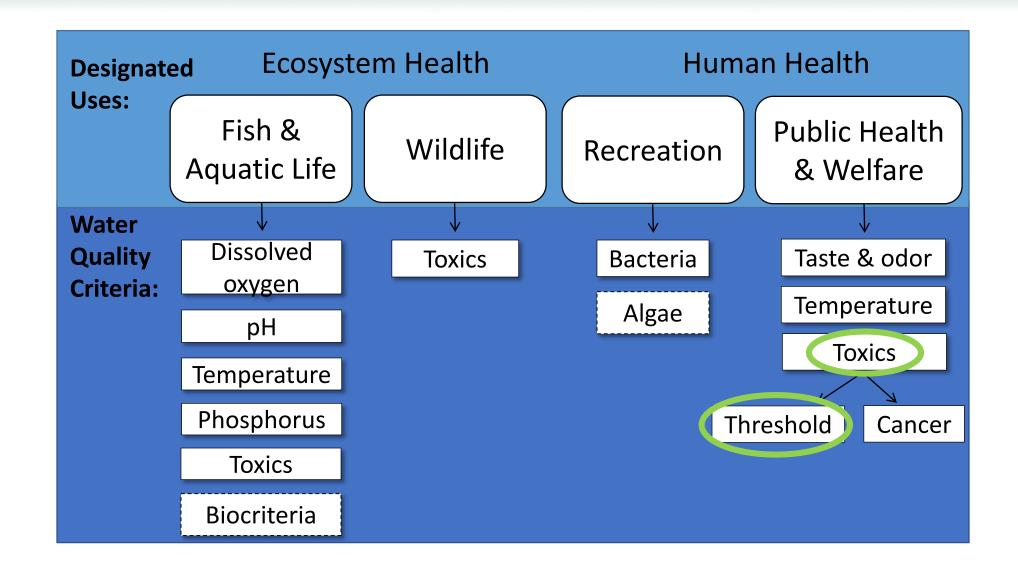
Today's presentation

- 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



ALLEN MANAGEMENT

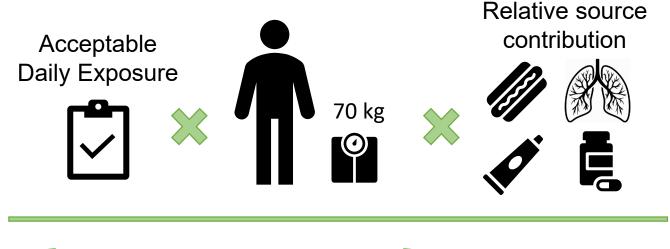
NR 105.08: Human Threshold criteria

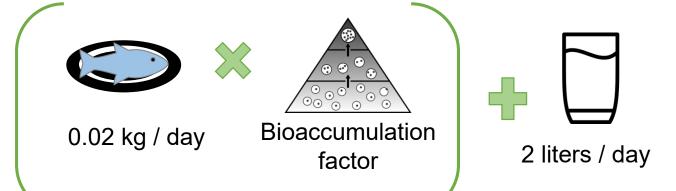
- Maximum concentration of a substance that will protect humans from adverse effects of:
 - Contact with or ingestion of surface water
 - Ingestion of aquatic organisms taken from those waters

 Science indicates a threshold below which no adverse effect is likely

NR 105.08: Human Threshold criteria

How are criteria calculated?







