In-Situ Stabilization of PFAS Contaminated Soils at Two Superfund Sites

Diana Bless, U.S. EPA, ORD; John McKernan, Sc.D., CIH; Ed Barth, Ph.D., PE, CIH; Carolyn Acheson, Ph.D.; Marc Mills, Ph.D.; Mark Johnson, PhD; Chunming Su, PhD; Diana Cutt; Robyn Henderek; Sharon Hartzell; U.S. EPA Region 2
Kavitha Dasu, Ph.D.; Ramona Iery, Ph.D.; Amy Dindal, PMP; Battelle Memorial Institute
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Outline

• What are PFAS?
• How are PFAS used?
• Where are they used?
• Production and transport
• Health effects and select U.S. regulatory activity
• Examination of treatment options
• What is solidification and stabilization
• Experimental background and methodology for studying sorbents for stabilization
What are PFAS?

- **Perfluorinated**
  
  Perfluorosulfonic Acids
  
  PFBS, PFHS, PFOS

  Perfluorocarboxylic Acids
  
  C₆ acid – C₁₂ acid
  
  PFOA C₈ acid

- **Polyfluorinated**
  
  Fluorotelomer Alcohols – produced chemical and manufacturing residual
  
  6:2, 8:2 and 10:2
More Examples of PFAS

• **Perfluoroalkyl Sulfonates**
  - PFBS \( n = 4 \)
  - PFPeS * \( n = 5 \)
  - PFHxS \( n = 6 \)
  - PFHpS \( n = 7 \)
  - PFOS \( n = 8 \)
  - PFNS * \( n = 9 \)
  - PFDS \( n = 10 \)

• **Fluorotelomer Sulfonates**
  - \( 4:2 \) FtS \( n = 4 \)
  - \( 6:2 \) FtS \( n = 6 \)
  - \( 8:2 \) FtS \( n = 8 \)

• **Perfluoroalkyl Carboxylates**
  - PFBA \( n = 4 \)
  - PFPeA \( n = 5 \)
  - PFHxA \( n = 6 \)
  - PFHpA \( n = 7 \)
  - PFOA \( n = 8 \)
  - PFNA \( n = 9 \)
  - PFDA \( n = 10 \)
  - PFuDA \( n = 11 \)
  - PFDaA \( n = 12 \)
  - PFTrA \( n = 13 \)
  - PTFteA \( n = 14 \)

• **Fluorotelomer Sulfonamides Amines**
  - \( 6:2 \) FtSaAm \( n = 6 \)
  - \( 8:2 \) FtSaAm \( n = 8 \)

• **Phosphate Esters**
  - \( n = 4,6,8 \)
How are PFAS used?

Physical and chemical properties:

- Oil and water repellence
- Thermal stability and temperature resistance
- Friction reduction

Products include:

- Coatings for textiles, paper, surfaces, and cookware
- Thermal resistant plastics
- Hydraulic fluids
Where are PFAS used?

Manufacturing
- Primary manufacturing of PFAS products
- Secondary manufacturing and industrial use
  - Textiles and papers – surface treatment to repel stains, oil, and water
  - Plastics – coatings, resins, and flame retardants
  - Metal Plating and Etching – corrosion prevention, mechanical wear prevention, fume suppressant, post-plating cleaner
  - Photolithography, semi-conductor – photoresists, etchants, wetting agents
  - Aqueous Film Forming Foams – fire suppression, fire training, flammable vapor suppression, and asphyxiation of diseased poultry CAFOs

Commercial and Consumer Use
- Textiles and paper products
- Hydraulic fluids
- Surface preparation agents - cleaning agents, polishes, paints, varnishes, dyes, and inks
- Medical Products
PFOS Production in 2000 by 3 M

- Firefighting foams: 3%
- Industrial surfactants, additives, and coatings: 10%
- Textile, leather, and carpet treatment: 37%
- Paper and packaging products: 41%
- Other: 9%

Schultz et al, 2003 Env Engr Sci
Transport in the environment

- Air and water discharges can carry PFAS contamination
- PFAS may deposit on soil and sediment which then become a source
- Previous remediation activities may affect transport at a site
- Mobility dependent on
  - Chain length
  - Geochemistry of water and soil and sediment, especially pH
  - Hydrology of the site
PFAS Health Effects

