PFAS Treatment Train
Developing Alternatives for PFAS Groundwater Treatment & Destruction

Presented at SAME Rhein-Main Post
Wiesbaden, Germany
March 21, 2019

woodplc.com
Presentation Outline

✓ Background, Exposure Pathways & Risk
✓ Factors Affecting F&T
✓ Remediation and Treatment Developments
✓ Takeaways
✓ Q&A
Background, Exposure
Pathways & Risk
Wood – The basis for our lessons learned

- Evaluating over 130 locations globally
- Canada, US, UK, Australia, Germany
- Strategic R&D Partnerships
- Policy development & review
- Author of Industry BMP documents
- Established Audit program
- New technology pilot system
- Fingerprinting and source identification
- Design/construction of Mitigation Systems
- Litigation support
What are PFAS? Sources/Uses

Oil and Gas Extraction

Electroplating (mist suppressants)

Manufacturing Processes/Intermediates/By-products

Consumer Products

Semiconductor Industry

Aqueous Film Forming Foams (AFFF)
The Heads and Tails of PFAS

*Per-* and *Poly-FluoroAlkyl Substances*

Xenobiotic, anthropogenic
>3,000 individual compounds
>40 chemical groups
Commercial use since ~1950s

Source: NGWA, 2017, figure 4.3
Nomenclature: What are PFAS?

Fluorinated Substances

Polyfluoroalkyl substance

Perfluoroalkyl substance (PFAAs)

Note:
This is a simplified representation of fluorinated substance sub-classes and in no way represents the entire fluorinated substances class


PFCA = perfluorocarboxylic acid
PFSA = perfluorosulfonic acid
PFCA = perfluoroalkyl acids
PFSA = per- and polyfluoroalkyl acids

A presentation by Wood.
### Physical and chemical properties of PFAS listed in UCMR3 list

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<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>PFOS</td>
<td>1763-23-1</td>
<td>&lt;1.0</td>
<td>0.52 – 0.57</td>
<td>6.43</td>
<td>2.4 – 4.7</td>
</tr>
<tr>
<td>PFHxS</td>
<td>355-46-4</td>
<td>-6 – -5</td>
<td>2.3</td>
<td>5.17</td>
<td>1.78</td>
</tr>
<tr>
<td>PFBS</td>
<td>375-73-5</td>
<td>-3.31</td>
<td>46.2 – 56.6</td>
<td>3.9</td>
<td>2.26</td>
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<tr>
<td>PFNA</td>
<td>375-95-1</td>
<td>-0.21</td>
<td>9.5</td>
<td>5.92</td>
<td>5.08</td>
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<tr>
<td>PFOA</td>
<td>335-67-1</td>
<td>-0.5 – 4.2</td>
<td>3.4 – 9.5</td>
<td>5.30</td>
<td>1.92 – 2.59</td>
</tr>
<tr>
<td>PFHpA</td>
<td>375-85-9</td>
<td>-2.29</td>
<td>4.2</td>
<td>4.67</td>
<td>1.52 – 2.82</td>
</tr>
</tbody>
</table>

