THE EMERGING ISSUE

PER- & POLYFLUOROALKYL SUBSTANCES (PFASs)

Big Picture, Challenges and Solutions

Ian Ross, Ph.D.

Global PFASs Lead
Arcadis
Contents

- PFASs News
- PFASs Chemistry
- Replacement Chemistry
- Regulatory Evolution
- State of UK waters
- Ingenious Treatment Solutions
- Conclusions
PFASs Introduction

PFAS comprises many thousands of compounds – multiple sources

PFAS are impacting drinking water worldwide

Some PFAS are classed as persistent organic pollutants

Advanced analytical methods are being adopted to measure PFAS

None of the PFASs biodegrade, some biotransform to daughter compounds that are extremely persistent

Dramatically increasing regulatory concern
Unique Characteristics of PFASs

**Longer chain PFASs stick their tails in the air** - the longer perfluoroalkyl chains migrate to the gas:liquid interface, so stratify in solution.

**PFASs bioaccumulate via interaction with proteins (not fats)** - PFASs bind to β-lipoproteins, as mistaken for fatty acids.

**PFASs tend to be soluble in water** - PFASs can be very mobile in the environment as water soluble, unlike most other POPs.

**Long chain PFASs are initially excreted in humans then reabsorbed** - humans have one the highest levels of renal reabsorption so fail to excrete long chain PFASs, whereas monkeys, mice and rats can excrete at faster rates.

**PFASs tend to stick together** - long chain PFAAs have been identified as layers on surfaces agglomerating by via “molecular brush”

**Increased concentrations of PFAAs observed at WWTP outflow vs inlet** – PFAA precursors are transformed in municipal / biological / oxidative treatment processes.
Detections of PFAS in drinking water has caused spiraling regulatory concern.
PFASs in US Public Water Supplies

US EPA has established the drinking water health advisory levels at 70 ng/L for PFOA/PFOS  19th May 2016

https://www.epa.gov/ground-water-and-drinking-water/drinking-water-health-advisories-pfoa-and-pfos

Detected in ~ 2% of large public water supplies

USEPA UMCR 3, May 2016
US ATSDR releases 'suppressed' PFAS tox profile

Study confirms EPA guidelines 'woefully underestimates risk', says NGO

21 June 2016 / PFAS, Toxicology, United States

The US Agency for Toxic Substances and Disease Registry has released a controversial draft toxicological profile on four per- and polyfluoroalkyl substances (PFAS). The move comes amid uproar over allegations that other federal agencies were suppressing its release.

Last month, internal EPA emails released under a public records request showed concern that the ATSDR was planning to publish a study with minimal risk levels (MRLs) for the PFAS far below those set by the EPA. One White House staffer feared this would result in a "public relations nightmare".

Erin Brockovich: It's Not Just Flint—America Has a Scary Water Problem

http://www.nytimes.com/2016/01/10/magazine/the-lawyer-who-became-duponts-worst-nightmare.html?_r=0

Willamtown RAAF PFOA/ PFOS contamination of fishing grounds.

http://www.willamtownraaf.com/PFOS/PFOA.html

http://www.willamtownraaf.com/PFAS/contamination.html
Toxic Secrets: Where the sites with PFAS contamination are near you

Sites under investigation

At least 90 sites across Australia are under investigation for elevated levels of per- and poly-fluoroalkyl [PFAS] chemicals.

The Sydney Morning Herald

Leaflet | Map tiles by Stamen Design, under CC BY 3.0. Data by OpenStreetMap, under CC BY SA.

Patrick Breysse, Director of the CDC’s National Centre for Environmental Health, described the chemicals as “one of the most seminal public health challenge for the next decades”.

Breysse estimated 10 million Americans were currently drinking contaminated water.

He said soon “we think that hundreds of millions of Americans will be drinking water with levels of these chemicals above levels of concern”
Coming Soon…

https://www.thedevilweknow.com/

https://www.genxthefilm.org/
**Perfluoroalkyl Acids (PFAAs)**

- **Perfluoroalkyl acids (PFAAs)** previously termed Perfluorinated Compounds (PFCs) generally are the and include:
  - Perfluoralkyl carboxylates (PFCAs) e.g. PFOA
  - Perfluoroalkyl sulfonates (PFSAs) e.g. PFOS
  - Perfluoroalkyl phosphinic acids (PFPiS); perfluoroalkyl phosphonic acids (PFPAs)
  - Perfluoroalkyl ethers e.g. GenX

- There are many PFAAs with differing chain lengths (generally C1-C18)

---

**Perfluoroalkyl Carboxylates (PFCA)**

- n=1 Perfluorohexanoic acid (PFHxA)
- n=2 Perfluorooctanoic acid (PFHxA)
- n=3 Perfluorobutanoic acid (PFBA)
- n=4 Perfluoropentanoic acid (PFPeA)
- n=5 Perfluorohexanoic acid (PFHxA)
- n=6 Perfluorohexanoic acid (PFHxA)
- n=7 Perfluorooctanoic acid (PFDA)
- n=8 Perfluorooctanoic acid (PFNA)
- n=9 Perfluorododecanoic acid (PFDoA)
- n=10 Perfluorodecanoic acid (PFDA)
- n=11 Perfluoroundecanoic acid (PFUdA)
- n=12 Perfluoroundecanoic acid (PFDoA)

**Perfluoralkyl Sulfonates (PFSA)**

- n=1 Perfluoromethanesulfonic acid (PFMeS)
- n=2 Perfluorooctanesulfonic acid (PFOS)
- n=3 Perfluoropropanesulfonic acid (PFPrS)
- n=4 Perfluorobutanesulfonic acid (PFBS)
- n=5 Perfluoropentanesulfonic acid (PFPeS)
- n=6 Perfluorohexanesulfonic acid (PFHxS)
- n=7 Perfluorohexanesulfonic acid (PFHxS)
- n=8 Perfluorooctanesulfonic acid (PFOS)
- n=9 Perfluorooctanesulfonic acid (PFOS)
- n=10 Perfluorododecanesulfonic acid (PFDoS)
- n=11 Perfluoroundecanesulfonic acid (PFUdS)
- n=12 Perfluoroundecanesulfonic acid (PFDoS)

* The final carbon atom in PFCA's unlike in PFSA's is part of the head group and not fluorinated.

