THE EMERGING ISSUE
PFAS POLY- AND PERFLUOROALKYL SUBSTANCES

Big Picture, Challenges and Solutions

August 2016

Ian Ross Ph.D.
ARCADIS
Contents

PFAS News
PFAS Uses & History
PFAS Chemistry
Exposure
Regulatory Evolution
Analytical Challenges / Advanced Analytical Solutions
Fate and Transport / Site Conceptual Model
Remediation Options
Case Study
PFAS comprise a group of thousands of man-made chemicals that have been manufactured in bulk quantities and used for various applications since the 1940s.

PFAS are commonly found as a man-made chemical class measured in human blood\(^1\).

PFAS have been used in a wide range of industrial applications and commercial and consumer products such as textile coatings, non-stick cookware, electronics, mist suppressants, and firefighting foams.

There is dramatically increasing regulatory concern over PFAS worldwide.

Some PFAS are extremely persistent, bio accumulative, and toxic and thus restricted under the Stockholm Convention and classed as persistent organic pollutants (POPs).

Many PFAS are not detected by commercial analytical methods.

PFAS do not biodegrade and are highly mobile in groundwater systems, as plumes can travel tens of miles.

Many industries are now showing concern over the potential threat PFAS pose to drinking water sources.

\(^1\) Karrman et al, Chemosphere 64 (2006) 1582–1591
PFAS News 2015 / 2016

Detections of PFAS in drinking water has caused spiraling regulatory concern
PFAS Sources

- Firefighting Foams
- Metal Plating
- Textiles
- Electronics
- Photography
- Paper Coatings
- Paints
- Hydraulic Fluids
Landfill leachate as sources of PFAS

The very wide and varied use of PFAS means there are many potential sources for release into the environment.

Many consumer goods containing PFAS will now be in landfills.

As PFAS do not biodegrade, they are expected to be present in leachates.
Potential Sources of PFAS Contamination

*Most cannot be detected by laboratory analysis

© Arcadis 2016

Property of Arcadis, all rights reserved
PFAS - Properties and Implications

PFAS plumes are generally longer as PFAS are generally:

- Highly soluble
- Low $K_{oc}$
- Recalcitrant – extreme persistence
- Mostly Anionic

<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 (@20-25°C), mg/L</td>
<td>0.0027</td>
<td>3400 – 9500</td>
<td>519</td>
<td>1100</td>
<td>1780</td>
</tr>
<tr>
<td>Vapor Pressure (@25°C), mmHg</td>
<td>4.05x10^{-5}</td>
<td>0.5-10</td>
<td>2.48x10^{-6}</td>
<td>77.5</td>
<td>97</td>
</tr>
<tr>
<td>Henry's Constant, atm-m^3/mol</td>
<td>4.6x10^{-3}</td>
<td>1.01x10^{-4}</td>
<td>3.05x10^{-9}</td>
<td>0.01</td>
<td>0.0056</td>
</tr>
<tr>
<td>Log $K_{oc}$</td>
<td>5 – 7</td>
<td>2.06</td>
<td>2.57</td>
<td>2.473</td>
<td>2.13</td>
</tr>
</tbody>
</table>
Perfluorinated compounds (PFCs)

- Perfluorinated Compounds (PFCs) generally are the Perfluoroalkyl acids (PFAAs)
- PFAAs include:
  - Perfluoralkyl carboxylates (PFCAs) e.g. PFOA
  - Perfluorooalkyl sulfonates (PFSAs) e.g. PFOS
  - Perfluorooalkyl phosphinic acids (PF Pi S); perfluorooalkyl phosphonic acids (PF Pi As)
- There are many PFAAs with differing chain lengths, PFOS and PFOA have 8 carbons (C8) - octanoates

Perfluoroalkyl Sulfonates

<table>
<thead>
<tr>
<th>Chain Length</th>
<th>PFBS</th>
<th>PFPeS</th>
<th>PFHxS</th>
<th>PFHpS</th>
<th>PFOS</th>
<th>PFNS</th>
<th>PFDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>C0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C8</td>
<td>PFBA</td>
<td>PFPeA</td>
<td>PFHxA</td>
<td>PFHpA</td>
<td>PFOS</td>
<td>PFNS</td>
<td>PFDS</td>
</tr>
<tr>
<td>C9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C11</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C12</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C13</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C14</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Zwitterionic, Cationic, and Anionic Fluorinated Chemicals in Aqueous Film Forming Foam Formulations and Groundwater from U.S. Military Bases by Nonaqueous Large-Volume Injection HPLC-MS/MS

Will J. Becke, Thomas C. Dry, and Jennifer A. Field

PFAAs totally resist biodegradation & biotransformation so are extremely persistent
Perfluorinated Compounds in Consumer Products

- Historical focus has mainly been on PFOA and PFOS, but PFAS-containing products contain a mixture of differing chain length PFAAs.
- In this study C5 to C12 perfluorinated carboxylates (PFCA) are detected in PFOA (C8) containing consumer products.
- Similar diversity of PFAA chain lengths may be expected in other PFAS-containing products and PFAS-contaminated areas.

Data from Guo et al. 2009, U.S. EPA; Polyfluorinated substances and perfluorinated sulfonates were not measured.
Polyfluorinated Compounds - Precursors

Thousands of polyfluorinated precursors to PFAAs have been commercially synthesized for bulk products.

The common feature of the precursors is that they will biotransform to make PFAA’s as persistent “dead end” daughter products.

PFAS do not biodegrade i.e. mineralise.

