A Green and Practical Approach for Removing PFAS from Contaminated Environments

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What are PFAS?

~ 3000-5000 PFAS

Polymer PFAS
Non-polymer PFAS

Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS)

Perfluoroalkyl and Polyfluoroalkyl Substances

Perfluoroalkyl acids (PFAAs)

Perfluoroalkyl carboxylic acids (PFCAs) and Perfluoroalkyl sulfonic acids (PFSAs)
# History and use of PFAS

## Preparation, Discovery and Manufacturing History of Select PFAS

<table>
<thead>
<tr>
<th>PFAS</th>
<th>Development Time Period</th>
<th>Pre-Invention of Chemistry / Initial Chemical Synthesis / Production</th>
<th>Commercial Products Introduced and Used</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTFE</td>
<td>Invented</td>
<td>Non-Stick Coatings</td>
<td>U.S. Reduction of PFOS, PFOA, PFNA (and other select PFAS³)</td>
</tr>
<tr>
<td>PFOS</td>
<td>Initial Production</td>
<td>Stain &amp; Water Resistant Products</td>
<td>Architectural Resins</td>
</tr>
<tr>
<td>PFOA</td>
<td>Initial Production</td>
<td>Protective Coatings</td>
<td>Predominant form of firefighting foam</td>
</tr>
<tr>
<td>PFNA</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fluorotelomers</td>
<td></td>
<td>Firefighting Foams</td>
<td></td>
</tr>
<tr>
<td>Dominant Process ³</td>
<td>Electrochemical Fluorination (ECF)</td>
<td></td>
<td>Fluoro-telomerization (shorter chain ECF)</td>
</tr>
</tbody>
</table>

### Notes:
1. This table includes fluoropolymers, PFAAs, and fluorotelomers. PTFE (polytetrafluoroethylene) is a fluoropolymer. PFOS, PFOA, and PFNA (perfluoronoanoic 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:
Detection and regulation

• Organic fluorine compounds were first detected in human serum in 1960s.

• In 2006, EPA invited eight major leading companies in the PFAS industry to join in a 2010/2015 PFOA global stewardship program.

• In 2009, US EPA: 400 parts per trillion (ppt) and 200 ppt for PFOA and PFOS, respectively

• In May 2016, US EPA updated drinking water guideline for PFOS and PFOA: lifetime health advisory, a max. 70 ng/L, separately or combined.

• New Jersey: Sept 4, 2018, MCL for PFNA of 13 ng/L; March 13, 2019, an interim specific GW quality standard for PFOA and PFOS, each at 10 ng/L.
Emerging awareness

Figure 3-1. Emerging awareness and emphasis on PFAS occurrence in the environment
(Source: J. Hale, Kleinfelder, used with permission)

Interstate Technology Regulatory Council (ITRC): History and Use of Per- and Polyfluoroalkyl Substances (PFAS), 2017.
Exposure to PFAS

Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS)

Frequently Asked Questions

What are PFAS?
Perfluoroalkyl and polyfluoroalkyl substances (PFAS) are a large group of manufactured chemicals that have been used in industry and consumer products worldwide since the 1950s.
- PFAS do not occur naturally, but are widespread in the environment.
- PFAS are found in people, wildlife, and fish at the top of the food chain.
- Some PFAS can stay in people’s bodies a long time.
- Some-PFAS break down slowly in the environment.

How can I be exposed to PFAS?
PFAS contamination may be in drinking water, food, indoor dust, some consumer products, and workplace. Most non-water exposure occur through thinking contaminated water or eating food that contains PFAS.
- Food packaging materials
- Nonstick cookware
- Antireflection coatings
- Water-resistant clothing
- Cleaning products
- Paints, varnishes, and sealants
- Firefighting foam
- Some cosmetics

How can I reduce my exposure to PFAS?
PFAS are present in hundreds of products and in the environment (so water, soil, etc.). If you prefer to avoid PFAS exposure altogether, you need to know sources of PFAS contamination, you can take steps to reduce your risk of exposure.
- If your drinking water contains PFAS, above the THL Lifetime Health Advisory, consider using an alternative or treated water source for any activity in which you might come into contact with PFAS:
  - drinking
  - food preparation
  - cooking
  - brushing teeth, and
  - preparing infant formula.
- Check if fish advisories for water bodies where you fish.
- Follow fish advisories that tell people to eat small to medium size fish from waterways contaminated with PFAS.
- Research has shown that the benefits of eating fish, so continue to eat fish from safe sources part of your healthy diet.


