PFAS Update

Practical Implications for Solid Waste Operations and Facility Development

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Agenda

• Background
• Chemistry (Lite)
• Regulatory Context
• Sampling/Monitoring Issues
• Analytical Issues
• Leachate Management
• Treatment
• Legal Issues
• PR Issues
• Due Diligence Implications
Focus on PFAS

• Per- and polyfluoroalkyl substances (PFAS) are a group man-made chemicals that includes PFOA, PFOS, GenX, and many other chemicals.

• PFAS have been manufactured and used in a variety of industries around the globe since the 1940's.
Why the Focus on PFAS?

- Commonly Found in Many Products
- USEPA Advisory (70 PPT total PFOA/PFOS)
- States Taking the Lead on Regulations (Inconsistent standards, enforcement, and site discovery activities)
- Legal Concerns / Uncertainty
- Multitude of Compounds that are Generally
  - Mobile in the Environment
  - Persistent
  - Bioaccumulative
  - Difficult and/or Costly to Remove/Destroy
  - Toxic / Regulated at Low Concentrations
• Certain PFAS are mobile, persistent, and bioaccumulative and are not known to degrade in the environment.
  • Most notably some of the perfluoroalkyl acids (PFAAs) such as:
    • Perfluorooctanoate (PFOA)
    • Perfluorooctane sulfonate (PFOS)
  • More complex PFAS can degrade to PFOA/PFOS (Terminal PFAS).
# Introduction to PFAS

<table>
<thead>
<tr>
<th>PFAS</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></td>
</tr>
<tr>
<td>Fluorotelomers</td>
<td></td>
</tr>
<tr>
<td>Dominant Process</td>
<td>Electrochemical Fluorination (ECF)</td>
</tr>
<tr>
<td>Pre-Invention of Chemistry / Production</td>
<td>Initial Chemical Synthesis / Production</td>
</tr>
</tbody>
</table>

**Notes:**
1. This table includes fluoropolymers, PFAAs, and fluorotelomers. PTFE (polytetrafluoroethylene) is a fluoropolymer. PFOS, PFOA, and PFNA (perfluoronanoic acid) are PFAAs.
2. Refer to Section 3.4.
3. The dominant manufacturing process is shown in the table; note, however, that ECF and fluorotelomerization have both been, and continue to be, used for the production of select PFAS.

**Sources:** Prevedouros et al. 2006; Concawe 2016; Chemours 2017; Gore-Tex 2017; US Naval Research Academy 2017
Where Are PFAS

- Food packaged in PFAS-containing materials, processed with equipment that used PFAS, or grown in PFAS-contaminated soil or water
Where are PFAS

- Commercial household products, including stain- and water-repellent fabrics, nonstick products (e.g., Teflon), polishes, waxes, paints, cleaning products, and fire-fighting foams (AFFF).
Where are PFAS

- Workplace, including production facilities or industries (e.g., chrome plating, electronics manufacturing or oil recovery) that use PFAS
Where are PFAS

- Drinking water, typically localized and associated with a specific facility (e.g., manufacturer, landfill, wastewater treatment, firefighter training facility)
Where are PFAS - Drinking Water

Hu et al. 2016
Where Are PFAS

• Living organisms, including fish, animals and humans, where PFAS have the ability to build up and persist over time.
Decreasing Trend In US Blood Levels