---

**PFAAs totally resist biodegradation – are ultra-persistent**
Polyfluorinated Compounds – PFAA Precursors

Fully fluorinated carbon-chain “tail”  Unfluorinated C2 “spacer”  Functional group

Fully fluorinated carbon-chain “tail”  Functional group

*e.g.* Poly-fluorinated - 6:2 Fluorotelomer sulfonate (6:2FtS)  *e.g.* Per-fluorinated - PFOS

Atoms: Green = Fluorine, Grey = Carbon, White = Hydrogen, Red = Oxygen, Yellow = Sulphur, non-fluorinated carbon atoms circled

Perfluoroalkyl group – the forever functional group

- Fluorotelomer alcohol, 8:2 FTOH
- Fluorotelomer Sulfonamido Betaines
- Perfluoroalkyl Sulfonamido Amines
- PFASs
- PFOS
- PFHxS
Poly- and Perfluoroalkyl Substances (PFASs)

Polyfluorinated compounds (~5,000 compounds)

Perfluorinated Compounds (PFCs) aka Perfluoroalkyl Acids (PFAAs)
~25 common individual compounds but ~100's compounds
PFOS, PFOA, PFHxS, PFBA, GenX

Microbial / Higher Organism Biotransformation

More Commonly Regulated
Discovery of 40 Classes of Per- and Polyfluoroalkyl Substances in Historical Aqueous Film-Forming Foams (AFFFs) and AFFF-Impacted Groundwater

Krista A. Barzen-Hanson,† Simon C. Roberts,† Sarah Choyke,§ Karl Oetjen,§ Alan McAlees,∥ Nicole Riddell,∥ Robert McCrindle,∥ P. Lee Ferguson,∥ Christopher P. Higgins,∥*† and Jennifer A. Field∥*#

<table>
<thead>
<tr>
<th>Class Number</th>
<th>Structure</th>
<th>nPFAS</th>
<th>Acronym</th>
<th>Confidence Level</th>
<th>AFFF Found In</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>![Image]</td>
<td>3-9</td>
<td>N-Tanp- FASA</td>
<td>2b</td>
<td>A, B, C, D, E, F, G</td>
</tr>
<tr>
<td>22</td>
<td>![Image]</td>
<td>6-8</td>
<td>N-PFAS</td>
<td>3</td>
<td>M, N</td>
</tr>
<tr>
<td>23</td>
<td>![Image]</td>
<td>1-10</td>
<td>UPFAS</td>
<td>3</td>
<td>A, B, C, D, E, M, N, P</td>
</tr>
<tr>
<td>24</td>
<td>![Image]</td>
<td>1-6</td>
<td>H-UPFAS</td>
<td>3</td>
<td>A, B, C, D, E, F, G, M</td>
</tr>
<tr>
<td>25</td>
<td>![Image]</td>
<td>0-8</td>
<td>H-PFAS</td>
<td>3</td>
<td>A, B, C, D, E, F, G, M, N, P</td>
</tr>
<tr>
<td>26</td>
<td>![Image]</td>
<td>5, 7</td>
<td>aPFAS</td>
<td>3</td>
<td>A, B, C, D, E, F, G, M, N, P</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Class Number</th>
<th>Structure</th>
<th>nPFAS</th>
<th>Acronym</th>
<th>Confidence Level</th>
<th>AFFF Found In</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>![Image]</td>
<td>3-8</td>
<td>N-SF- FASA</td>
<td>2b</td>
<td>B, C</td>
</tr>
<tr>
<td>14</td>
<td>![Image]</td>
<td>3-8</td>
<td>N-SFAP- FASA</td>
<td>2b</td>
<td>A, B, C, F</td>
</tr>
<tr>
<td>15</td>
<td>![Image]</td>
<td>3-8</td>
<td>N-SHOPA- FASA</td>
<td>3</td>
<td>C, D, E, F, G</td>
</tr>
<tr>
<td>16</td>
<td>![Image]</td>
<td>3-8</td>
<td>N-CMAp- FASA</td>
<td>2b</td>
<td>D, E, F, G</td>
</tr>
<tr>
<td>17</td>
<td>![Image]</td>
<td>3-8</td>
<td>N-CMAp- FASA</td>
<td>2b</td>
<td>D, E, F, G</td>
</tr>
<tr>
<td>18</td>
<td>![Image]</td>
<td>3-8</td>
<td>N-CMAp- FASA</td>
<td>2b</td>
<td>L</td>
</tr>
<tr>
<td>19</td>
<td>![Image]</td>
<td>3-8</td>
<td>CMApD-FA</td>
<td>2b</td>
<td>L</td>
</tr>
<tr>
<td>20</td>
<td>![Image]</td>
<td>3-8</td>
<td>CMApD-FA</td>
<td>2b</td>
<td>L</td>
</tr>
<tr>
<td>21</td>
<td>![Image]</td>
<td>3-8</td>
<td>CMApD-FA</td>
<td>2b</td>
<td>L</td>
</tr>
<tr>
<td>22</td>
<td>![Image]</td>
<td>3-8</td>
<td>CMApD-FA</td>
<td>2b</td>
<td>L</td>
</tr>
<tr>
<td>23</td>
<td>![Image]</td>
<td>3-8</td>
<td>CMApD-FA</td>
<td>2b</td>
<td>L</td>
</tr>
<tr>
<td>24</td>
<td>![Image]</td>
<td>3-8</td>
<td>CMApD-FA</td>
<td>2b</td>
<td>L</td>
</tr>
<tr>
<td>25</td>
<td>![Image]</td>
<td>3-8</td>
<td>CMApD-FA</td>
<td>2b</td>
<td>L</td>
</tr>
<tr>
<td>26</td>
<td>![Image]</td>
<td>3-8</td>
<td>CMApD-FA</td>
<td>2b</td>
<td>L</td>
</tr>
</tbody>
</table>