• PFOA and PFOS
  ▪ Low birth weights for infants
  ▪ Affects the immune and thyroid systems, cholesterol metabolism
  ▪ Kidney and testicular cancer

• Other PFAS
  ▪ Data gaps exist
  ▪ Cross Agency Human Health/Toxicity work group - gather information from literature and conduct studies
  ▪ Other parts of U.S. Govt. (ATSDR) evaluating PFAS toxicity
  ▪ Other nations (e.g., Australia) also evaluating PFAS toxicity
Levels of Concern

Selected Concentrations at Military Bases Sampled

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Ground Water/Surface Water</th>
<th>Soil/Sediment (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>US EPA</td>
<td>State X&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>PFOA</td>
<td>70 ng/L&lt;sup&gt;a&lt;/sup&gt;</td>
<td>400 ng/L</td>
</tr>
<tr>
<td>PFOS</td>
<td>70 ng/L&lt;sup&gt;a&lt;/sup&gt;</td>
<td>400 ng/L</td>
</tr>
<tr>
<td>PFBS</td>
<td>380 µg/L&lt;sup&gt;b&lt;/sup&gt;</td>
<td>-</td>
</tr>
</tbody>
</table>

<sup>a</sup> EPA 2016 “Drinking Water Health Advisory for Perfluorooctane Sulfonate (PFOS)”, EPA 2016 “Drinking Water Health Advisory for Perfluorooctanoic Acid (PFOA)”

<sup>b</sup> EPA 2016 Regional Screening Level. [https://www.epa.gov/risk/regional-screening-levels-rsls-generic-tables-may-2016](https://www.epa.gov/risk/regional-screening-levels-rsls-generic-tables-may-2016)

<sup>c</sup> EPA risk-based screening levels calculated using the EPA Regional Screening Level calculator at [https://epa-prgs.ornl.gov/cgi-bin/chemicals/csl_search](https://epa-prgs.ornl.gov/cgi-bin/chemicals/csl_search). (US EPA, OLEM)

<sup>d</sup> State X. 2016.
Why Examine PFAS Treatment Options?

• The problem seems insurmountable!
  – Industrial societies have used PFAS compounds since the 1940s-50s
  – They don’t degrade substantially when released into the environment
  – Health implications – Prior slide on Levels of Concern
  – PFAS compounds are found in an ever increasing number of sites and media

• Treatment options
  – A number of treatment options have been suggested, but few are proven for use in the number of media found to be impacted
    • RO, activated carbon, and anion exchange resins are being used successfully to treat for PFAS in drinking water
  – Other media such as solids (soils and sediments) not studied thoroughly
PFAS Stabilization Literature Review

- Review of soil sorption technologies was conducted and published in The Military Engineer, Jan-Feb 2018 issue

- Literature review further indicated promise for the concept of binders to solidify PFAS in soil and sediment

Solidification/Stabilization Technology Application

- Solidification and stabilization (S/S) utilized at a number of Superfund contaminated sites since the program’s inception
- Process where contaminated soil or sediment are ‘contained’ within a low-porosity matrix to reduce or eliminate leaching
- Immobilizes and encapsulates contaminants (does not destroy)
- Certain refuse materials from industrial processes can be ‘beneficially reused’ when concrete is used in the S/S process (e.g., fly ash)
- Low-porosity of treated, stabilized matrix keeps contaminants in the matrix and out of
  - Soils
  - Sediments
  - Surface water
  - Ground water
Experimental Approach for Testing Sorbents for S/S

Task 1
Task 1a Identify sorbents
Task 1b Sorbent Characterization

5 Sorbents plus control for initial screening

Task 2 (using PFAS mix)
Task 2a Sorbent Screening Kinetic study (5 sorbents plus Ottawa sand as control)
Task 2b Batch Sorption (1 sorbent) (out of 5 sorbents tested in Task 2a)