Some precursors are fluorotelomers.

Some are cationic (positively charged) or zwitterionic (mixed charges) – this influences their fate and transport in the environment.

Cationic / zwitterionic PFAS tend to be less mobile than anionic PFAAs and so can potentially be retained longer in “source zones”.

Environmental fate and transport will be complex as PFAS comprise multiple chain lengths and charges.
Diversity of PFAS Characterised in AFFF – to Date.
PFOS or PreFOS? Are perfluoroctane sulfonate precursors (PreFOS) important determinants of human and environmental perfluoroctane sulfonate (PFOS) exposure?†

Jonathan W. Martin,⁎⁎ Brian J. Asher,⁎ Sanjay Becsoom,⁎ Jonathan P. Benskin⁎ and Matthew S. Ross⁎

(VII)

FOSSAAs
a. R=methyl, N-methyl perfluoroctanesulfonamidoacetate, NMeFOSAA
b. R=ethyl, N-ethyl perfluoroctanesulfonamidoacetate, NEtFOSAA
c. R=H; Perfluoroctanesulfonamidoacetate, FOSAA

(VIII)

FCSE Phosphates (di-ester shown)
a. R=methyl, d-NEtFOSA Phosphate
b. R=ethyl, di-NEtFOSA phosphate (mono- and tri- also manufactured)

(IX)

FCSE Acrylate Esters
a. R=methyl, R'=H, NMeFOSA acrylate
b. R=ethyl, R'=H, NEtFOSA acrylate
c. R=methyl, R'=methyl, NMeFOSA methacrylate
d. R=ethyl, R'=methyl, NEtFOSA methacrylate

(III) Perfluoroctanesulfonamido propanium salts

(IV) Perfluoroctanesulfonamido alkyl amine oxide salts
Biodegradation of $N$-Ethyl Perfluoroctane Sulfonamido Ethanol (EtFOSE) and EtFOSE-Based Phosphate Diester (SAmPAP Diester) in Marine Sediments

Jonathan P. Benskin, Michael G. Ilonomou, Frank A. P. C. Gobas, Timothy H. Begley, Million B. Woudneh, and John R. Cosgrove

Useful Graphics

$25^\circ$  $t_{1/2} = 44$ days

ARCADIS
Design & Consultancy for natural and built assets

Property of Arcadis, all rights reserved
Aerobic Precursor Biotransformation to PFAAs

PFAS do not biodegrade – i.e. mineralize, they biotransform and many parent or intermediate compounds are not detected by conventional analytical methods.

© Arcadis 2016

Property of Arcadis, all rights reserved
## PFAS Exposure, Distribution, and Elimination in Humans

### Exposure
- **Most exposure** is likely from ingestion of contaminated food or water.
- Exposure can also come from:
  - Breast milk
  - Air
  - Dust (especially for children)
  - Skin contact with various consumer products

### Distribution
- PFAS bind to proteins, not to fats.
- Highest concentrations are found in blood, liver, kidneys, lung, spleen and bone marrow.
- Long chain PFAS such as PFOS, PFHxS and PFOA have bioaccumulative properties.
- Shorter chain PFAS generally have a lower bioaccumulation potential, although there may be some exceptions.

### Elimination
- Elimination of PFOS, PFHxS and PFOA from the human body takes some years, whereas elimination of shorter chain PFAS are in the range of days.
- Apart from chain length, blood half-lives of PFAS are also dependent on gender, PFAS-structure (branched vs. straight isomers), PFAS-type (sulfonates vs. carboxylates) and species.
- Elimination mainly by urine.

Member State Legislation: November 2015. The EQS shall be met by End of 2027.

Bioaccumulation

The PFAS web


© Arcadis 2016

Property of Arcadis, all rights reserved
Toxicity for Humans

- Exposure mainly by ingestion
- PFAS bind to proteins (not to lipids / fats) and are mainly detected in blood, liver and kidneys
- Study with 656 children demonstrated elevated exposure to PFOS & PFOA are associated with reduced humoral immune response [1]
- Large epidemiological study of 69,000 persons found probable link between elevated PFOA blood levels and the following diseases: high cholesterol, ulcerative colitis, thyroid disease, testicular cancer, kidney cancer and preeclampsia –C8 science panel [2]
- European Food Safety Authority (2008):) established a TDI for PFOS and PFOA of 150 ng/kg bw/day and 1,500 ng/kg bw/day
- USEPA has selected a Reference Dose for PFOS and PFOA of 20 ng/kg bw/day (May 2016)


Bioacumulation Potential

Table 3: Elimination half-life ($t_{1/2}$, days) of perfluorobutanoic acid (PFBA), perfluorobutane sulfonic acid (PFBS), perfluorohexanoic acid (PFHxA), perfluorohexane sulfonic acid (PFHxS), perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) in serum in rat, monkey and human. Figures are derived from the Refs. 15,83-94

<table>
<thead>
<tr>
<th></th>
<th>$t_{1/2}$, days</th>
<th>PFBA</th>
<th>PFBS</th>
<th>PFHxA</th>
<th>PFHxS</th>
<th>PFOA</th>
<th>PFOS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rat</td>
<td>0.3</td>
<td>0.2</td>
<td>0.05–0.2</td>
<td>7</td>
<td>5</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>Monkey</td>
<td>2</td>
<td>4</td>
<td>1</td>
<td>100</td>
<td>21</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>Human</td>
<td>3–4</td>
<td>26</td>
<td>&lt;28</td>
<td>3000</td>
<td>1000</td>
<td>1500</td>
<td></td>
</tr>
</tbody>
</table>