PFAS contaminated sites close to Albany, NY

Specific industries:
- St Gobain Performance Plastics, Honeywell at Hoosick Falls: PFOA, PFBA, PFHxA, PFHpA, PFPeA, PFNA, PFOS
- Taconic Plastics at Town of Petersburgh, PFOA dominant

Use of Aqueous Film Forming Foam (AFFF)
- Stewart Air National Guard Base, DOD, City of Newburgh, PFOS and many other PFAS

http://www.dec.ny.gov/chemical/108831.html
PFOA in contaminated aquifer

https://www.dec.ny.gov/docs/administration_pdf/mccdatasummary.pdf
How to remove PFAS?

PFAS remediation technologies

Non-destructive

- Sorption
  - Activated carbon, Resins, Polymers, Nanomaterials, Minerals, Biochar
- Coagulation/flocculation
  - Conventional coagulants, Specialty coagulants, Electrocoagulation
- Membrane filtration
  - RO, Nanofiltration, Membrane filtration, Microfiltration, Electrodialysis

Destructive

- Chemical reaction
  - Ozone, Sonochemical, electrochemical, metal, thermochemical, plasma, photolysis
- Biodegradation
  - Aerobic, Anaerobic, pure strains, mixed community
Phytoremediation – plant-microbe-soil interactions

Truua et al., Phytoremediation And Plant-Assisted Bioremediation In Soil And Treatment Wetlands: A Review. The Open Biotechnology Journal, Volume 9, 2015
**Juncus effusus – hydroponic experimental design**

<table>
<thead>
<tr>
<th>Plant</th>
<th>Conc. range (µg/L)</th>
<th>Harvest time (days)</th>
<th>Replicates</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yes</td>
<td>0</td>
<td>21</td>
<td>3</td>
<td>No PFAS control</td>
</tr>
<tr>
<td>Yes</td>
<td>1x</td>
<td>7</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Yes</td>
<td>1x</td>
<td>14</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>Yes</td>
<td>1x</td>
<td>21</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>Yes</td>
<td>10x</td>
<td>7</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Yes</td>
<td>10x</td>
<td>14</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Yes</td>
<td>10x</td>
<td>21</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>No</td>
<td>10x</td>
<td>21</td>
<td>6</td>
<td>No plant control</td>
</tr>
<tr>
<td>No</td>
<td>10x</td>
<td>21</td>
<td>3</td>
<td>With sodium azide (8 mM)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>PFAS</th>
<th>Abbr.</th>
<th>Designed Conc. 1x (µg/L)</th>
<th>Designed Conc. 10x (µg/L)</th>
<th>Real Conc. in each bottle 1x (µg/L)</th>
<th>Real Conc. in each bottle 10x (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perfluoropentanoic acid</td>
<td>PFPA (C5)</td>
<td>66</td>
<td>660</td>
<td>76.44±6.30</td>
<td>604.46±62.83</td>
</tr>
<tr>
<td>Perfluorobutanesulfonic acid</td>
<td>PFBS (C4)</td>
<td>110</td>
<td>1100</td>
<td>115.00±7.61</td>
<td>1172.28±113.83</td>
</tr>
<tr>
<td>Perfluorohexanoic acid</td>
<td>PFHxA (C6)</td>
<td>120</td>
<td>1200</td>
<td>115.29±8.70</td>
<td>1183.03±96.59</td>
</tr>
<tr>
<td>Perfluoroheptanoic acid</td>
<td>PFHpA (C7)</td>
<td>75</td>
<td>750</td>
<td>80.40±7.25</td>
<td>810.31±73.16</td>
</tr>
<tr>
<td>Perfluorohexanesulfonic acid</td>
<td>PFHxS (C6)</td>
<td>290</td>
<td>2900</td>
<td>272.19±20.20</td>
<td>2876.20±267.57</td>
</tr>
<tr>
<td>Perfluorooctanoic acid</td>
<td>PFOA (C8)</td>
<td>250</td>
<td>2500</td>
<td>288.72±25.29</td>
<td>3065.86±144.08</td>
</tr>
<tr>
<td>Perfluorooctanesulfonic acid</td>
<td>PFOS (C8)</td>
<td>4300</td>
<td>43000</td>
<td>4104.59±466.43</td>
<td>44088.64±3822.62</td>
</tr>
</tbody>
</table>
Experimental procedure

- Mesocosms were established in a greenhouse.
- Plants were harvested on day 7, 14, and 21.
- For PFAS analysis, roots and shoots are separated, freeze-dried and subject to extraction and analysis by LC/MS/MS.
- For stress study, fresh roots and shoots were separated and homogenized on ice and subject to analysis of H₂O₂ content, activities of superoxide dismutase (SOD) and catalase (CAT).