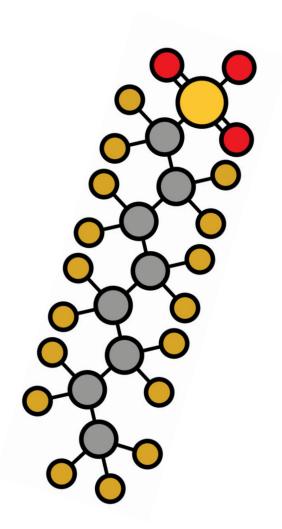
NR 105.08: Human Threshold criteria

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

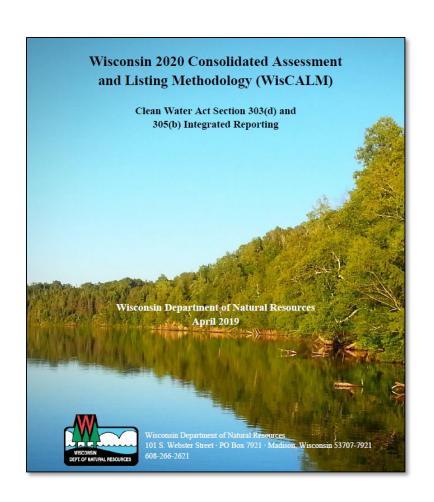
Today's presentation

- 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

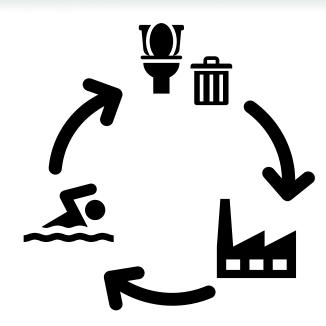


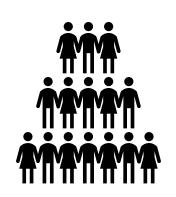
Affected entities

- 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

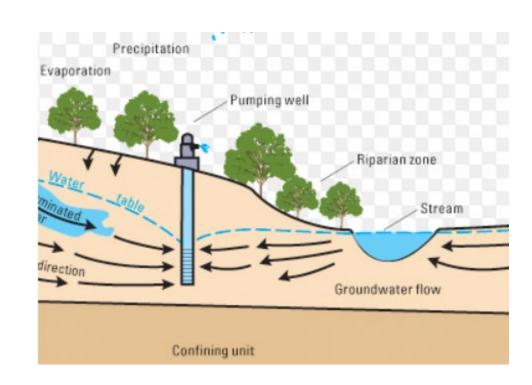
- Authority for groundwater quality standards
- What guides groundwater standard development?
- Chapter revisions
- How will these standards be used?



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

- 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

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



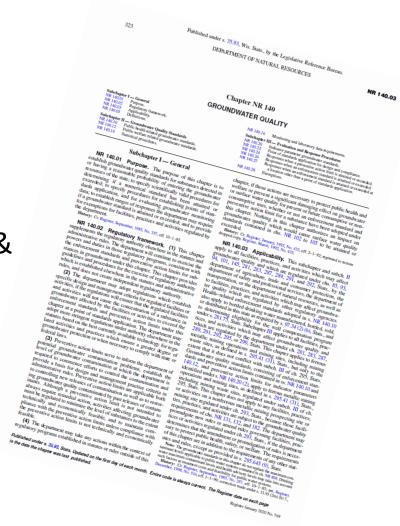
"Cycle 10" Revisions

- 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



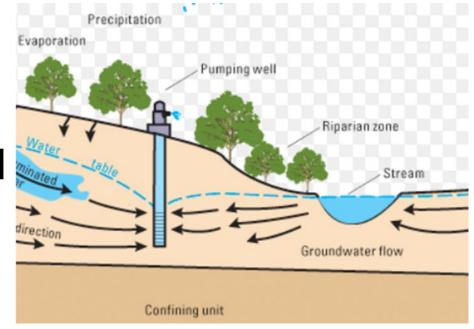
"Cycle 10" Revisions

- "Cycle 10" list: 27 proposed public heath 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



	~ -	_		
Substance	New or	Enforcement Standard		Preventive Action Limit
Substance	existing	existing Recommen		Recommended Value
1,1-Dichloroethane	Existing	No change	850 μg/L	85 μg/L
1,2,3-Trichloropropane	Existing	1	0.3 ng/L	0.03 ng/L
1,4-Dioxane	Existing	↓	$0.35~\mu g/L$	0.035 μg/L
Aluminum	Existing	No change	200 μg/L	20 μg/L
Bacteria (Total coliform)	Existing	No change	0	0
Bacteria (E. coli)	New	n/a	0	0
Barium	Existing	No change	2 mg/L	$0.4~\mathrm{mg/L}$
Boron	Existing	1	$2,000~\mu g/L$	400 μg/L
Clothiandin	New	n/a	$1,000~\mu g/L$	200 μg/L
Cobalt	Existing	No change	40 μg/L	4 μg/L*
Daethal MTP and TPA	New	Combine	70 μg/L	7 μg/L*
degradates		with dacthal		
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	$0.2~\mu g/L$	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	1	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

- 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