1 Sorbent selected for soil treatability study

Task 3 (using PFAS mix)
Task 3a Physico-chemical properties of 2 PFAS-contaminated field soils
Task 3b Soil-Sorbent Treatability Studies using SPLP protocol in 2 PFAS-contaminated field soils plus Ottawa sand control
Sorbent Screening Kinetics Study

5 sorbents selected

5.0 mg: 50 mL sorbent to solution 0.01 M NaCl background electrolyte

Triplicates for all treatments including blanks and controls

Spike PFAS target analytes Initial conc. 500 µg L⁻¹

Sample dilution Surrogates & Internal standard spiked

Analysis on LC-MS/MS

Shaked at 125 rpm, 23±1°C and sampled over 0-20 d
Analytical Method and List of Six Native Analytes

- AB Sciex QTRAP 5500 Triple Quadrupole MS
- LC equipped with PEEK™ tubing and solvent delay column
- Negative electrospray ionization mode with MRM
- Column: Kinetex 2.6 μm C18 100 A 50 x 4.6 mm
- Run time: 10 minutes
- Quantitation Method: Isotope Dilution
- Dark blue – tested in kinetics studies

<table>
<thead>
<tr>
<th>Native Analyte</th>
<th>Mass-labelled Surrogates</th>
<th>Internal Standards</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFBA</td>
<td>13C4-PFBA</td>
<td>13C3-PFBA</td>
</tr>
<tr>
<td>PFHxA</td>
<td>13C5-PFHxA</td>
<td>13C2-PFOA</td>
</tr>
<tr>
<td>PFOA</td>
<td>13C8-PFOA</td>
<td>13C2-PFOA</td>
</tr>
<tr>
<td>PFNA</td>
<td>13C9-PFNA</td>
<td>13C2-PFOA</td>
</tr>
<tr>
<td>PFBS</td>
<td>13C3-PFBS</td>
<td>13C4-PFOS</td>
</tr>
<tr>
<td>PFOS</td>
<td>13C8-PFOS</td>
<td>13C4-PFOS</td>
</tr>
</tbody>
</table>
Sorbent Screening Kinetics Testing

**PFASs Tested**
- PFHxA
- PFOA
- PFNA
- PFBS
- PFOS

**5 Selected Sorbents**
- Activated Carbon
- Biochar
- Fe amended biochar
- Trade name mineral binder 1 (B1)
- Trade name mineral binder 2 (B2)
  * Ottawa sand control
Sorbent Screening Kinetics Testing

Tested equilibrium concentrations (Isotherm/Partitioning) for all 5 sorbents
- Prepared solution of all 5 PFASs
- Added equal amount of solution to each of the 5 sorbents
- Determined concentrations of 5 PFASs left in solution after set time periods (2 hrs to > 400 hrs)
- B2 equilibrated after 24 hrs
- Others equilibrated at 120 hrs (5 days)
Sorbent Screening Kinetics Testing

Sorbents performed differently among the 5 PFASs tested:
- Surface area (BET and micropore) or Pore volume do not fully elucidate results
- pH, surface charge, hydrophobicity or other physicochemical effects may help in understanding results
- Better understanding of performance characteristics needed

<table>
<thead>
<tr>
<th>Sorbents</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Act. Carbon</td>
<td>6.2</td>
</tr>
<tr>
<td>Biochar</td>
<td>7.0</td>
</tr>
<tr>
<td>Fe-Biochar</td>
<td>4.6</td>
</tr>
<tr>
<td>B1</td>
<td>5.2</td>
</tr>
<tr>
<td>B2</td>
<td>5.2</td>
</tr>
<tr>
<td>Ottawa Sand</td>
<td>4.7</td>
</tr>
</tbody>
</table>
Next Steps

- Continue reviewing Laboratory Isotherm/Partitioning study results
- Select sorbent for use in solidifying/stabilizing (S/S) two contaminated site soils from PFAS-contaminated sites (EPA Region 2 and EPA Region 8)
- Conduct EPA Synthetic Precipitation Leaching Procedure (SPLP) on these two S/S soils
- Analyze all data and prepare final technical report summarizing results of the tested sorbents to stabilize PFAS-contaminated field soils.