What’s wrong with persistence - don’t we want to build things to last?

Ian Ross Ph.D.
Global PFAS Practice Lead
Tetra Tech
The main challenges for PFAS – their management and regulation – within the UK context.

• What are PFAS
• How to measure PFAS
• Replacement of one PFAS with another
• Regulatory frameworks
• PFAS point sources
• UK waters
• PFAS destruction
• Green Chemistry Solutions
• Summary
Poly- and Perfluoroalkyl Substances (PFASs)
(~4,730 manufactured compounds)

Polyfluorinated “Precursors” - Proprietary PFASs

Thousands of individual parent compounds, sharing common daughters e.g. 6:2 FTS, 5:3 acid

Perfluorinated Compounds (PFCs) or Perfluoroalkyl Acids (PFAAs)

~25 common individual compounds, terminal daughters i.e. “forever chemicals”
e.g. PFOS, PFOA, PFHxS, PFBA, PFHxA

Environmental / Higher Organism Biotransformation
Perfluoroalkyl group – confers extreme persistence

Fluorotelomer alcohol, 8:2 FTOH

Fluorotelomer Sulfonamido Betaines

Perfluoroalkyl Sulfonamido Amines

PFOS

PFHxS

PFOA
Fluorotelomer Foam

Breakdown products of the C6 FT Foam: short-chain PFCAs

Precursor

Stable Intermediate

Source: Weiner et.al. 2013
PFASs in Landfill Leachate

The elephant in the room: potential biopersistence of short-chain PFAS

Estimated PFAS Mass Flows in U.S. Landfill Leachate in 2013 (kg/yr)

- Wet <10 yrs.
- Wet >10 yrs.
- Temperate <10 yrs.
- Temperate >10 yrs.
- Arid

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 stoichiometrically converts PFAA precursors to PFAA’s
- TOP assay indirectly measures total precursors as a result of increased PFAAs formed after oxidation vs before.

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

PFCA (and increase after TOP Assay)

- PFTeDA C14
- PFTrDA C13
- PFDoDA C12
- PFUnDA C11
- PFDA C10
- PFNA C9
- PFOA C8
- PFHpA C7
- PFHxA C6
- PFPeA C5
- PFBA C4

Sample 1: 7,497
Sample 2: 7,306
S1 TOP A: 1,912,294 (255x)
S2 TOP A: 2,018,226 (276x)

Data Courtesy of Nigel Holmes Queensland DEHP
Chemical “Whack a Mole”

Exposure from one PFAS replaced by another
Next Generation PFASs

Science Inventory

You are here: EPA Home > Science Inventory > Assessing Generated In Vitro Toxicokinetic Data of Per- and Polyfluoroalkyl Substances (PFAS) with In Vitro-In Vivo Extrapolation (IVIVE)

Assessing Generated In Vitro Toxicokinetic Data of Per- and Polyfluoroalkyl Substances (PFAS) with In Vitro-In Vivo Extrapolation (IVIVE)

Citation:

Impact/Purpose:
This presentation will be given at the annual Fall meeting for the North Carolina chapter of the Society of Toxicology and is focused on utilizing in vitro toxicokinetic assays with PFAS. This meeting is being held virtually over three separate days in September 2020. Plasma protein binding for more than 50 PFAS was determined by ultracentrifugation. Hepatic clearance data from collaborators at NTP was also included to then perform IVIVE to predict systemic concentrations. Future work will examine toxicokinetic differences based on functional group and may help inform risk-based chemical safety assessment.

Fluorinated alternatives to long-chain perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkane sulfonic acids (PFSAs) and their potential precursors

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Fluoropolymer manufacture

Metal plating
**PBT Applicability?**

- For drinking water quality, PBT-based regulations are only marginally effective.

- PBT aimed to protect food chain, not drinking water?

- In contrast, persistent and mobile organic compounds (PMOCs) are more of a concern for water quality because, like PCBs, they can persist in the environment, but they are not removed from water by sorption processes due to their high polarity and thus excellent water solubility.

- Therefore, they may end up in drinking water, posing a potential risk to human health.

- Umweltbundesamt (UBA) suggesting alternative assessment frameworks:
  - PMT **Persistent Mobile Toxic**
  - vPvM very **Persistent and very Mobile** as potential Substances of Very High Concern.
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
Regulation of PFHxA

- EU proposal to limit the use of PFHxA related substances (precursors) – December 2019;
- Rationale:
  - “Fulfils the P-criterion and vP-criterion”
  - “Mobility and long range transport potential” and “unpredictable and irreversible adverse effects on the environment or human health over time”
- Exemptions (5 years) are in place for certain uses:
  - Hard chrome plating;
  - Photographic coatings;
  - Firefighting foams – Emergency use only
  - There is no exemption for testing (unless all releases contained) or training with fire fighting foams.
- Exemptions (12 year) are in place for Class B firefighting foams used to protect storage tanks with a surface area above 500m²
- Military users exempted – Requirement that during training foam contained and disposed of safely
- The EU considers the restriction practical as it is affordable, implementable, and manageable
Potential Locations of PFAS Point Source Contamination

- Primary Manufacturing (e.g. for PTFE)
- Product manufacturing: carpets, paints, paper coating, leather tanneries, metal plating, textiles
- Fire Training Sites: Airports, Civil, Defence, Petrochemical, Rail Yards
- Sites of hydrocarbon fires, since late 1960’s e.g. Buncefield
- Car wash/wax, dry cleaners, ash pits
- Sprinkler systems -warehouses, aircraft hangars, car workshops, pharmaceutical plants
- Wastewater treatment plants – biosolid waste
- Landfills
Soils / Concrete are Long Lasting Sources of PFASs