PFASs
© Arcadis 2016
Digest AFFF precursors and measure the hidden mass: TOP Assay

Microbes slowly make simpler PFAA’s (e.g. PFOS / PFOA) from PFAS (PFAA precursors) over 20+ years

Need to determine precursor concentrations as they will form PFAAs

Too many PFAS compounds and precursors – so very expensive analysis

Oxidative digest convert PFAA precursors to PFAA’s

Indirectly measure precursors as a result of the increased PFAAs formed

Analytical tools fail to measure the hidden PFAS precursor mass, the TOP assay solves this
TOP Assay Applied to Surface Water from Recent C6 Fluorotelomer Foam Loss

Data Courtesy of Nigel Holmes Queensland DEHP
Aerobic Biotransformation Funnel: Conversion of Polyfluorinated Precursors to PFAAs
Tolerable Daily Intake (TDI)

ng/kg/body weight/d

<table>
<thead>
<tr>
<th>Source</th>
<th>TDI PFOS (ng/kg bw/day)</th>
<th>TDI PFOA (ng/kg bw/day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EFSA, 2008</td>
<td>150</td>
<td>1500</td>
</tr>
<tr>
<td>EPA, 2009</td>
<td>80</td>
<td>190</td>
</tr>
<tr>
<td>Denmark, 2015</td>
<td>30</td>
<td>100</td>
</tr>
<tr>
<td>EPA, 2016 (RfD)</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>RIVM, 2016</td>
<td>in progress</td>
<td>12.5</td>
</tr>
<tr>
<td>Australia, 2017</td>
<td>20</td>
<td>160</td>
</tr>
<tr>
<td>ATSDR 2018 (proposed RfD)</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>EFSA 2018</td>
<td>determined</td>
<td>determined</td>
</tr>
</tbody>
</table>

Evolution of Regulatory PFAS Values

**COMPOUND REGULATED AND CHAIN LENGTH KEY**

- **PFOS** O=8
- **PFHxS** Hx=6
- **PFHxA** H=8
- **PFHpA** Hp=7
- **PFBS** B=4
- **PFOSA** O=6
- **PFBA** B=4
- **PFPeA/S** Pe=5
- **PFHxA** H=6

**REGULATORY PFAS VALUES**

- **DENMARK** (Drinking & Groundwater): 0.09
- **FEDERAL GERMANY** (Drinking Water): 0.1
- **UK** (Drinking Water): 0.07
- **AUSTRALIA** (Drinking Water): 0.07
- **ITALY** (Drinking Water): 0.07
- **STATE OF BADEN-WÜRTTEMBERG** (Groundwater): 0.3
- **EUROPEAN SURFACE WATERS (PFOS)**: 0.00065
- **Queensland**: 0.25
- **Australian Surface Waters (PFOS)**: 0.00023

**PROPERTY OF ARCADIS, ALL RIGHTS RESERVED**
Global Regulatory PFAS Tracker

PFAS Global Standards

- Asia
- Australia
- Europe
- North America

Proposed or Promulgated: All

Compound: All

Standards: 1765

[Map showing global distribution of PFAS standards with regions highlighted in Asia, Australia, Europe, and North America.]
Human Exposure to PFASs

Drinking Water
And Food

House dust
Indoor air
Outdoor air
Consumer products
  • Fluoropolymers inc. side chain polymers
  • Fluorosurfactants
  • Performance chemicals
  • Product residuals

Long Chain Human Bioaccumulation Half Life:
  PFHxS  8.5 years
  PFOS   4.2 years
  PFOA   3.8 years

Precursor
PFAA
Emissions from manufacturing plant had impacted groundwater used by municipal and private supplies.

Study commissioned by court as part of a class action against manufacturer.

Three epidemiologists studied links between PFOA and various health outcomes.

55 health outcomes studied, 4 reports issued between 2011 and 2012.

Information collected (69,030 individuals):

- Blood biomarkers, 10 PFAA
- Health questionnaire / medical records

Study aim was to establish “Given available scientific evidence, is it more probable than not that a connection is present between C8 (PFOA) exposure and disease?”
C8 Science Panel - Findings

• Study found mean PFOA levels of 82.9 ng/L and PFOS levels of 23.6 ng/L in serum samples.
• Probable links were identified for 6 of the 55 health outcomes.