OECD/UNEP Global PFC Group

Synthesis paper on per- and polyfluorinated chemicals (PFCs)
Evolving Regulatory PFAS Values – Overview

Drinking, Surface and Ground Water (µg/l)

**COMPOUND REGULATED AND CHAIN LENGTH KEY**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chain Length</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFOS</td>
<td>O=8</td>
</tr>
<tr>
<td>PFOA</td>
<td>O=8</td>
</tr>
<tr>
<td>PFBS</td>
<td>B=4</td>
</tr>
<tr>
<td>PFBA</td>
<td>B=4</td>
</tr>
<tr>
<td>PFPaA/S</td>
<td>Pe=5</td>
</tr>
<tr>
<td>PFHxA</td>
<td>Hx=6</td>
</tr>
<tr>
<td>PFHxS</td>
<td>Hx=6</td>
</tr>
<tr>
<td>PFHpA</td>
<td>Hp=7</td>
</tr>
<tr>
<td>PFOSA</td>
<td>O=8</td>
</tr>
<tr>
<td>PFNA</td>
<td>N=9</td>
</tr>
<tr>
<td>PFDA</td>
<td>D=10</td>
</tr>
</tbody>
</table>

**European Surface Waters (PFOS) 0.00065**

**Australian Surface Waters (PFOS) 0.00023**
### Evolving Regulatory PFAS Values

#### Drinking Water Criteria in µg/l in European Countries

<table>
<thead>
<tr>
<th></th>
<th>Denmark¹</th>
<th>Germany²</th>
<th>The Netherlands</th>
<th>Sweden³</th>
<th>U.K.⁴</th>
<th>Italy⁵</th>
<th>Australia</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFOS</td>
<td>(0.1)</td>
<td>(0.1)</td>
<td>0.53</td>
<td>(0.09)</td>
<td>0.3</td>
<td>0.03</td>
<td>0.5</td>
</tr>
<tr>
<td>PFOA</td>
<td>(0.1)</td>
<td>-</td>
<td>-</td>
<td>(0.09)</td>
<td>-</td>
<td>0.5</td>
<td>5</td>
</tr>
<tr>
<td>PFBS</td>
<td>(0.1)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PFBA</td>
<td>(0.1)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PFPeA</td>
<td>(0.1)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PFHxA</td>
<td>(0.1)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PFNA</td>
<td>(0.1)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PFDA</td>
<td>(0.1)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6:2 FTS</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

#### Drinking Water Criteria in µg/l U.S.⁶

<table>
<thead>
<tr>
<th></th>
<th>Minnesota</th>
<th>New Jersey</th>
<th>Vermont⁷</th>
<th>U.S. EPA⁸</th>
<th>Canada</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFOS</td>
<td>0.3</td>
<td>-</td>
<td>(0.02)</td>
<td>(0.07)</td>
<td>0.6</td>
</tr>
<tr>
<td>PFOA</td>
<td>0.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.2</td>
</tr>
<tr>
<td>PFBS</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>15</td>
</tr>
<tr>
<td>PFBA</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>30</td>
</tr>
<tr>
<td>PFPeA</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.2</td>
</tr>
<tr>
<td>PFHxA</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.2</td>
</tr>
<tr>
<td>PFNA</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.2</td>
</tr>
<tr>
<td>PFDA</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.2</td>
</tr>
</tbody>
</table>

### Groundwater Criteria in µg/l in European Countries

<table>
<thead>
<tr>
<th></th>
<th>Denmark¹</th>
<th>State of Bavaria⁹</th>
<th>State of Baden-Württemberg¹⁰</th>
<th>The Netherlands</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFOS</td>
<td>(0.1)</td>
<td>0.23/(0.3)</td>
<td>0.23/(0.3)</td>
<td>0.023*</td>
</tr>
<tr>
<td>PFOA</td>
<td>(0.1)</td>
<td>(0.3)</td>
<td>(0.3)</td>
<td>-</td>
</tr>
<tr>
<td>PFBS</td>
<td>(0.1)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PFBA</td>
<td>(0.1)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PFPeA</td>
<td>(0.1)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PFHxA</td>
<td>(0.1)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PFNA</td>
<td>(0.1)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PFDA</td>
<td>(0.1)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6:2 FTS</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

### Groundwater Criteria in µg/l in U.S.

<table>
<thead>
<tr>
<th></th>
<th>New Jersey</th>
<th>Texas, Residential</th>
<th>Soil Criteria in mg/kg in European Countries, U.S.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFOS</td>
<td>-</td>
<td>-</td>
<td>Denmark¹</td>
</tr>
<tr>
<td>PFOA</td>
<td>0.1</td>
<td>-</td>
<td>Norway</td>
</tr>
<tr>
<td>PFBS</td>
<td>-</td>
<td>-</td>
<td>The Netherlands</td>
</tr>
<tr>
<td>PFBA</td>
<td>-</td>
<td>-</td>
<td>Italy Resil Ind</td>
</tr>
<tr>
<td>PFPeA</td>
<td>-</td>
<td>-</td>
<td>Texas, Residential</td>
</tr>
<tr>
<td>PFHxA</td>
<td>-</td>
<td>-</td>
<td>Denmark</td>
</tr>
<tr>
<td>PFNA</td>
<td>-</td>
<td>-</td>
<td>Norway</td>
</tr>
<tr>
<td>PFDA</td>
<td>-</td>
<td>-</td>
<td>The Netherlands</td>
</tr>
<tr>
<td>6:2 FTS</td>
<td>-</td>
<td>-</td>
<td>Italy Resil Ind</td>
</tr>
</tbody>
</table>