- **Ingestion**
- **Direct Contact**
How are PFAS different? Characteristics

<table>
<thead>
<tr>
<th>Chemical Properties</th>
<th>PCB (Arochlor 1260)</th>
<th>PFOA</th>
<th>PFOS</th>
<th>TCE</th>
<th>Benzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Weight</td>
<td>357.7</td>
<td>414.07</td>
<td>538</td>
<td>131.5</td>
<td>78.11</td>
</tr>
<tr>
<td>Solubility</td>
<td>0.0027 mg/L @24°C</td>
<td>3400–9500 mg/L @25°C</td>
<td>519 mg/L @20°C</td>
<td>1100 mg/L @ 20°C</td>
<td>1780 mg/L @20°C</td>
</tr>
<tr>
<td>Vapor Pressure (25°C)</td>
<td>4.05x10⁻⁵ mmHg</td>
<td>0.5-10 mmHg</td>
<td>2.48x10⁻⁶ mmHg</td>
<td>77.5 mmHg</td>
<td>97 mmHg</td>
</tr>
<tr>
<td>Henry’s Constant</td>
<td>4.6x10⁻³ atm-m³/mol</td>
<td>0.0908 atm-m³/mol</td>
<td>3.05x10⁻⁶ atm-m³/mol</td>
<td>0.0103 atm-m³/mol</td>
<td>0.0056 atm-m³/mol</td>
</tr>
<tr>
<td>Organic Carbon Part. Coeff. (Log K&lt;sub&gt;oc&lt;/sub&gt;)</td>
<td>4.8-6.8</td>
<td>2.06</td>
<td>2.57</td>
<td>2.42</td>
<td>2.15</td>
</tr>
</tbody>
</table>

- High solubility, low volatility in water
- High detection frequency in soil and sediment
PFAS Risks vs. Perceived Risks

- **Science**
  - Risk = Unacceptable Concentration (Hazard) + Complete Exposure Pathway

- **Public Risk Perception**
  - Risk = Perceived Hazard + Outrage

- **Public PFAS Perception**
  - Risk = **Any PFAS** + Outrage
Risk Drivers – Drinking Water & Ecological Receptors
Factors Affecting F&T
PFAS Fate/Transport in Soil

- Sorption not the only process influencing F&T
- Electrostatic attraction also a factor
  - Cationic, Anionic, and Zwitterionic PFAS
  - PFAS can accumulate in residual NAPL and at air/water interface
  - Air-water interfacial partitioning also likely contributing to vadose zone retardation
  - Presence of a surface cover and surface soil type also affects the degree of PFAS flushing

Brusseau, M. L.; 2018 - Science of the Total Environment; 176-185

Anderson et al 2019 – Journal of Contaminant Hydrology; 59-65
Chemical Complications

- AFFFs met MilSpec – formulations changed with and without name changes
  - 9 primary formulations, many used/released at the same location (e.g. FTAs)
  - 100s of PFAS
- PFOA used as surfactant in emulsion polymerization of PTFE (Secondary Mfg. use PFOA vs. produce it)
  - PFOA phased out over time
  - GenX (C6) is PFOA replacement in fluoropolymer
Chemical Considerations

- Many and varying sources
- Numerous common co-contaminants with varying characteristics
- 100s of environmentally relevant PFAS
- Changing/inconsistent laboratory methods
- Laboratory advances: more analytes & lower detection limits
- New regulatory thresholds addressing more analytes
- Changing/lower regulatory thresholds (e.g. TX changed 4x)
- Significant Litigation – PFAS in drinking water & blood serum
Additional Chemical Considerations

Different Classes of PFAS will behave differently – don’t lump them in same bucket characteristically! They are not all thermally, chemically, and biologically stable.

- Short Chain vs. Long Chain
- PFCAs vs. PFSAs
- Poly-fluorinated Precursors
- Metabolites that we can’t even analyze
- Redox, TOC, ionic compounds (e.g. chlorides, calcium), pH all influence F&T in groundwater
- As diverse as hydrocarbons!
Biological Influences on F&T

• Fully fluorinated PFAS are biologically resistant to attenuation (e.g. PFOS/PFOA)

• Long-chain poly-fluorinated precursor PFAS (e.g. 8:2 FTOH) may biotransform (i.e. oxidize) and dead end at fully- or perfluorinated PFAS
  o Dissolved oxygen in aerobic aquifer may facilitate this oxidation

• Note: Even if microorganisms could biodegrade PFOS/PFOA they would not be happy/hungry microorganisms within the mid plume or downgradient where average PFAS concentrations are usually very low
TOP Assay as F&T Tool – Use with Caution