## Where PFAS is Used?

<table>
<thead>
<tr>
<th>Fluoropolymer coatings</th>
<th>Product Uses/Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>□ Plastics/polymers</td>
<td>□ Some grease-resistant paper</td>
</tr>
<tr>
<td>□ Oil, stain, water repellent (Stainmaster® carpets, Scotch Gard™ and Gore-Tex®)</td>
<td>□ Fast food containers/wrappers (27 fast food chains)</td>
</tr>
<tr>
<td>□ Surfactants used in firefighting foams</td>
<td>□ Microwave popcorn bags</td>
</tr>
<tr>
<td>□ Mist suppressants for metal plating operations</td>
<td>□ Pizza boxes</td>
</tr>
<tr>
<td>□ Photomicroolithography process to produce semiconductors</td>
<td>□ Candy wrappers</td>
</tr>
<tr>
<td>□ Photography and film products</td>
<td>□ Non-stick cookware such as Teflon™-coated pots/pans</td>
</tr>
<tr>
<td></td>
<td>□ Used on carpets, upholstery, and other fabrics</td>
</tr>
<tr>
<td></td>
<td>□ Water-resistant clothing - Hush Puppy Shoes (Wolverine Worldwide)</td>
</tr>
<tr>
<td></td>
<td>□ Adhesives</td>
</tr>
<tr>
<td></td>
<td>□ Aviation hydraulic fluids</td>
</tr>
<tr>
<td></td>
<td>□ Cleaning products</td>
</tr>
<tr>
<td></td>
<td>□ Personal care products such as shampoo, dental floss, and cosmetics (nail polish, eye makeup)</td>
</tr>
<tr>
<td></td>
<td>□ Paints, varnishes and sealants</td>
</tr>
</tbody>
</table>
PFAS Found in Food 20 years ago!

• 3M Commissioned Study reported in 2001 – PFOA and PFOS in beef, pork, chicken, milk, green beans, eggs, bread, and others in 6 cities in US southeast
  - Levels from 500 to 14,700 ppt
• FDA study 2019 – PFAS in meat, seafood, dairy, sweet potatoes, pineapples, leafy greens, chocolate cake with icing –
  - **17,640 parts per trillion (ppt) of perfluoro-n-pentanoic acid (PFPeA) in chocolate cake with icing.**
  - If regulated at same level as proposed NY drinking water guidelines of 10 ppt, cake would contaminate thousands of gallons of water.
Chemistry... It’s Complicated...

- Numerous Compounds (~3,000)
  - Perfluoroalkyl Acids (PFAAs)
  - Perfluoroalkane Sulfonamides (FASAs)
  - Fluorotelomer Substances
  - Perfluoroalkane Sulfonamide Substances
- Historically Inconsistent Naming
- ITRC Has Proposed Standardized Terminology (March 2017)
Regulatory Climate

• Geography Matters
• States are Taking the Lead with Setting Standards
• Inconsistent
• USEPA Drinking Water Health Advisory for PFOA/PFOS
PFAS REGULATIONS - USEPA

- EPA has established health advisory levels of 70 parts per trillion for PFOA and PFOS combined in drinking water.
  - “…based on the best available peer-reviewed studies of the effects of PFOA and PFOS on laboratory animals (rats and mice) and were also informed by epidemiological studies of human populations that have been exposed to PFASs.” FACT SHEET - PFOA & PFOS Drinking Water Health Advisories, USEPA, November 2016, EPA 800-F-16-003.
USEPA Advisory

• 70 ppt (ng/l), May 2016, Applies to Total PFOS/PFOA
• Basis: Reference Dose From Lau et al. 2006 Developmental Study in Mice
  • Lowest effects level of 1 mg/kg-d adjusted to 0.0053 mg/kg-d to account for much longer half-life in humans
  • Safety/uncertainty factor totaling 300 applied to get reference dose of 0.00002 mg/kg-d = 20 ng/kg-d
Adverse health effects due to exposure to PFOA and PFOS over certain levels may result in:

- developmental effects to fetuses during pregnancy or to breastfed infants (e.g., low birth weight, accelerated puberty, skeletal variations),
- cancer (e.g., testicular, kidney),
- liver effects (e.g., tissue damage),
- immune effects (e.g., antibody production and immunity),
- thyroid effects, and
- other effects (e.g., cholesterol changes).
Dear Waste Site Cleanup Stakeholder (and other interested parties),

Today, the Baker-Polito Administration and the Department of Environmental Protection (MassDEP) are filing two rules with the Secretary of State related to PFAS: a FINAL soil and groundwater cleanup rule and a DRAFT drinking water rule. The rules will be published by the Secretary of State on December 27th, but are available now on the MassDEP website.

Massachusetts is one of only a small number of states with formal PFAS cleanup standards (under the MA Contingency Plan). The standards require parties that are responsible for contamination to clean up groundwater that could be used as drinking water to meet a limit standard of 20 parts per trillion (ppt) for the sum of six PFAS compounds. The cleanup standard also establishes specific PFAS limits for soils.