## Optimized LC/MS/MS parameters for target PFAAs

<table>
<thead>
<tr>
<th>Compound</th>
<th>Retention time (min)</th>
<th>Quantitation transition (m/z)</th>
<th>Collision energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFPA</td>
<td>7.60</td>
<td>263→219.0</td>
<td>12</td>
</tr>
<tr>
<td>PFBS</td>
<td>8.78</td>
<td>299.0→80.0</td>
<td>40</td>
</tr>
<tr>
<td>PFHxA</td>
<td>8.57</td>
<td>313.0→269.0</td>
<td>12</td>
</tr>
<tr>
<td>PFHpA</td>
<td>9.40</td>
<td>363.0→319.0</td>
<td>13</td>
</tr>
<tr>
<td>PFHxS</td>
<td>10.42</td>
<td>399.0→80.0</td>
<td>40</td>
</tr>
<tr>
<td>PFOA</td>
<td>10.18</td>
<td>413.0→369.0</td>
<td>13</td>
</tr>
<tr>
<td>PFOS</td>
<td>11.98</td>
<td>499.0→80.0</td>
<td>40</td>
</tr>
<tr>
<td>13C-PFHxA</td>
<td>8.57</td>
<td>315.0→270.0</td>
<td>12</td>
</tr>
<tr>
<td>13C-PFOA</td>
<td>10.18</td>
<td>415.0→370.0</td>
<td>13</td>
</tr>
<tr>
<td>13C-PFOS</td>
<td>11.98</td>
<td>503.0→80</td>
<td>40</td>
</tr>
</tbody>
</table>
Plant growth
PFAS mass recovery
Results – Plant uptake

Variable | Factor | p value |
--- | --- | --- |
PFPA conc. in shoots | TimePoint | <0.001*** |
| Conc. | <0.001*** |
| TimePoint × Conc. | 0.113 |
PFHS conc. in shoots | TimePoint | <0.001*** |
| Conc. | <0.001*** |
| TimePoint × Conc. | 0.045* |
PFHxA conc. in shoots | TimePoint | <0.001*** |
| Conc. | <0.001*** |
| TimePoint × Conc. | <0.001*** |
PFHpA conc. in shoots | TimePoint | 0.036* |
| Conc. | <0.001*** |
| TimePoint × Conc. | 0.104 |
PFHxS conc. in shoots | TimePoint | 0.191 |
| Conc. | <0.001*** |
| TimePoint × Conc. | 0.102 |
PFDA conc. in shoots | TimePoint | <0.001*** |
| Conc. | <0.001*** |
| TimePoint × Conc. | 0.001*** |
PFOS conc. in shoots | TimePoint | 0.013* |
| Conc. | <0.001*** |
| TimePoint × Conc. | 0.287 |
Bioconcentration factor (BCF) and translocation factor (TF)
PFAAs removal efficiency
Correlation between carbon chain length of PFAAs and translocation factors (TF)
Correlation between logKow and logBCF of PFAAs
Plant response

[Graphs showing plant response metrics such as H_2O_2 level, SOD activity, and CAT activity for shoots and roots at Day-14 and Day-21 with control, 1x, and 10x treatments.]

Legend:
A > B > C > D
A indicates the highest value, followed by B, then C, and D.
Results

- Approximately 11.4% of spiked PFAAs were removed by *J. effusus* when it was exposed to PFAAs at a total of 4.635 mg/L for 21 days.
- Except PFOS, the other six PFAAs had higher concentrations in the shoots than those in the roots.
- Accumulation in shoots increased with decreased carbon-chain length.
- No visible impacts to plant growth was observed.
- Exposure to PFAAs stimulated anti-oxidative defense system in *J. effusus* shoots but inhibited the superoxide dismutase (SOD) and catalase (CAT) activities and damaged the anti-oxidative defense system in *J. effusus* roots.
Further studies

• Since this study was performed in December with a daylight time of < 9 hours, it would be interesting to evaluate plant uptake in summer.
• Plant uptake with a longer duration needs to be investigated.
• Real PFAS-contaminated water needs to be studied considering the possible presence of other non-PFAS compounds.
• Other plant species needs to evaluated for PFAS remediation.
• Plant-microbe-soil interactions deserve to be studied.
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