Probable Link

• High Cholesterol
• Ulcerative Colitis
• Thyroid Disease
• Testicular Cancer
• Kidney Cancer
• Pregnancy-Induced Hypertension

No Probable Link

• Hypertension/Coronary Artery Disease
• Chronic Kidney, Liver, Parkinson’s, Autoimmune* Diseases
• Osteoarthritis
• Common Infections
• Neurodevelopmental Disorders/Stroke
• Asthma
• Birth Defects/Preterm/Low Birth Weight
• Miscarriage or Stillbirth

*rheumatoid arthritis, lupus, Type I and II diabetes, Crohn’s disease, multiple sclerosis
Toxicity for Humans

- 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]

Perfluoroalkyl Acid Distribution in Various Plant Compartments of Edible Crops Grown in Biosolids-Amended soils

Andrea C. Blaine,† Courtney D. Rich,† Erin M. Sedlacko,† Lakhwinder S. Hundal,† Kuldeep Kumar,‖ Christopher Lau,§ Marc A. Mills,∥ Kimberly M. Harris,∥ and Christopher P. Higgins†§

PFASs
© Arcadis 2016

Figure 2. Concentrations of PFAAs in greenhouse radish (a), celery (b), tomato (c), and pea (d) grown in industrially impacted soil. Values for tomato fruit are from a previous study. Bars represent means and standard errors of five determinations. Values less than the LOQ are denoted by <; LOQs for respective matrix and analyte are listed in SI Table S4 and Table S5.
Concerns over short chain PFAS - Overview

**Persistent**
- Based on read-across from long chain PFAS
- Long-range transport and findings in remote areas

**Mobility and Exposure of Organisms**
- Potential to contaminate drinking water resources
- Difficult to be removed from water
- Binding to proteins
- Non-negligible half-lives in organisms
- Enrichment in plants

**Toxic**
- No indications of ecotoxicity
- Toxicity in humans to be assessed
- Potential endocrine disruptor

- Representatives of European Authorities agreed: Properties are of concern (BA-Workshop in October 2016)
- However, non-classical combination of concerns so far not covered by REACH


Umwelt Bundesamt

Regulation needs support from research: Short-chain PFASs under REACH

Lena Vierke, Claudia Staude, Éva Fetter, Stephan Brendel, Annegret Biegel-Engler
Section IV 2.3 – Chemicals
German Environment Agency (UBA), Germany
PFAS Foams being Replaced

- C8 (PFOS and PFOA) phased-out
- C8 replaced with compounds with shorter (e.g., C4, C6) perfluorinated chains
- C4, C6 PFAS are less bioaccumulative, still extremely persistent and more mobile in aquifer systems vs C8 - more difficult and expensive to treat in water.
- Solutions for characterizing all PFAS species important to cover current and future risks / liabilities
- Regulations addressing multiple chain length PFAS (long and short) are evolving globally
- Fluorine free (F3) foams contain no persistent pollutants
- F3 foams pass ICAO tests with highest ratings for extinguishment times and burn-back resistance, so are widely available as replacements to AFFF
PFASs in Landfill Leachate

Figure 1. Group 1 PFAS release in U.S. landfill leachate for 2013 demonstrating a dominance of compounds with five fluorinated carbons (PFHxA and 5:3 FTCA). Releases were calculated from mean concentrations in each climate and age category (Table 3). The individual columns are based on eq. 1 while the total is based on eq. 2.
Concerns over short chain PFAS (cont.)

Internal exposure-based pharmacokinetic evaluation of potential for biopersistence of 6:2 fluorotelomer alcohol (FTOH) and its metabolites

Shruti V. Kabadi\textsuperscript{a}, Jeffrey Fisher\textsuperscript{b}, Jason Aungst\textsuperscript{b}, Penelope Rice\textsuperscript{a}

\textsuperscript{a} JPL/CRAN/OSA/CPSC, 5001 Campus Drive, HFS 275, College Park, MD 20740, United States
\textsuperscript{b} EPA/NCTR, 3300 COTR Road, Jefferson, AR 72079, United States

FDA scientists voice concerns over metabolites of food contact substance

Focus on metabolites of 6:2 fluorotelomer alcohol

"Our work represents the first step towards identifying the mechanism by which 6:2 FTOH, similar C6-PFCs, and its metabolites could accumulate in the body to potentially cause adverse effects," write the researchers in the journal \textit{Food and Chemical Toxicology}.

useful for biomonitoring purposes and toxicological evaluation. More importantly, we determined that 5:3 A is an important biomarker for assessment of long-term exposure to 6:2 FTOH as 5:3 A had the highest internal exposure and slowest clearance across species. Furthermore, we concluded that 5:3 A has the potential to reach steady state upon repeated exposure to 6:2 FTOH as its clearance was determined to reduce with increasing 6:2 FTOH exposure. We also identified specific
Polyfluorinated Compounds – PFAA Precursors

Bioactive – metabolised via reactive aldehydes and creates secondary molecule – increased toxicity vs inert PFAA
Estimating human exposure to PFOS isomers and PFCA homologues: The relative importance of direct and indirect (precursor) exposure

Wouter A. Gebbink, Urs Berger, Ian T. Cousins

Department of Applied Environmental Science (TIM), Stockholm University, SE-106 91 Stockholm, Sweden

Fig. 1. Schematic of direct and indirect (precursor) exposure pathways for PFOS and PFCAs.
A Never-Ending Story of Per- and Polyfluoroalkyl Substances (PFASs)?

Zhanyun Wang, Jamie C. DeWitt, Christopher P. Higgins, and Ian T. Cousins

**ABSTRACT:** More than 3000 per- and polyfluoroalkyl substances (PFASs) are, or have been, on the global market, yet most research and regulation continues to focus on a limited selection of rather well-known long-chain PFASs, particularly perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA) and their precursors. Continuing to overlook the vast majority of other PFASs is a major concern for society. We provide recommendations for how to proceed with research and cooperation to tackle the vast number of PFASs on the market and in the environment.