The draft drinking water standard would establish a Maximum Contaminant Level (MCL) for drinking water of the sum of 20 ppt for six PFAS compounds. The proposed standards cover a larger subgroup of compounds than any other state and provide a greater degree of protection, particularly for sensitive subgroups including pregnant women, nursing mothers, and infants.


As of July 1, 2019. From Bryan Cave Leighton Paisner LLP.
## Drinking Water Standards

<table>
<thead>
<tr>
<th>Compound</th>
<th>USEPA Health Advisory Tox Values</th>
<th>Other States EPA Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFOS</td>
<td>70 sum</td>
<td>Guidance Goals</td>
</tr>
<tr>
<td>PFOA</td>
<td>11 sum</td>
<td>Regulatory Standards</td>
</tr>
<tr>
<td>PFNA</td>
<td>10 sum</td>
<td>Drinking Water</td>
</tr>
<tr>
<td>PFHxS</td>
<td>70 sum</td>
<td>Health Based</td>
</tr>
<tr>
<td>PFHpA</td>
<td>51 sum</td>
<td>Regulatory Standard</td>
</tr>
<tr>
<td>PFBS</td>
<td>70 sum</td>
<td>Water Board Notification</td>
</tr>
<tr>
<td>PFDA</td>
<td>70 sum</td>
<td>Current ORSG</td>
</tr>
<tr>
<td>PFHxA</td>
<td>51 sum</td>
<td>MCL or Proposed</td>
</tr>
<tr>
<td>GenX</td>
<td>70 sum</td>
<td>Health Advisory/</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Emergency Rules</td>
</tr>
</tbody>
</table>

### New York (NY) Regulations
- Recommended MCL: 10
- Proposed MCL: 7

### New Jersey (NJ) Regulations
- MCL or Proposed MCL: 13
- Emergency: 7

### Vermont (VT) Health Advisory/Other Rules
- Health Advisory: 20
- Proposed MCL: 13

### Massachusetts (MA) Regulations
- Current ORSG: 16
- Proposed ORSG: 6.5

### Connecticut (CT) Regulations
- Water Board Notification: 70

### California (CA) Regualtory Standard
- Regulatory Standard: 6.5, 51, 400,000

### Michigan (MI) Health Based Guidelines
- Health Based Guidelines: 10, 6

### Minnesota (MN) Drinking Water Guidelines
- Drinking Water Guidelines: 38

### New Hampshire (NH) Regulations
- Regulatory Standard: 10

### New Mexico (NM) Guidelines
- Guidelines: 10

### North Carolina (NC) Guidelines
- Guidelines: 10
Groundwater Sampling/Monitoring

- Do Your Homework
  - Follow local state guidance (if available)
  - Supplement with useful info from other sources (Michigan guidance is a good starting point, ITRC guidance, lab instructions, company SOPs)

- Keep It Simple
  - Less sampling materials are generally better
  - Dedicated equipment can be a good idea

- Special Considerations
  - Prohibited equipment and clothing
  - Personal care products
  - Consider alternative bug spray and sunscreen

- Use Duplicates, Field/Equipment Blanks Frequently
Sources of Sample Contamination

• Almost Anything
  • Teflon Equipment/Containers
  • Field Books
  • Field Forms
  • Post-It Notes
  • Lunch
  • Tyveks
  • Clothing
  • Personal Care Products

• Use Duplicates, Field/Equipment Blanks Frequently
• What Will All This Cost?
  • If PFAS sampling becomes required, additional analytical cost a certainty
  • Labor costs premiums will be more variable depending upon site conditions (e.g. deep groundwater, low-flow sampling requirements in permit/monitoring plan, etc.)
  • Possible “first round” preparation costs
• Observations to Date
  • Sampling can be done effectively without cross-contamination
  • Results from wells over time fairly reproducible with similar variation as other contaminants (same lab)
  • Field duplications show good reproducibility
  • Rinseate blanks have not shown contamination from sampling equipment, which is critical for credibility of data
Surface Water Sampling

- What is in your waders? PFD?
- Possible to work from shore?
- “Invisible Sheen”
Analytical - Part Per Trillion

1 drop in a half cup of water = 1 part per hundred
pph = 1 / 100

1 drop in a quart of water = 1 part per thousand
ppth = 1 / 1000

1 drop in two tubs of water = 1 part per million
ppm = 1 / 1,000,000

1 drop in an Olympic size swimming pool = 1 part per billion
ppb = 1 / 1,000,000,000

1 drop in a lake = 1 part per trillion
ppt = 1 / 1,000,000,000,000

Click on each red drop of contaminant to add it to the measure of water. Observe how the concentration differs in each quantity of water.