- No standard procedure – details and QC differ between labs
- No agreement on how to evaluate data quality and usability
- Challenging to interpret...
  - Can show formation of multiple low molecular PFAS and other PFAS with no action levels – how do you apply that information?
- Only provides information on what may form under the very aggressive oxidation used
  - Aggressive oxidation likely more significant than what can be facilitated in natural environment (i.e. aerobic aquifer)
- Results are likely to require extensive and complicated explanation, and may raise more questions than they answer

“Standardized (TOP) methods are urgently needed”

Martin et al 2019 – Talanta 195, pages 533-542
Physical/Analytical Testing in Support of F&T

Low cost physical and analytical testing available to evaluate PFAS transport:

- **Soil**
  - Grain-size analysis
  - Cationic Exchange Capacity (CEC)
  - Anionic Exchange Capacity (AEC)
  - pH
  - Total Organic Carbon (TOC)

- **Groundwater**
  - Dissolved Oxygen (DO) and Oxidation-Reduction Potential (ORP)
  - TOC
Atmospheric Transport

- Particle phase/aerosol transport
- Wet deposition of particle-associated PFAS
- PFOA associated with small particles (<0.14 μm)
- PFOS associated with larger particles (1.38 to 3.81 μm)

- Vapor phases transport (mainly neutral precursors)
- Dry deposition of particle-associated PFAS
- Atmospheric transformation of precursors to other PFAS by reaction with NOx, OH•, O3, O2

- Shorter transport potential
  ≈3-5 days atmospheric lifetime (PM2.5)

- Longer transport potential
  ≈20 days atmospheric lifetime (8:2 FtOH)

- Wet deposition of vapor-phase PFAS

A presentation by Wood.
Surface Water Source Areas

- >95% detection in Stormwater across all samples collected
- Non-point source contribution
- Stormwater as source to GW impacts
- Management via
  - passive treatment
  - collection and treatment
  - retention

Program-Wide Data Evaluation Summary

<table>
<thead>
<tr>
<th>Sampled Media</th>
<th># of samples</th>
<th>PFOS Frequency of Detects</th>
<th>PFOS Median / Maximum (ppb)</th>
<th>PFOA Frequency of Detects</th>
<th>PFOA Median / Maximum (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stormwater samples</td>
<td>80</td>
<td>96.30%</td>
<td>0.140 / 3.70</td>
<td>67.50%</td>
<td>0.040 / 0.940</td>
</tr>
</tbody>
</table>
Evolving Definition/Understanding of Source Areas

• Increasing appreciation for significance of Surface Water pathway
  o Including as source to offsite groundwater impacts
• Increasing appreciation for Potential Air Transport
  o e.g. Mfg. Stacks, Cooling Towers, Air Strippers
    – Generally: Water + PFAS + Heat = Air Releases/Transport
• Large AFFF Sites may have enough disparate contributing sources to consider “Whole Site” as a Source
• Site Construction and Remediation activities may redistribute or change sources
  o FTA excavation
  o Aerobic Bio/ISCO oxidation of polyfluorinated precursors
Unaltered Source Area

✓ High Retention Areas Remain
  o Near Surface
  o Capillary Fringe
✓ Leaching from Retention Areas
  o High Concentrations in Source Area Remain
  o Resulting in High PFAS Flux Rate
✓ Source Area Remediation
  More Likely to:
  o Reduce Flux
  o Eliminate unacceptable risks to receptors
Altered/Excavated Source Area

- High Retention Areas Excavated

- No significant leaching from Retention Areas
  - Highest GW concentrations downgradient from Source Area
  - Lower Flux Rate

A presentation by Wood.
Remediated PFAS Source Area

complex fate and transport at AFFF sites

- fluoro-surfactants emulsify LNAPL
- delayed precursor oxidation
- PFAA concentration
- natural O₂ induced PFAS hot spot — precursor biotransformation
- natural O₂ recharge
- PFAS concentration
- hydrocarbons attenuate rapidly PFASs expand

- highly anaerobic PFASs and fuel
- remediation induced oxidation
- PFAA hotspot — precursor oxidation
- PFAS concentration
- groundwater flow