Fluorinated alternatives to long-chain perfluoroalkyl carboxylic acids (PFCA), perfluorooalkane sulfonic acids (PFSA) and their potential precursors

Zhanyun Wang, Jan T. Cousins, Martin Scheringer, Konrad Hungerbühler

- Institute for Chemical and Bioengineering, ETH Zurich, Wolfgang-Pauli-Strasse 10, CH-8093 Zurich, Switzerland
- Department of Applied Environmental Science (FSU), Stockholm University, SE-10691 Stockholm, Sweden

**Fluoropolymer manufacture**

<table>
<thead>
<tr>
<th>PFAS</th>
<th>Formula</th>
<th>CAS No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADONA</td>
<td>F₃C(OOCH₂CH₃)₂F</td>
<td>958445-44-8</td>
</tr>
<tr>
<td>GenX</td>
<td>F₃C(OOCH₂CH₃)₂F</td>
<td>62037-80-3</td>
</tr>
<tr>
<td>Asahi's product</td>
<td>F₃C(OOCH₂CH₃)₂F</td>
<td>908020-52-5</td>
</tr>
<tr>
<td>Solvay's product</td>
<td>F₃C(OOCH₂CH₃)₂F</td>
<td>322938-24-6</td>
</tr>
</tbody>
</table>

**Metal plating**

<table>
<thead>
<tr>
<th>PFAS</th>
<th>Formula</th>
<th>CAS No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NEt₄PFBS</td>
<td>(C₄F₉)₂N⁺CF₃SO₃⁻</td>
<td>25628-08-4</td>
</tr>
<tr>
<td>F₅₃</td>
<td>F₅₃⁺</td>
<td>27619-97-2</td>
</tr>
<tr>
<td>F₅₃</td>
<td>F₅₃⁻</td>
<td>74026-64-7</td>
</tr>
<tr>
<td>F₅₃B</td>
<td>F₅₃⁻</td>
<td>73606-19-6</td>
</tr>
</tbody>
</table>
Plasma concentrations reveal transition from identifiable PFASs to unidentified organofluorine.

Leo W. Y. Yeung and Scott A. Mabury

Are humans exposed to increasing amounts of unidentified organofluorine?
Criteria to Categorize Safety of Chemicals

• Persistence (P): Compounds that do not break down in the environment over long periods of time (i.e., they do not readily biodegrade).

• Bioaccumulative (B): Compounds that build up and are retained in organisms at a faster rate than they can be removed or expelled.

• Mobility (M): Compounds that can travel long distances in groundwater or surface waters from their point of release.

• Toxicity (T): Compounds impart an adverse health effect to an organism at a relatively low concentration of exposure.

• Biopersistence: Compounds that tend to remain inside an organism, rather than being expelled or broken down.

• Biomagnification: The increased concentration of a compound, such as a toxic chemical, in the tissues of organisms at successively higher levels in the food chain –through trophic levels.

Stockholm Convention on Persistent criteria to define persistent organic pollutants (POPs), based on PBT

Suggestion that other criteria are more relevant by UBA under REACH: PMT, vPvB, vPvM

The Precautionary Principle

Principle 15 of the Rio Declaration on Environment and Development as follows:

“Where there are threats of serious or irreversible damage, lack of full scientific certainty shall not be used as a reason for postponing cost-effective measures to prevent environmental degradation”

Comparisons are made to the medical Hippocratic Oath – “Do No Harm”

Multiple ways to apply this concept: Persistent Bioaccumulative and Toxic (PBT), very persistent and very bioaccumulative (vPvB), very mobile very persistent (vPvM), Persistent Mobile Toxic (PMT) or poorly reversible exposure

Poor Reversibility of Exposure (Conceptual)

Poorly reversible exposure of a chemical can occur two ways:

- The chemical has slow elimination kinetics in organisms (bioaccumulative)
- Due to environmental recalcitrance, exposure is steady (extreme persistence)

(Cousins et al. Environ. Int. 2016)
Major Locations of PFAS Point Source Contamination

• Primary Manufacturing (e.g. PTFE)
• Secondary Manufacturing (Application of PFASs to other products) – Tanneries, Paper Mills, Firefighting Foam Blending, Metal Plating Facilities
• Fire Training Sites
  o Airports
  o Civil
  o Defence
  o Oil and Gas
  o Large Rail Yards
• Wastewater treatment plants
• Landfills
Groundwater Risks to Receptors

**Source** – **Pathway** – **Receptor**

- **Source**
  - High concentration, spill site, route via groundwater to receptor
  - e.g. drinking water well

- **Pathway**
  - ?

- **Receptor**

**Diffuse**
- Ground level impacts and ground/surface water

**Landfill Leachate**
- Municipal / Domestic WWTP
- Industry & Manufacturing
- Agricultural Land
- Commercial / Domestic Products
- Metal Plating
- ASTs – Fuel storage (FFF / FP)

**AFFF / FFFP / FP**
- Fire training
- Incident Response

**Grasshopper effect**
- via widening of source zones
- e.g. concentrated plume intercepts crop spray irrigation to make secondary wider source area for more dilute plume
Occurrence of PFAAs in UK Waters

- Environment Agency PFAA monitoring 2008
- Groundwater sampling
  - Conducted at 219 sites in England and Wales (6.5% EA network)
  - The majority of sites were in areas of potential sources eg. airfields
  - “Low risk rural sites” comprised 5%
- Surface water sampling
  - Drinking water abstractions (42 sites)
  - “Higher risk sites” (39 sites) eg. effluents from sewage works
- Limits of detection were 0.1 ug/L so well above the new US EPA standards at 0.07 ug/L
Groundwater

- PFCs detected in 26% of groundwater sites
- Detection even at “low risk” sites

Surface Water

- PFCs detected at 52% of surface water sites (drinking water abstractions)
- PFCs detected at 67% “high risk” sites