Certifiable Environmental Curriculum (CEC) 2018
• How do you Confidently Measure 0.020 µg/L?
• USEPA Method 537 Rev 1.1 LC/MS in Drinking Water
  • 14 Compounds Typical (>3,000 targets)
  • Up to 25 Compounds (DOD ELAP Cert)
• TOP (Total Oxidizable Precursor) Assay may be something to consider in certain circumstances
• Difficult Matrices (Leachate?) – Discuss with your lab
• PFOA and PFOS Replacements – Discuss with your lab
Leachate Management

• Outlets for off-site disposal are narrowing
• More on-site treatment likely
Treatment

• Technologies Work on Some of the Compounds
• Multiple Ionic States
• Variable Isomers
• Differing Alkyl Groups
Current Water Technologies

- Most Amenable to Ex-situ Treatment
  - Carbon
  - Resin
  - RO

Source: NH Business Review 2018

Source: Australian DOD 2018
PFAS Treatment Technologies

- Activated Carbon
- Ion Exchange
- Reverse Osmosis
- Deep Well Injection
- Innovative Technologies
  - Advanced Remediation Catalysis (ARC)
  - Advanced Reduction Processes (ARP)
  - Non-Thermal Plasma Reduction
  - Advanced Oxidation – Persulfate; Nano-ZVI
  - Plasma Arc
  - Etc
  - Etc
  - Etc
PFAS Remediation Options for Pump & Treat

- Membrane Filtration
- Carbon Adsorption
- Methanol/Brine Regenerable Resin
- Single-Use Resin
GAC Adsorption

• With GAC, adsorption occurs on the surface of the interior graphite platelets which are the solid part of the porous structure of the granules
• Adsorption is an equilibrium process and capacity is concentration dependent
• Exhausted GAC can often be sent to a reactivation furnace to destroy the adsorbates and produce a reusable product – air emissions?
GAC Perfluorinated Compound Adsorption

- GAC has been in use at Minnesota sites for groundwater treatment for many years in this service
- Spent GAC can be successfully reactivated from this service for a minimum of waste generation
- As is typical of GAC adsorption, smaller and lower formula weight compounds tend to adsorb less strongly than larger, heavier compounds with similar structures.
GAC PFAS Adsorption

So absorption characteristics depend on type of PFAS!! – See vertical scale on both graphs.
IX - Single-Use Selective Resin + Incineration

PFAS in water → Cement Kiln Incineration
1400°C to 2000°C
→ PFAS –free water

Short Contact Time ~3 mins
Simple & Effective - Operator Preferred.

Complete Destruction of PFAS
Must Consider Negative Impact of Leachate Chemistry on GAC & IX

Table 1  The chemical composition of leachate.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Measured characteristic</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOD5</td>
<td>3400 PPM</td>
</tr>
<tr>
<td>COD</td>
<td>8250 PPM</td>
</tr>
<tr>
<td>pH</td>
<td>8.24</td>
</tr>
<tr>
<td>Turbidity</td>
<td>1400 NTU</td>
</tr>
<tr>
<td>TS</td>
<td>29942 PPM</td>
</tr>
<tr>
<td>TDS</td>
<td>26612 PPM</td>
</tr>
<tr>
<td>Conductivity</td>
<td>59400</td>
</tr>
<tr>
<td>SO₄</td>
<td>34712 PPM</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>6365 PPM</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>1308 PPM</td>
</tr>
<tr>
<td>NO₃</td>
<td>3.95 PPM</td>
</tr>
<tr>
<td>NH₄</td>
<td>3745 PPM</td>
</tr>
</tbody>
</table>

Some constituents interfere more than others!!