#### Soil Criteria in mg/kg in European Countries, U.S.

<table>
<thead>
<tr>
<th></th>
<th>Denmark¹</th>
<th>Norway</th>
<th>The Netherlands</th>
<th>Italy Resil Ind</th>
<th>Texas, Residential</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFOS</td>
<td>(0.4)</td>
<td>0.1</td>
<td>0.0023</td>
<td>-</td>
<td>1.5</td>
</tr>
<tr>
<td>PFOA</td>
<td>(0.4)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.6</td>
</tr>
<tr>
<td>PFBS</td>
<td>(0.4)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.058</td>
</tr>
<tr>
<td>PFBA</td>
<td>(0.4)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>73</td>
</tr>
<tr>
<td>PFPeA</td>
<td>(0.4)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>150</td>
</tr>
<tr>
<td>PFHxA</td>
<td>(0.4)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5.1</td>
</tr>
<tr>
<td>PFNA</td>
<td>(0.4)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5.1</td>
</tr>
<tr>
<td>PFDA</td>
<td>(0.4)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.5</td>
</tr>
<tr>
<td>6:2 FTS</td>
<td>(0.4)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.76</td>
</tr>
<tr>
<td>PFHxS</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.96</td>
</tr>
<tr>
<td>PFPeS</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4.8</td>
</tr>
</tbody>
</table>

#### Notes:

1. \( \Sigma 12 \text{PFAS} = 0.100 \, \mu g/L \), includes PFBS, PFHxS, PFOS, PFOSA, 6:2 FTS, PFPeA, PFHpA, PFNA, PFDA.
2. \( \Sigma \text{PFOS and PFOA} = 0.100 \, \mu g/L \); Composite precautionary guidance value for long term exposure.
3. \( \Sigma 7 \text{PFAS} = 0.090 \, \mu g/L \), includes PFBS, PFHxS, PFOS, PFPeA, PFHxA, PFHpA, PFOA.
4. Tier 1 values.
5. \( \Sigma 8 \text{PFAS} = 0.500 \, \mu g/L \), includes PFHxS, PFPeA, PFHxA, PFPeS, PFPeS; Separate standards for PFBA, PFBS, PFOA.
6. Alaska Department of Environmental Conservation published chemical toxicity parameters to support development of PFOS and PFOA cleanup levels on May 15, 2016.
7. \( \Sigma \text{PFOS and PFOA} = 0.020 \, \mu g/L \).
8. \( \Sigma \text{PFOS and PFOA} = 0.070 \, \mu g/L \).
9. \( \Sigma \text{PFOS, PFOA, PFHxS} = 0.3 \, \mu g/L \).
10. \( \Sigma 12 \text{PFAS} < 1 \, \mu g/L \), includes PFBS, PFHxS, PFOS, PFOSA, 6:2 FTS, PFPeA, PFHpA, PFNA, PFDA; PFOS standard changes to 0.3 \, \mu g/L if multiple PFAS present.

Values in parentheses indicate the analytes are considered as a sum concentration.
ANALYTICAL TOOLS
Analytical Challenges

- PFAS from commercial products may comprise many thousands of individual perfluorinated and polyfluorinated compounds
- AFFF contained many hundreds of PFASs including polyfluorinated precursors to PFAAs
- Current conventional analytical methods (i.e. LCMSMS) only examine a small fraction of the compounds present (16 - 39 individual compounds)
- Microbes the attack the non-fluorinated of the PFAS precursor molecules making PFAAs as dead end daughter products, so precursors will form compounds (PFAAs) that are being regulated and persist
- The analytical costs to assess the concentration of each of these PFAS individually will be substantial as analytical standards for each one would be required
Advanced Analytical Techniques
Expanding analytical tool box to assess total PFAS

- **Total oxidizable precursor (TOP) Assay**
  - Initial LC-MS/MS analysis with re-analysis following oxidative digest
  - Detection limits to ~ 2 ng/L (ppt)
  - Commercially available in UK, Australia, under development in US

- **Particle-induced gamma emission (PIGE) Spectroscopy**
  - Isolates organofluorine compounds on solid phase extraction, measures total fluorine
  - Detection limits to ~ 15 ug/L (ppb) F
  - Commercially available in US

- **Adsorbable organofluorine (AOF)**
  - Isolates organofluorine compounds with activated carbon and measures F by combustion ion chromatography
  - Detection limits to ~ 1 ug/L (ppb) F
  - Commercially available in Germany, Australia

- **Time of Flight MS (LCQTOF) MS**
  - Identifies multiple precursors via mass ions capture and accurate mass estimation (to 0.0001 of a Dalton) to give empirical formulae (e.g. C_{10}F_{21}O_{3}N_{2}H_{4})
  - Semi quantitative
Total Oxidizeable Precursor Assay (TOP)

Oxidation of Precursors to PFAAs with OH•

PFSA Precursors

\[ \text{S}_2\text{O}_8^{2-} \rightarrow 2 \text{SO}_4^{2-} + \text{OH}^- \]

{pH > 11}

\[ \text{SO}_4^{2-} + \text{OH}^- \]

[85 °C]