A presentation by Wood.
Remediation and Treatment Developments
Remediation & Treatment Scenarios

1. Surface soil
2. Subsurface soil
3. Source area GW
4. Downgradient GW containment
5. Stormwater infrastructure containment
6. Surface water
7. Sediment
8. Offsite GW impacted by surface water
9. Residential well GW treatment
10. Production well GW treatment

Focus Thus Far
Targeted Future Focus
### Remediation/Treatment – Tested Technologies

<table>
<thead>
<tr>
<th>Ex-Situ</th>
<th>In-Situ</th>
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<tbody>
<tr>
<td>GAC</td>
<td>Isolation (e.g., capping)</td>
</tr>
<tr>
<td>RemBind</td>
<td>PlumeStop</td>
</tr>
<tr>
<td>Ion Exchange Resin</td>
<td>Phytoremediation</td>
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<tr>
<td>Modified Zeolites</td>
<td></td>
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<tr>
<td>Coagulation/Electrocoagulation</td>
<td></td>
</tr>
<tr>
<td>Reverse Osmosis</td>
<td></td>
</tr>
<tr>
<td>Nano-/Ultra- Membrane Filtration</td>
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**Separation**

- Chemical Oxidation
- Chemical Reduction
- Microbial Biodegradation
- Fungal Degradation
- Enzymatic Catalyzed

**Destruction**

- Water or Groundwater Treatment Technology
- Soil Treatment Technology
- AFFF Stockpile Treatment Technology

A presentation by Wood.
Available Full Scale Soil Remediation Alternatives

• Excavation and encapsulation
  – Effective but expensive, generally used with higher volumes of soil at lower PFAS concentrations

• Incineration
  – Generally used with low volumes of soil at higher concentrations, requires at least 1100°C

• Immobilization
  – RemBind
    o Proprietary powdered reagent – Activated Carbon, Organic Matter, and Aluminum Hydroxide
    o Added to soil at a ratio of 1-10% by weight
    o Binding occurs in 24 hrs; bench and pilot shows >98.5% reduction
  – MatCARE
    o Modified clay adsorbent
    o Immobilizes PFOS in soil and groundwater
    o pH, clay content and organic content influence PFOS release from soil
Available Full Scale Water Remediation/Treatment Alternatives

- **Granular Activated Carbon Sorption**
  - Most ubiquitously used for water

- **Ion Exchange (IX) Resin Sorption**
  - Effective removal of PFOS when calcium is present

- **Reverse Osmosis (Membrane)**
  - Efficient for PFOS concentrations ranging from 0.5 to 1600 ppm.

Wood Full Scale Pease AFB IX Pump and Treat System Under Construction
Results of the Pease AFB Pilot Study

Volume Treated Before Breakthrough: All Observed PFAS

- 6:2 FS
- 8:2 FS
- PFBS
- PFBA
- PFHpS
- PFHxS
- PFHxA
- PFOA
- PFOS
- PFPeA

- GAC (5-min EBCT)
- Resin (5-min EBCT)
Pilot Study Regeneration Success and Full-scale Construction

- Lifecycle cost evaluation performed for full-scale 200 gpm system at Pease AFB
- Capital cost for resin system is ~15% higher than GAC
  - Media cost
  - Regeneration system
- O&M cost is ~50% lower than GAC
  - Resin has higher capacity
  - No media replacement
- Even without regeneration, lifecycle cost of resin system is lower, depending upon PFAS mix
- Pease full-scale system scheduled to start up this fall
Pease AFB IX Treatment, Regen, & Recovery Systems

IX Resin System

In-vessel IX Resin Regeneration System

Distillation Regeneration Recovery System

A presentation by Wood.
Multi-Media Bench-Scale Trials

Study Results

Illustrative curves for GAC and IX media for total PFAS from site-specific groundwater