**Table 3.1 Perfluorinated compounds in groundwater by aquifer type**

<table>
<thead>
<tr>
<th>Aquifer</th>
<th>Number of sites monitored</th>
<th>Sites with detected PFX</th>
<th>Number of sites</th>
<th>Max PFX (ug L⁻¹) excluding non detections</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>% sites</td>
<td>Min</td>
</tr>
<tr>
<td>Drift</td>
<td>6</td>
<td>1</td>
<td>16.7</td>
<td>0.2</td>
</tr>
<tr>
<td>Minor</td>
<td>75</td>
<td>18</td>
<td>24.0</td>
<td>0.12</td>
</tr>
<tr>
<td>Chalk</td>
<td>36</td>
<td>13</td>
<td>36.1</td>
<td>0.1</td>
</tr>
<tr>
<td>L’wer GS</td>
<td>3</td>
<td>0</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>Jur’s Lst</td>
<td>3</td>
<td>2</td>
<td>66.7</td>
<td>0.22</td>
</tr>
<tr>
<td>FT stt</td>
<td>72</td>
<td>14</td>
<td>19.4</td>
<td>0.1</td>
</tr>
<tr>
<td>Mag Lst</td>
<td>7</td>
<td>3</td>
<td>42.9</td>
<td>0.1</td>
</tr>
<tr>
<td>Carb Lst</td>
<td>16</td>
<td>6</td>
<td>37.5</td>
<td>0.12</td>
</tr>
</tbody>
</table>
PFAS in European Surface Waters

<table>
<thead>
<tr>
<th>River</th>
<th>PFOS (ng/l)</th>
<th>Flow (m³/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scheldt (Be, NL)</td>
<td>154</td>
<td>-</td>
</tr>
<tr>
<td>Seine (Fr)</td>
<td>97</td>
<td>80</td>
</tr>
<tr>
<td>Severn (UK)</td>
<td>238</td>
<td>33</td>
</tr>
<tr>
<td>Rhine (Ge)</td>
<td>32</td>
<td>1,170</td>
</tr>
<tr>
<td>Krka (SI)</td>
<td>1,371</td>
<td>50</td>
</tr>
</tbody>
</table>

EU-wide survey of polar organic persistent pollutants in European river waters

Table 5.2: EQS of the European Commission for PFOS and its derivatives

<table>
<thead>
<tr>
<th>Name of substance</th>
<th>AA-EQS¹ (µg/l)</th>
<th>MAC-EQS² (µg/l)</th>
<th>EQS (µg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perofluorooctane sulfonate and its derivatives (PFOS)</td>
<td>0,00065</td>
<td>0,00013</td>
<td>36, 7, 9, 1</td>
</tr>
</tbody>
</table>

¹AA: Annual average  
²MAC: Maximum allowable concentration
Worldwide Distribution of Novel Perfluoroether Carboxylic and Sulfonic Acids in Surface Water

Figure 2. Mean concentrations (ng/L) of legacy PFASs (PFCAs and PFASs) and fluorinated alternatives (PFECAs, PFESAs, and FTSAs) in the studied rivers and lakes: Chao Lake (n = 13), Tai Lake (n = 15), Yangtze River (n = 35), Pearl River (n = 13), Liao River (n = 6), Huai River (n = 9), Yellow River (n = 15), Thames River (n = 6), Rhine River (n = 20), Delaware River (n = 12), Han River (n = 6), and Malaren Lake (n = 10).
Sampling and a data review was conducted by the Drinking Water Inspectorate in 2007.
Review found only 4 of 29 water companies had PFAS testing data to share with the DWI.
The sampling drinking water at raw, mid treatment, and final stage of process.
- Fifteen “high risk” sites based on surrounding land use (usually airfields).
- Five lower risk “control” sites.

http://dwi.defra.gov.uk/research/completed-research/reports/DWI70_2_212PFOS.pdf
### Table 6.2 PFOS results (in µg/l) of sampling in 2007 at the perceived higher-risk sites for all four sampling sessions.

<table>
<thead>
<tr>
<th>Site</th>
<th>Source</th>
<th>Description</th>
<th>Airfield</th>
<th>Airfield</th>
<th>Borehole 3</th>
<th>Borehole 4</th>
<th>Borehole 5</th>
<th>GAC feed water</th>
<th>GAC 1</th>
<th>GAC 2</th>
<th>GAC 3</th>
<th>GAC 4</th>
<th>GAC 5</th>
<th>GAC 6</th>
<th>GAC 7</th>
<th>GAC 8</th>
<th>GAC 9</th>
<th>GAC 10</th>
<th>GAC 11</th>
<th>GAC 12</th>
<th>Post GAC (all)</th>
<th>After chlorine contact</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>Groundwater (UC)</td>
<td>Ultrafiltration membranes and chlorination using chlorine gas.</td>
<td>Before last chlorination</td>
<td>After Cl contact tanks</td>
<td>Raw</td>
<td>0.016</td>
<td>0.020</td>
<td>&lt;0.011</td>
<td>0.013</td>
<td>Raw</td>
<td>0.016</td>
<td>0.023</td>
<td>&lt;0.011</td>
<td>-</td>
<td>Raw</td>
<td>0.016</td>
<td>0.019</td>
<td>&lt;0.011</td>
<td>0.014</td>
<td>Raw</td>
<td>0.154</td>
<td>0.020</td>
</tr>
<tr>
<td>9</td>
<td>Groundwater (UC)</td>
<td>None on site: water pumped by raw water pumping main to another treatment works, which has GAC (not in operation), super chlorination using gas and dechlorination.</td>
<td>Raw</td>
<td>Raw</td>
<td>Raw</td>
<td>0.182</td>
<td>-</td>
<td>0.183</td>
<td>-</td>
<td>Raw</td>
<td>0.152</td>
<td>0.124</td>
<td>0.205</td>
<td>0.135</td>
<td>0.162</td>
<td>-</td>
<td>-</td>
<td>0.208</td>
<td>-</td>
<td>Final</td>
<td>0.154</td>
<td>-</td>
</tr>
<tr>
<td>15</td>
<td>Groundwater (UC)</td>
<td>GAC and chlorination by on-site electrolytic generation using food grade salt stored in HDPE. 12 GAC beds.</td>
<td>Large use of PFOS-containing fire fighting foam</td>
<td>Large use of PFOS-containing fire fighting foam</td>
<td>Borehole 3</td>
<td>0.059</td>
<td>0.076</td>
<td>0.052</td>
<td>Off line</td>
<td>Borehole 4</td>
<td>0.029</td>
<td>0.028</td>
<td>0.018</td>
<td>Off line</td>
<td>Borehole 5</td>
<td>0.038</td>
<td>0.029</td>
<td>0.030</td>
<td>Off line</td>
<td>GAC feed water</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
### Available *In Situ* Groundwater Treatment Technologies