Dilute Sample pH > 12

NaOH + K₂S₂O₈

8

PFCA Precursors

PFPA Precursors

Approach described in Houtz and Sedlak, *ES&T*, 2012

Property of Arcadis, all rights reserved
Figure 1. Average concentrations of perfluorinated sulfonates and carboxylates in AFFF formulations analyzed before (a) and after oxidation (b). Dates represent the years of manufacture of AFFF formulations analyzed in each category.
Total Oxidisable Precursor (TOP) Assay

Fire Training Area

**Soil Composite**
- 240% increase

**Groundwater Composite**
- 75% increase
TOP Assay – Fire Training Area

% Change in PFAS compounds Following TOP Assay
Soil Composite

© Arcadis 2016
Comparison of AOF & TOP Assay with AFFF Impacted Groundwater

\[ R^2 = 0.8034 \]
Poly- and perfluoroalkyl substances in wastewater: Significance of unknown precursors, manufacturing shifts, and likely AFFF impacts

Erika F. Houtz a, b, *, Rebecca Sutton c, June-Soo Park a, Margaret Sedlak c

Fig. 2. Molar percentage of measured precursors, unknown precursors, and total measured PFCAs, PFSAs, and PFPAAs in WWTP effluent samples. The concentration of unknown precursors is the total concentration of PFAAs generated upon oxidation, less the oxidation products expected from the precursors directly measured.
Advanced Analytical Tools are needed to understand the CSM
PFAS Groundwater Remediation

Evolving technologies

- Stronger anion exchange resins
- Precipitation
- Sonolysis
- Proprietary combinations of zeolites, GAC, clay
- Organoclays

PFAS Soil Remediation

- Excavation and landfill (landfill leachate will contain PFAS)
- Stabilization / Immobilization – cement / proprietary reagents
- Capping – prevent leaching
- Incineration, high temperatures (> 1,100 °C) are needed to cleave the stable C-F-bonds
PFAS Groundwater Remediation

- Granular activated carbon (GAC) can be effective in removing PFOS/PFOA, however sorption is low and competition occurs (much higher costs than for conventional contaminants)
- GAC shown to have 80x less sorptive capacity for PFOS vs BTEX
- GAC increasingly less effective as PFAS chain length diminishes
  - Breakthrough PFBA>PFHxA>PFOA>PFOS>PFHxS
- Column testing required to determine mass of GAC needed to treat PFAS
- GAC requirements are site specific:
  - Which PFASs are present
  - Competition from TOC, precursors and other contaminants

Alternative water treatment options

<table>
<thead>
<tr>
<th>Compound</th>
<th>M.W. (g/mol)</th>
<th>Aeration</th>
<th>Coagulation</th>
<th>Coagulation Flocculation Sedimentation Filtration</th>
<th>Conventional Oxidation (MnO₄, O₃, ClO₂, CLM, UV-AOP)</th>
<th>Anion Exchange (select resins tested)</th>
<th>Granular Activated Carbon</th>
<th>Nano Filtration</th>
<th>Reverse Osmosis</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFBA</td>
<td>214</td>
<td>assumed</td>
<td>assumed</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PFPeA</td>
<td>264</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PFHxA</td>
<td>314</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PFHpA</td>
<td>364</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PFOA</td>
<td>414</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PFNA</td>
<td>464</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PFDA</td>
<td>514</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PFBS</td>
<td>300</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PFHxS</td>
<td>400</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PFOS</td>
<td>500</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FOSA</td>
<td>499</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>assumed</td>
<td>assumed</td>
<td></td>
</tr>
<tr>
<td>N-MeFOSAA</td>
<td>571</td>
<td>assumed</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>assumed</td>
<td>assumed</td>
<td></td>
</tr>
<tr>
<td>N-EtFOSAA</td>
<td>585</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>assumed</td>
<td>assumed</td>
<td>assumed</td>
</tr>
</tbody>
</table>


- Conventional Treatment
  - > 90% removal
  - > 10%, < 90% removal
  - < 10% removal
  - unknown

- Specialized Treatment
Injecting GAC to Aquifers

- Distribution - clogging?
- GAC does not retain shorter chains as well as longer
- GAC has low binding capacity for PFOS/PFOA vs BTEX etc.
- Longevity of treatment
- PFAS don’t biodegrade so GAC will saturate and desorb mass, making a secondary source
- How is injected GAC removed when saturated?
Treatment of PFAS in Soils

Soil

- Excavation and disposal at approved landfill sites (lingering liabilities)
- High-temperature thermal incineration (1100 °C)
- Solidification and stabilization
- Containment through capping
- Soil washing (sands/gravels)
- Thermal Desorption?

Considerations:

- No final solution; concentrated in another phase (no degradation)
- Landfill leachate is not typically being evaluated for PFOS, and therefore may pose additional threats to groundwater quality
**Nanofiltration (NF)**

- Literature evidence high performance close to RO (>95%)
- May not be as effective against smaller species PFBS, and PFPeA
- The fouled membrane performed better than the virgin membrane (other literature find opposite performance)
- Organic matter may increase rejection at the membrane surface

### Table 3.4 PFAA percent rejection by bench-scale nanofiltration.

Molecular weights (g/mol) are listed below chemical names.

