PFAS Overview and Water Quality Program Update

Nate Willis
Wastewater Engineer
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

PFASs:
- perfluoroalkyl acids (PFAAs)
- perfluorooalkane sulfonic acids (PFSAs)
- perfluoroalkyl phosphonic acids (PFPPAs)
- perfluoroalkyl phosphinic acids (PFPIAs)

PFAAs:
- perfluoroalkyl carboxylic acids (PFCAs), $C_{n,F_{2n+1}}COOH$
- perfluoroalkane sulfonic acids (PFSAs), $C_{n,F_{2n+1}}SO_3H$
- perfluoroalkyl phosphonic acids (PFPPAs), $C_{n,F_{2n+1}}PO_3H_2$
- perfluoroalkyl phosphinic acids (PFPIAs), $(C_{n,F_{2n+1}})(C_{m,F_{2m+1}})PO_2H$

PFSAs:
- perfluoroalkane sulfonamides (PFSAs), $C_{n,F_{2n+1}}SO_2R$, R = NH, NHCH_2CH_2OH, etc.

PFPIAs:
- perfluoroalkyl phosphonamides (PFPIAs)
- perfluoroalkyl phosphonamidates (PFPIAs)

PFCAs:
- perfluoroalkyl carboxylic acids (PFCAs)
- e.g., $C_2F_5OC_2F_5OCF_2COOH$

PFPPAs:
- perfluoroalkyl phosphonic acids (PFPPAs)
- e.g., $C_2F_5OCF_2CF_2SO_3H$

PFPIAs:
- perfluoroalkyl phosphonic acids (PFPIAs)
- e.g., $C_2F_5OCF_2CF_2SO_3H$

* These polymers are based on monomers derived from PASFs or fluorotelomer-based raw materials.
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?

- Many PFAS are surfactants
  - Tail is hydrophobic, oleophobic and lipophobic, head is polar and hydrophilic
  - Readily form films

What are PFAS and where did they come from?

<table>
<thead>
<tr>
<th>PFAS¹</th>
<th>Development Time Period</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1930s</td>
</tr>
<tr>
<td>PTFE</td>
<td>Invented</td>
</tr>
<tr>
<td>PFOS</td>
<td>Initial Production</td>
</tr>
<tr>
<td>PFOA</td>
<td>Initial Production</td>
</tr>
<tr>
<td>PFNA</td>
<td>Initial Production</td>
</tr>
<tr>
<td>Fluorotelomers</td>
<td>Initial Production</td>
</tr>
<tr>
<td>Dominant Process²</td>
<td>Electrochemical Fluorination (ECF)</td>
</tr>
</tbody>
</table>

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
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?

Source: Wang, Cousins, Scheringer, Buck, Hungerbuhler, Global Emission Inventories for C4-C14 PFCA Homologues from 1951 to 2030, Part I: Production and Emissions from Quantifiable Sources, 2014
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 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)
  – 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

Source: [Hhttps://stud.epsilon.slu.se/8158/13/ostlund_a_150709.pdf](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
  – 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
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

- Menominee R @ Marinette
- Starkweather Creek
- "Middle" Wisconsin R
- Mississippi R
- La Crosse R nr Fort McCoy

Maximum PFOS concentrations:
- 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
- Mississippi R: Max 4.2 ng/L PFOS
- La Crosse R nr Fort McCoy: Max 43 ng/L PFOS

*Note: The '*' symbol indicates additional information or conditions related to the PFOS concentration.
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
• 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

- **DNR**
  - 1. Review Existing Rules
  - 2. Revise Rules to Achieve Compliance with Standards (Public Input)
  - 3. Enforce Standards
## Cycle 10 Recommendations

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

* 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

<table>
<thead>
<tr>
<th></th>
<th>Groundwater (all values in ppt)</th>
<th>Groundwater Standard/Guideline Policy Type</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PFOA</td>
<td>PFOS</td>
</tr>
<tr>
<td><strong>Colorado</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>70</td>
</tr>
<tr>
<td><strong>Delaware</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>70</td>
</tr>
<tr>
<td><strong>Massachusetts</strong></td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td><strong>Michigan</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>16</td>
</tr>
<tr>
<td><strong>Minnesota</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>15</td>
</tr>
<tr>
<td><strong>New Hampshire</strong></td>
<td>12</td>
<td>15</td>
</tr>
<tr>
<td><strong>New Jersey</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td><strong>Vermont</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td><strong>Wisconsin</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>20</td>
</tr>
</tbody>
</table>
Surface Water Quality Standards

• Triennial Standards Review

A: In Progress
B: New Priorities
C: Priorities, but limited progress expected
D: Barriers to progress
E: Not Priorities
Water Quality Standards Development Process

- Relative source contribution
- Human Health Surface Water Quality Criteria

RfD 70 kg

Bioaccumulation factor

0.02 kg / day

2 liters / day
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?

Nate Willis
(608) 266-3221
nathaniel.willis@wisconsin.gov