<table>
<thead>
<tr>
<th>Breakthrough (C/C₀)</th>
<th>Mass Treated (mg/g)</th>
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<tbody>
<tr>
<td>GAC lowest initial leakage due to longer EBCT</td>
<td></td>
</tr>
<tr>
<td>Steep GAC curve</td>
<td></td>
</tr>
<tr>
<td>GAC (10 min EBCT)</td>
<td></td>
</tr>
<tr>
<td>Shallow IX curves</td>
<td></td>
</tr>
<tr>
<td>Non regenerable IX (2 min EBCT)</td>
<td></td>
</tr>
</tbody>
</table>

| Regenerable IX (2 min EBCT) |
| GAC (10) |
| PFBA |
| Shallow IX |
| GAC lowest initial leakage due to |
| Non regenerable IX |

Note: Site-specific pilot testing recommended to determine media performance
Focus Areas - Water Treatment R&D

- **Electrochemical Treatment/Destruction**
  - Perchlorate byproduct

- **Sonolytic Treatment/Destruction**
  - Equipment up time challenges, duplicate infrastructure required?

- **Plasma Treatment/Destruction**
  - For direct treatment of low concentration PFAS
  - Destruction of concentrated PFAS in regenerant solution from Ion Exchange
Wood Plc - On-going Research and Development

Strategic Environmental Research and Development Program (SERDP) U.S. DoD Basic and Applied Research Program

Awarded: “Combined In Situ / Ex Situ Treatment Train for Remediation of PFAS Contaminated Groundwater”

Environmental Security Technology Certification Program (ESTCP) U.S. DoD Technology Demonstration and Validation

Awarded: “Removal and Destruction of PFAS and Co-Contaminants from Groundwater”
Ongoing R&D – PLASMA

✓ Plasma is an ionized gas consisting of a quasi-neutral mixture of neutral species, positive ions, negative ions, and electrons.

✓ Electrical discharge plasma formed directly in or above water makes use of OH radicals to oxidize and aqueous electrons to chemically reduce organic and inorganic compounds.

✓ Benefits of plasma-based water treatment:
  ✓ Wide variety of reactive chemical species (OH, $e_{aq}^-$, $e^-$, O, H, H$_2$O$_2$, O$_2$, HO$_2$).
  ✓ Physical effects such as generation of ultraviolet-range radiation (UV), shockwaves capable of inducing cavitation, and high temperatures capable of thermally decomposing molecules.
  ✓ No chemical additives are required.

A presentation by Wood.

Pictures: Plasma Research Laboratory, Clarkson University
Next Steps – Onsite destruction of high-C PFAS

Potential no-waste solution

Treatment of high C still bottom waste

A presentation by Wood
Plasma Formation

Plasma in argon gas contacting water

Courtesy of: Plasma Research Laboratory, Clarkson University

$S_l$ = liquid solute  $S_g$ = gas solute
Proactive Considerations - Is there a problem?

Evaluation of Vulnerabilities

- Develop a systematic approach to identifying and prioritizing potential PFAS sources
  - USEPA – PFAS usage listing (Feb. 2017)
  - National American Industrial Classification System (NCAIS)
  - Evaluate for landfills and/or registered tanks
  - Source location receptor evaluation

- Location prioritization and selection for further evaluation

- Measurement and validation of PFAS locations (FY2019)

A presentation by Wood.
Takeaways

✓ PFAS seem to be “everywhere”

✓ PFAS does not equal PFAS

✓ Developing technologies
  Destructive treatment technologies

✓ Treatability and pilot studies important

✓ “Treatment trains” should be considered

✓ Evaluate your vulnerabilities early and prioritize
Questions and General Discussion

Marc Soellner  
European PFAS Leader  
marc.soellner@woodplc.com  
+49 173 662 8936

Dave Woodward, V.P.  
Global PFAS Technical Director  
david.woodward@woodplc.com  
+1 717 659 0434

Shalene Thomas  
Global Emerging Contaminants Program Manager  
PFAS Work Group Leader  
shalene.thomas@woodplc.com  
+1 612 490 7606