<table>
<thead>
<tr>
<th>Membrane/water</th>
<th>Pressure (psi)</th>
<th>Permeate Flow (ml/min)</th>
<th>Permeate Flux (L/m²-h)</th>
<th>J0¹</th>
<th>PPBA (214)</th>
<th>PPFPeA (264)</th>
<th>PPFixA (314)</th>
<th>PFtA (414)</th>
<th>PFNA (464)</th>
<th>PFDA (514)</th>
<th>PFBS (300)</th>
<th>PFHeS (400)</th>
<th>PFOS (500)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MRL (ng/L)</td>
<td>25</td>
<td>4.5</td>
<td>17</td>
<td>1</td>
<td>&gt; 94</td>
<td>&gt; 97</td>
<td>&gt; 95</td>
<td>&gt; 97</td>
<td>&gt; 98</td>
<td>&gt; 97</td>
<td>&gt; 99</td>
<td>&gt; 99</td>
<td>&gt; 99</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>9</td>
<td>33</td>
<td>1</td>
<td>&gt; 94</td>
<td>&gt; 97</td>
<td>&gt; 95</td>
<td>&gt; 97</td>
<td>&gt; 97</td>
<td>&gt; 99</td>
<td>&gt; 99</td>
<td>&gt; 99</td>
<td>&gt; 99</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>13.5</td>
<td>50</td>
<td>1</td>
<td>&gt; 94</td>
<td>&gt; 97</td>
<td>&gt; 95</td>
<td>&gt; 97</td>
<td>&gt; 98</td>
<td>&gt; 97</td>
<td>&gt; 99</td>
<td>&gt; 99</td>
<td>&gt; 99</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>16</td>
<td>59</td>
<td>1</td>
<td>&gt; 95</td>
<td>&gt; 97</td>
<td>&gt; 95</td>
<td>&gt; 97</td>
<td>&gt; 98</td>
<td>&gt; 97</td>
<td>&gt; 99</td>
<td>&gt; 99</td>
<td>&gt; 99</td>
</tr>
<tr>
<td></td>
<td>125</td>
<td>20.5</td>
<td>75</td>
<td>1</td>
<td>&gt; 94</td>
<td>&gt; 97</td>
<td>&gt; 95</td>
<td>&gt; 97</td>
<td>&gt; 98</td>
<td>&gt; 97</td>
<td>&gt; 99</td>
<td>&gt; 99</td>
<td>&gt; 99</td>
</tr>
<tr>
<td>AGW-Virgin</td>
<td>40</td>
<td>4.5</td>
<td>17</td>
<td>0.63</td>
<td>&gt; 95</td>
<td>&gt; 97</td>
<td>&gt; 95</td>
<td>&gt; 97</td>
<td>&gt; 98</td>
<td>&gt; 97</td>
<td>&gt; 99</td>
<td>&gt; 99</td>
<td>&gt; 99</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>9</td>
<td>33</td>
<td>0.71</td>
<td>&gt; 94</td>
<td>&gt; 97</td>
<td>&gt; 95</td>
<td>&gt; 97</td>
<td>&gt; 98</td>
<td>&gt; 97</td>
<td>&gt; 99</td>
<td>&gt; 99</td>
<td>&gt; 99</td>
</tr>
<tr>
<td></td>
<td>96</td>
<td>13.5</td>
<td>50</td>
<td>0.78</td>
<td>&gt; 94</td>
<td>&gt; 97</td>
<td>&gt; 95</td>
<td>&gt; 97</td>
<td>&gt; 98</td>
<td>&gt; 97</td>
<td>&gt; 99</td>
<td>&gt; 99</td>
<td>&gt; 99</td>
</tr>
<tr>
<td></td>
<td>110</td>
<td>16</td>
<td>59</td>
<td>0.91</td>
<td>&gt; 94</td>
<td>&gt; 97</td>
<td>&gt; 95</td>
<td>&gt; 97</td>
<td>&gt; 98</td>
<td>&gt; 97</td>
<td>&gt; 99</td>
<td>&gt; 99</td>
<td>&gt; 99</td>
</tr>
<tr>
<td></td>
<td>140</td>
<td>20.5</td>
<td>75</td>
<td>0.89</td>
<td>&gt; 94</td>
<td>&gt; 97</td>
<td>&gt; 95</td>
<td>&gt; 97</td>
<td>&gt; 98</td>
<td>&gt; 97</td>
<td>&gt; 99</td>
<td>&gt; 99</td>
<td>&gt; 99</td>
</tr>
<tr>
<td>AGW-Fouled</td>
<td>40</td>
<td>4.5</td>
<td>17</td>
<td>0.63</td>
<td>&gt; 95</td>
<td>&gt; 97</td>
<td>&gt; 95</td>
<td>&gt; 97</td>
<td>&gt; 98</td>
<td>&gt; 97</td>
<td>&gt; 99</td>
<td>&gt; 99</td>
<td>&gt; 99</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>9</td>
<td>33</td>
<td>0.71</td>
<td>&gt; 94</td>
<td>&gt; 97</td>
<td>&gt; 95</td>
<td>&gt; 97</td>
<td>&gt; 98</td>
<td>&gt; 97</td>
<td>&gt; 99</td>
<td>&gt; 99</td>
<td>&gt; 99</td>
</tr>
<tr>
<td></td>
<td>96</td>
<td>13.5</td>
<td>50</td>
<td>0.78</td>
<td>&gt; 94</td>
<td>&gt; 97</td>
<td>&gt; 95</td>
<td>&gt; 97</td>
<td>&gt; 98</td>
<td>&gt; 97</td>
<td>&gt; 99</td>
<td>&gt; 99</td>
<td>&gt; 99</td>
</tr>
<tr>
<td></td>
<td>110</td>
<td>16</td>
<td>59</td>
<td>0.91</td>
<td>&gt; 94</td>
<td>&gt; 97</td>
<td>&gt; 95</td>
<td>&gt; 97</td>
<td>&gt; 98</td>
<td>&gt; 97</td>
<td>&gt; 99</td>
<td>&gt; 99</td>
<td>&gt; 99</td>
</tr>
<tr>
<td></td>
<td>140</td>
<td>20.5</td>
<td>75</td>
<td>0.89</td>
<td>&gt; 94</td>
<td>&gt; 97</td>
<td>&gt; 95</td>
<td>&gt; 97</td>
<td>&gt; 98</td>
<td>&gt; 97</td>
<td>&gt; 99</td>
<td>&gt; 99</td>
<td>&gt; 99</td>
</tr>
<tr>
<td>DI-Virgin</td>
<td>25</td>
<td>5.5</td>
<td>20</td>
<td>1</td>
<td>&gt; 93</td>
<td>&gt; 97</td>
<td>&gt; 95</td>
<td>&gt; 97</td>
<td>&gt; 98</td>
<td>&gt; 97</td>
<td>97</td>
<td>&gt; 97</td>
<td>&gt; 99</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>7.5</td>
<td>28</td>
<td>1</td>
<td>&gt; 93</td>
<td>&gt; 97</td>
<td>&gt; 95</td>
<td>&gt; 97</td>
<td>&gt; 98</td>
<td>&gt; 98</td>
<td>98</td>
<td>&gt; 98</td>
<td>&gt; 99</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>12</td>
<td>44</td>
<td>1</td>
<td>&gt; 93</td>
<td>&gt; 97</td>
<td>&gt; 95</td>
<td>&gt; 97</td>
<td>&gt; 95</td>
<td>&gt; 97</td>
<td>96</td>
<td>&gt; 97</td>
<td>&gt; 99</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>16</td>
<td>59</td>
<td>1</td>
<td>&gt; 94</td>
<td>&gt; 97</td>
<td>&gt; 95</td>
<td>&gt; 97</td>
<td>&gt; 98</td>
<td>&gt; 98</td>
<td>96</td>
<td>&gt; 96</td>
<td>&gt; 99</td>
</tr>
<tr>
<td></td>
<td>125</td>
<td>19</td>
<td>70</td>
<td>1</td>
<td>&gt; 95</td>
<td>&gt; 97</td>
<td>&gt; 95</td>
<td>&gt; 97</td>
<td>&gt; 98</td>
<td>&gt; 98</td>
<td>95</td>
<td>&gt; 96</td>
<td>&gt; 99</td>
</tr>
</tbody>
</table>