Reverse Osmosis

• Should work effectively
• Membrane Based Separation Process.
• Separates Water from Organic and Inorganic Compounds.
• Effluent for reuse or disposal.
• What to do with Reject???
• If recirculation is allowed, returns the contaminants to the landfill where they were originally deposited.
• Solidification – Lime, others?
• Evaporation – Crystallization
  • Heat needed
  • Air Emissions
Reverse Osmosis

- Membrane Based Separation Process.
- Separates Water from Organic and Inorganic Compounds.
- If recirculation is allowed, returns the contaminants to the landfill where they were originally deposited.
- Effluent for reuse or disposal.
### Summary of Water Treatment Options for Various PFAS Compounds

| Compound                        | Acronym | Molecular Weight (g/mole) | Aeration | Coagulation Dissolved Air Floatation | Coagulation Flocculation Sedimentation Filtration | Conventional Oxidation (MnO₂, O₃, ClO₂, CLM, UV-AOP) | Anion Exchange (Select Resins Tested) | Granular Activated Carbon | Nano Filtration | Reverse Osmosis |
|---------------------------------|---------|---------------------------|----------|-------------------------------------|--------------------------------------------------|--------------------------------------------------|-------------------------------------|-------------------------------|----------------|----------------|----------------|
| Perfluorobutanesulfonic Acid    | PFBS    | 300                       |          |                                     |                                                  |                                                  |                                    |                               |                |                |
| Perfluorooctanoic Acid          | PFOA    | 414                       |          |                                     |                                                  |                                                  |                                    |                               |                |                |
| Perflurohexanesulfonic Acid     | PFHxS   | 400                       |          |                                     |                                                  |                                                  |                                    |                               |                |                |
| Perfluorooctane Sulfonate       | PFOS    | 500                       |          |                                     |                                                  |                                                  |                                    |                               |                |                |
| Perfluorohexanoic Acid          | PFHpA   | 364                       |          |                                     |                                                  |                                                  |                                    |                               |                |                |
| Perfluorononanoic Acid          | PFNA    | 464                       |          |                                     |                                                  |                                                  |                                    | assumed                      |                |                |
| Perfluorododecanoic Acid        | PFDA    | 418                       |          |                                     |                                                  |                                                  |                                    | assumed                      |                |                |

Table modified from E. Dickenson and C. Higgins 2016

Litigation is Becoming Active

• Citizen Suit Claims
• CERCLA Cost Recovery
• Toxic Tort
Public Relations

• PFAS is a hot topic
• Public relations issues are similar to all other issues of environmental contamination
• But… PFAS has all of the elements that cause people to have a higher perception of risk.
  • Man-made chemicals
  • Exotic chemical names and properties
  • Ubiquitous
  • Potential Carcinogen
  • In your blood
Due Diligence

• PFAS has become an issue on nearly every solid waste due diligence project and will become a “way of life” in solid waste industry transactions

• Talk to your consultant… Will PFAS be a REC? Regardless, let them know you care!

• Consider whether data is available and the relative benefits of baseline data

• Is PFAS present now? Is it attributable to the property? If not, could the condition be “blamed” on the property in the future?

• What receptors are present nearby? Private or public wells?

• What state are you in? What are the rules today? Consult your “Crystal Ball” regarding tomorrow!

• Estimate risk…
Summary

• PFAS – A Group of Many Compounds that do not all behave the same
• PFAS Compounds are Ubiquitous in Consumer Products & the Environment
• Regulation is Developing at the State Level and Variable
• Future Sampling at Solid Waste Facilities Likely and Must be Done with Care
• Analytical Methods are Development – Know What Compounds You Are Looking For
Summary

• Leachate Management Will Be Challenging – Pretreatment and Treatment Trains May Be More Common
• Treatment – Carbon is Most Common at Present, Lot’s of Interest in New Technologies
• Legal Issues – Same as all Other Contaminants, but Exposure Could be More Common
• PR Issues – Same as all Other Contaminants, but More “Scary”
• Due Diligence Implications – Think about baseline conditions and estimating risk
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