<table>
<thead>
<tr>
<th>Technology</th>
<th>Likelihood of Success?</th>
<th>Rationale</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerobic Biodegradation</td>
<td>Low</td>
<td>Biotransformation does not proceed past PFAA</td>
</tr>
<tr>
<td>Anaerobic Biodegradation</td>
<td>Low</td>
<td></td>
</tr>
<tr>
<td>Phytoremediation</td>
<td>Low</td>
<td>PFAA not volatile; depth limitations</td>
</tr>
<tr>
<td>Air Sparging/Vapor Extraction</td>
<td>Low</td>
<td>PFAA not volatile nor biodegradable</td>
</tr>
<tr>
<td>In-Situ Thermal Treatment</td>
<td>Low</td>
<td>Required temperature economically impractical; ex-situ waste management</td>
</tr>
<tr>
<td>Chemical Oxidation/Reduction</td>
<td>Moderate</td>
<td>Bench-tests confirm viable mechanisms exist; field evidence conflicting; potential for treatment train</td>
</tr>
<tr>
<td>Monitored Natural Attenuation</td>
<td>Moderate</td>
<td>PFAA do not biodegrade (dilution via advection, adsorption are viable mechanisms)</td>
</tr>
<tr>
<td>Groundwater Extraction and Ex-Situ Treatment</td>
<td>High</td>
<td>Presumptive remedy for PFAS to-date, focus of this discussion; ex-situ waste management</td>
</tr>
<tr>
<td>Permeable Reactive Barriers</td>
<td>High</td>
<td>Apply ex-situ sorption technologies with a funnel &amp; gate; change outs required</td>
</tr>
</tbody>
</table>
No “silver bullet” for PFAS remediation; treatment train is current state of the practice
Tentatively identified PFAS as a main ingredient is 6:2 FTSAS (fluorotelomermercaptoalkylamido sulfonate).

PFASs
© Arcadis 2016
Foam Cleanout/Decontamination

Sewer Decontamination Trial

Sequential

- Control
- 1st H₂O
- Caustic
- 2nd H₂O
- Solvent
- 3rd H₂O

PFOS Concentration (ng/L)

0 10,000 20,000 30,000 40,000

PFOS

2 1,900 970 1,000 44

Total PFAS (ng/L)

0 50,000 100,000 150,000 200,000 250,000 300,000 350,000

Foam Tank Cleanout – TOP Assay

Sequential

- Pre-TOP
- Post TOP

Baseline Water

Solvent

Final Water

1,900 970 1,000 44

326,000

153,000

3,880

2,480 3,840 78

© Arcadis 2016
The Challenge

- **+ 15 ML** - Sewage, Tradewaste, Brackish Creek Water, Chemical Flush Fluids, and Stormwater
- **Emergency Response** – full-scale onsite in three weeks
- FF Foam Concentrate – Precursors, 5,000 µg/L PFAS
- Multiple Contaminants (1,500 mg/L COD)
- Small Footprint
- Treatment Objective: 0.25 µg/L sum of PFAS by TOP assay
Emergency Response

2 weeks permitted

3 weeks system onsite

4 weeks installed
Ozofractionation – Case Study

Large volume high COD, high PFAS impacted wastewater

- ~3.6 million gallons of water
- Total [PFAS] ~ 3,950 µg/L; targeted discharge [PFAS] = <1 µg/L
- Laboratory analysis includes total oxidizable precursor (TOP) assay per country-specific regulations

Treatment train operation selected

- Ozofractionation with engineered polish
- Polish necessary for low discharge limit
- Foam concentrate to be thermally destroyed offsite
Ozofractionation - Concept

Photos courtesy Michael Dickson July 2017
## Ozofractionation – Case Study

Ozofractionation highly effective at removing PFOS, PFOA, and C6 PFAA precursors.

<table>
<thead>
<tr>
<th>Identification</th>
<th>Influent (µg/L)</th>
<th>Ozofraction % Removal</th>
<th>Adsorbent % Removal</th>
<th>Treated Water (µg/L)</th>
<th>Total % Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFOS</td>
<td>2.61</td>
<td>98.2%</td>
<td>81.3%</td>
<td>0.009</td>
<td>99.7%</td>
</tr>
<tr>
<td>PFOA</td>
<td>1.37</td>
<td>97.4%</td>
<td>94.4%</td>
<td>0.002</td>
<td>99.9%</td>
</tr>
<tr>
<td>6:2 FtS</td>
<td>87.4</td>
<td>95.6%</td>
<td>89.2%</td>
<td>0.416</td>
<td>99.5%</td>
</tr>
<tr>
<td>PFPeA</td>
<td>2.08</td>
<td>-66.3%</td>
<td>83.4%</td>
<td>0.575</td>
<td>72.4%</td>
</tr>
<tr>
<td>PFHxA</td>
<td>6.91</td>
<td>-66.4%</td>
<td>99.7%</td>
<td>0.034</td>
<td>99.5%</td>
</tr>
<tr>
<td>Sum PFAS</td>
<td>103</td>
<td>78.8%</td>
<td>95.1%</td>
<td>1.07</td>
<td>99.0%</td>
</tr>
<tr>
<td>Total PFAS, TOPA</td>
<td>3,950</td>
<td>99.6%</td>
<td>89.6%</td>
<td>1.76</td>
<td>99.96%</td>
</tr>
</tbody>
</table>

Ozofractionation converted some C6 precursors to PFHxA, PFPeA – net production of these compounds.