¹ Normalized specific flux change where J0 is the specific permeate flux at time 0 (i.e. constant flux normalized to net driving pressure, ΔP).
Sonolysis - Summary

• Applying sound energy to treatment liquid.
• Ultrasonic frequencies (>20 kHz) are usually used (smaller bubbles).
• Mechanism appears to be thermal decomposition.
  • Ultrasound causes and collapses bubbles in water (cavitation)
  • High temperatures during cavitation (4000-1000K)
  • 400 million bubbles per second per litre (188m²/min surface area)!
  • May also create hydroxyl radical
  • Rate depends of frequency need to balance number of events vs. event energy
  • PFOA rate>PFOS rate, PFOS requires higher temperature to cleave head group
PerfluorAd

- Produced by Cornelsen (UK/Germany);
- Designed to help protect GAC by treating high concentrations (>20ppb) to extend GAC lifetime;
- Modified cellulose based polymer with quaternary ammonium salt at C6
- Adsorption by electrostatic and hydrophobic interactions
- Injected as a liquid into the water stream causing precipitation/filtration of PFAS as a sludge.
- Not intended as a reusable technology, sludge disposal costs
- A second stage with a conventional GAC filter is required to remove low concentrations.
Resin developed by DOW
Bench and field scale testing showed effective removal of PFAS from groundwater
Claims to be 4 to 8 times more effective than GAC for PFOS/PFOA
Regeneration with solvent/brine (proprietary process)
Pilot trial Pease AFB vs a GAC treatment train
- Shorter contact time than GAC
- Higher treatment rate than GAC
- Significantly better performance than GAC for long chain
- Short chain PFAS performance similar to GAC
Resins – Anion Exchange

Zaggia et al. Water Res. 2015 137-146

- Pilot scale studies using water with inorganic ions and a range of PFAS.
- Breakthrough
  - A600 72,000bv PFOS; 3,200bv PFBA
  - A520 111,000bv PFOS; 11,000bv PFBA
  - A532E 160,000bv PFOS; 16,000bv PFBA
- Resins notes to be less effective than GAC but A532E close.
- Carbon data from real WWTP

<p>| Table 2 |
|-----------------|-----------------|</p>
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.5</td>
</tr>
<tr>
<td>Nitrates</td>
<td>19 mg L⁻¹</td>
</tr>
<tr>
<td>Sulfates</td>
<td>44 mg L⁻¹</td>
</tr>
<tr>
<td>Chlorides</td>
<td>24 mg L⁻¹</td>
</tr>
<tr>
<td>PFBA</td>
<td>212 ng L⁻¹</td>
</tr>
<tr>
<td>PFPeA</td>
<td>133 ng L⁻¹</td>
</tr>
<tr>
<td>PFHxA</td>
<td>109 ng L⁻¹</td>
</tr>
<tr>
<td>PFHpA</td>
<td>24 ng L⁻¹</td>
</tr>
<tr>
<td>PFOS</td>
<td>430 ng L⁻¹</td>
</tr>
<tr>
<td>PFOA</td>
<td>&lt;1 ng L⁻¹</td>
</tr>
<tr>
<td>PFOA</td>
<td>1 ng L⁻¹</td>
</tr>
<tr>
<td>PFOA</td>
<td>&lt;1 ng L⁻¹</td>
</tr>
<tr>
<td>PFOA</td>
<td>&lt;1 ng L⁻¹</td>
</tr>
<tr>
<td>PFOA</td>
<td>171 ng L⁻¹</td>
</tr>
<tr>
<td>PFOA</td>
<td>13 ng L⁻¹</td>
</tr>
<tr>
<td>PFOA</td>
<td>27 ng L⁻¹</td>
</tr>
</tbody>
</table>

- A600 and A520 can be regen with strong base and salts
- A532E needs alcohol to overcome hydrophobic alkyl chains
- Regeneration problem for A532E if treating drinking water as alcohols toxic?
- A600 50% effective after 2nd regen A520 15% at same point

Note: Carbon C is bitumen based. Carbon S and J coconut based, NOM effect likely in differences
Reverse Osmosis (RO)

- Uses a semi-permeable membrane to remove dissolved solids including low molecular wt. compounds
- In conventional osmosis water will pass through a membrane from a low concentration to a high concentration solution driven by osmotic pressure.
- If a pressure greater than the osmotic pressure is applied to the concentrated side of the membrane water can be forced the other way.
- Literature evidence very high performance (>99%)
- Complete removal of all chain lengths including PFBA
- Can be subject to fouling silica, NOM, metal oxides – pre treatment may help
- Costly systems and treatment of concentrate still required
Treatment of PFAS in Soils

Soil

- Excavation and disposal at approved landfill sites (lingering liabilities)
- High-temperature thermal incineration (1100 °C)
- Solidification and stabilization
- Containment through capping

Considerations:

- No final solution; concentrated in another phase (no degradation)
- Landfill leachate is not typically being evaluated for PFOS, and therefore may pose additional threats to groundwater quality
RemBind/RemBind Plus

- Produced by Australian company Ziltek
- Soil stabilisation agent (typically added at 5% and blended)
- Contains activated carbon, aluminium hydroxide (amorphous), Kaolin clay, and proprietary additives
- Treats a range of CoC (TPH, PAH, PCB), RemBind Plus more suited to PFAS as it has a stronger binding capacity.
- Activated carbon binds through adsorption (Van der Waals, covalent, and electrostatic), alumina through electrostatic mechanisms

- Trails show reduction in leachability (PFOS/PFOA)
  - Minimises off site disposal costs
  - Potentially reclassifies water material
  - Does not destroy the PFAS, therefore long term stability key.
  - Sort chain PFAS apparently retained but require higher dosing especially PFCA’s.
Peroxide-based Oxidation

Modification of traditional Fenton’s chemistry for peroxide-based radical oxidation

- The conventional approach: hydroxyl radical (OH•), a strong oxidant
- Both PFOA and PFOS are oxidation-resistant

The alternative:

- Superoxide radical (O₂•⁻), a reductant and nucleophile
- Hydroperoxide anion (HO₂⁻), a reductant and nucleophile

Figure 1. Degradation of PFOA in CHP systems [100 μg/L PFOA, 0.5 mM iron(III), 0 M (control), 0.25 M, 0.5 M, or 1 M hydrogen peroxide at pH 3.5, 0 or 1 M 2-propanol, total volume of 40 mL, 20 ± 2 °C].
Peroxide-based Oxidation

Hydroperoxide destruction using sole reactive species with base-catalyzed (pH 12.8) peroxide

- Peroxide concentration dependent

- Equivalent fluoride concentrations generated during reaction indicates complete PFOA destruction in absence of intermediates
- No detectable PFOA degradation products observed in any peroxide bench tests
• ScisoR® – Smart Combined *In Situ* Oxidation and Reduction
• Developed, tested and patented and by ARCADIS NL lead by Tessa Pancras
• Initial lab test have show removal of PFAS
  • Effective at ambient temperature
  • Soluble reagents can be injected or mixed with impacted soil and groundwater
• Comprises a specifically activated persulfate
• Potential for *in situ* / on site remediation of PFAS
ScisoR® Evaluation

Environment Canada Evaluation
• 100 µg/L PFOS spike test in water with ScisoR®

![Graphs showing PFOS and PFOA levels over treatment days.](image)
Summary

- PFAS do not biodegrade (mineralise) but biotransform to PFAAs as dead-end daughter products
- Regulations surrounding PFAS are evolving with lowering drinking water standards and a focus on increased interest in additional PFAAs
- PFAA precursor mass (“Dark Matter”) and multiple PFAAs likely accompany PFOS & PFOA in sources and plumes –depending on exact nature of source material
- Analysis of just PFAA’s may significantly underrepresent the actual PFAS mass
- Methods to determine the sum PFAS mass are available commercially via ARCADIS and show good initial correlation
- TOP Assay correlates well with AOF; TOP Assay appears more comprehensive
- A CSM is proposed based on TOP, AOF and PIGE data from an FTA source and plume
- Remediation options are evolving
Contacts

Ian Ross Ph.D.
Global PFAS Lead
Arcadis UK
ian.ross@arcadis.com

Jeff Burdick
North America PFAS Lead
Arcadis US
jeff.burdick@arcadis.com

Tessa Pancras
European PFAS Lead
Arcadis NL
tessa.pancras@arcadis.com

Download at:
https://www.concawe.eu/publications/558/40/Environmental-
fate-and-effects-of-poly-and-perfluoroalkyl-substances-
PFAS-report-no-8-16