Polishing adsorption stage was effective at removing PFHxA and, to a lesser extent, PFPeA; PFBA was not detectable in these samples.

Ozofractionation and engineered polish achieve 99.96% PFAS removal, post TOP.
Reconcentrate

- Total Volume Treated (L)
- Concentration (µg/L)
- Stage 1: 97% Reduction
  - 650 Tanks
- Stage 2: 91% Reduction
  - 21 Tanks
  - 2 Tanks

- Raw feed
- Concentrate
- Super Concentrate
Sonolysis

**Applicability:**
- Ultrasound applied to water results in successive rarefaction/compression of microbubbles ultimately yielding cavitation with extremely high temperatures on the surfaces of the bubbles resulting in pyrolysis of PFAS.

**Benefits:**
- Can reliably destroy concentrated PFAS waste streams with literature supported fluoride mass balance.
- Opportunities to use green energy sources as technology develops (i.e., solar power).

**Limitations:**
- PFOA rate > PFOS rate. PFOS will require longer residence times and/or more energy. Effective below 10,000 ppt?
- Requires specialized equipment and skilled implementation.
- High energy consumption and low flow rates.

---

**Assumes $0.12/kW-hr and 10 hr/d operation time**

<table>
<thead>
<tr>
<th>FLOW RATE (GPM)</th>
<th>ENERGY COST (USD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>$100,000</td>
</tr>
<tr>
<td>0.5</td>
<td>$10,000</td>
</tr>
<tr>
<td>5</td>
<td>$1,000</td>
</tr>
<tr>
<td>50</td>
<td>$100</td>
</tr>
<tr>
<td>500</td>
<td>$10</td>
</tr>
<tr>
<td>0.3 kW-hr/L</td>
<td></td>
</tr>
</tbody>
</table>

Property of Arcadis, all rights reserved
Sonolysis – Proof of Concept Testing

Initial Sum PFOS 17.5uM/L

Potential Fluoride in PFOS 297.5uM/L

92-99% Stoichiometric Fluoride Release (B-DKHz)

91-97% Sum PFOS Concentration Reduction (B-DKHz)
Engineered Regenerable Sorbents to Selectively Remove PFASs
SERDP Research 2018

Silica-based porous solids with aryl and fluoro groups will lead to effective adsorption sites for PFASs by interaction with the fluoroalkyl chain.
Engineered Regenerable Sorbents to Selectively Remove PFASs
SERDP Research 2018

RESULTS: PFOS ADSORPTION ISOTHERM (90 BTEB / 10 TDF-TMS)
Summary

- Significant press attention & public concern on PFASs as a result of impacts to drinking water
- Significant decreases in drinking water standards globally
- Site assessment with TOP assay redefines the PFASs CSM
- How to apply the precautionary principle to be protective of human health & the environment, proportionate and sustainable?
- Risk based contaminated site management essential
- Emerging remedial technologies provide ingenious solutions for PFASs
A review of emerging technologies for remediation of PFASs

Ian Ross  Jeffrey McDonough  Jonathan Miles  Peter Storch  Parvathy Thelakkat Kochanarayanan  Erica Kalve  Jake Hurst  Soumitr S. Dasgupta  Jeff Burdick

Correspondence
Ian Ross, Arcadis, 34 York Way, London N1 9YH, UK. Email: Ian.Ross@arcadis.com

Abstract
The need for remediation of poly- and perfluoroalkyl substances (PFASs) is growing as a result of more regulatory attention to this new class of contaminants with diminishing water quality standards being promulgated, commonly in the parts per trillion range. PFASs comprise >3,000 individual compounds, but the focus of analyses and regulations has generally been PFASs in most perfluorooctanoic acid (PFOA), which are all extremely persistent, can be highly mobile, and are increasingly being reported to bioaccumulate, with understating of its toxicity evolving. However, there are thousands of perfluorinated (“PFAs”) precursors, which can transform in the environment and produces persistent PFASs as persistent daughter products. Some PFASs can travel miles from their point of release, as they are mobile and persistent, potentially creating large plumes. The use of a conceptual site model (CSM) to define risks posed by specific PFASs to potential receptors is considered essential. Granular activated carbon (GAC) is commonly used as part of interim remedial measures to treat PFASs present in water. Many alternative treatment technologies are being adopted for PFASs or innovative solutions developed. The diversity of PFASs and associated with use of multiple PFASs in commercial products is not commonly assessed. Remedial technologies, which are adsorptive or destructive, are considered for both soils and wastes with challenges to their commercial application outlined. Biological approaches to treat PFASs report bioremediation which creates persistent PFASs, and PFASs can bioaccumulate. Water treatment technologies applied as sites could be used in a treatment train approach, for example, to concentrate PFASs and then destroy them on-site. Dynamic groundwater treatment systems can greatly enhance containment mass removal via groundwater pumping. This review of technologies for remediation of PFASs describes that:

- GAC may be effective for removal of long-chain PFASs, but does not perform well on short-chains PFASs and its use for removal of precursors is reported to be less effective;
- Anion exchange media can remove a wider range of long- and short-chain PFASs, but struggle to treat the shorter chain PFASs and removal of most PFAS precursors has not been evaluated.

DOI: 10.1002/wat25513

RESEARCH ARTICLE