• The unsaturated zones continue to be a source of PFASs to the groundwater after 18 years (FTA-1) and 20 years (infiltration beds) of inactivity.
• Some precursors are mobile at this field site
• Results indicate that shorter chain length PFAAs are more mobile than PFOS both vertically and horizontally.
• Significant long PFOS retained at the surface (top 0.5 cm) of 12 cm concrete core
• Long term leaching of PFOS from concrete surfaces is an ongoing issue with potential for impacted run off and surface water impacts for >80 years
Figure 2. Mean concentrations (ng/L) of legacy PFASs (PFCAs and PFASs) and fluorinated alternatives (PFECAs, PFESA, 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 Mälaren Lake (n = 10).
# Principle Exposure Route – Drinking Water

## Third Unregulated Contaminant Monitoring Rule

The third Unregulated Contaminant Monitoring Rule (UCMR 3) was published on March 1, 2012. UCMR 3 required monitoring for 80 contaminants. PFAS chemicals and PFOA were included between 2013 and 2015, using analytical methods developed by EPA, consensus organizations, or both. This monitoring provides early data for follow-up regulatory actions to protect public health.

- [Final Rule Notice: Final Revision to the UCMR 3 for Public Water Systems, March 1, 2012](#)
- [U.S. EPA: Toxic Information Fact Sheet](#)
- [EPA Approved Laboratories for PFAS](#)

## Six Perfluorinated Compounds

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>CAS Registry Number</th>
<th>Minimum Reporting Level</th>
<th>Sampling Points</th>
<th>Analytical Methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>perfluorooctanesulfonic acid (PFOS)</td>
<td>1763-23-1</td>
<td>0.04 μg/L</td>
<td>EPTDS</td>
<td>EPA 537 Rev 1.1</td>
</tr>
<tr>
<td>perfluorooctanoic acid (PFOA)</td>
<td>335-67-1</td>
<td>0.02 μg/L</td>
<td>EPTDS</td>
<td>EPA 537 Rev 1.1</td>
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<tr>
<td>perfluorononanoic acid (PFNA)</td>
<td>375-95-1</td>
<td>0.02 μg/L</td>
<td>EPTDS</td>
<td>EPA 537 Rev 1.1</td>
</tr>
<tr>
<td>perfluorohexanesulfonic acid (PFHxS)</td>
<td>355-46-4</td>
<td>0.03 μg/L</td>
<td>EPTDS</td>
<td>EPA 537 Rev 1.1</td>
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<tr>
<td>perfluorooctanoic acid (PFHpA)</td>
<td>375-85-9</td>
<td>0.01 μg/L</td>
<td>EPTDS</td>
<td>EPA 537 Rev 1.1</td>
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<tr>
<td>perfluorobutanesulfonic acid (PFBS)</td>
<td>375-73-5</td>
<td>0.09 μg/L</td>
<td>EPTDS</td>
<td>EPA 537 Rev 1.1</td>
</tr>
</tbody>
</table>
Fifth Unregulated Contaminant Monitoring Rule

The Safe Drinking Water Act (SDWA) requires that every five years EPA issue a new list of unregulated contaminants to be monitored by public water systems (PWSs). The proposed Fifth Unregulated Contaminant Monitoring Rule (UCMR 5) was published on March 11, 2021. UCMR 5, as proposed, would require sample collection for all chemical contaminants between 2022 and 2025 using analytical methods developed by EPA and consensus organizations. This proposed action would provide EPA, states, and communities with scientifically valid data on the national occurrence of these contaminants in drinking water. The proposed UCMR 5 would provide new data that is critically needed to improve EPA’s understanding of the frequency that PFAS are found in the nation’s drinking water systems and at what levels. EPA will accept public comment on the proposed UCMR 5 for 60 days, following publication in the Federal Register. EPA will also hold a virtual stakeholder meeting twice during the public comment period.

- Online Questionnaire: Issue Action to Address PFAS in Drinking Water (PDF)
- UCMR 5 Fact Sheet
- Public Stakeholder Meeting (Webinar): April 6 and 7, 2021
Groundwater Risks to Receptors

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

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

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

**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
Incineration

- 1,000 to 1,200 °C required to completely degrade PFOS
- Lower temperature incineration of PFASs can produce toxic intermediates (e.g. perfluoroisobutylene)
- Not proven effective for liquid wastes, potential for steam expansion i.e. AFFF concentrates – U.S. litigation
- Incinerator ash pits source of PFAS to groundwater
- Potent greenhouse gases (CF₄, C₂F₆ etc.) require 1,400 °C for destruction – above incineration temperatures
- Comprehensive analysis of all gaseous emissions required for any thermal treatment
- Cement kilns one potential solution but several technologies potentially applicable – sonolysis, plasma, electrochemical oxidation, supercritical water etc.

Biosolids as a PFAS Source to Groundwater / Milk

Kent County, Grand Rapids, Grand Rapids Water Resource Recovery Facility, Former Incinerator Ash Lagoon

Congress: Tell the Pentagon to halt incineration of toxic forever chemicals

By MARGARET KENNER / @HILLKENNER
The Pentagon is not doing enough to stop the incineration of toxic forever chemicals.

For 50 years, the Department of Defense (DoD) has buried the military-grade firefighting foam, known as AFFF or ARFF, in toxic waste sites.

The DoD has announced that it will phase out its use of AFFF in the near future, but it has not yet committed to halting incineration.

What makes AFFF toxic is its class of intermediate chemicals known as PFAS, which are known for their persistence and ability to find their way into groundwater.

Exposure to PFAS is associated with a variety of health risks, including cancer, thyroid dysfunction, and reproductive and developmental harms.

Congress is taking action to stop the DoD from incinerating toxic waste sites.


https://www.michigan.gov/pfasresponse/0,9038,7-365-86511-95645-529272--,00.html

New Mexico
‘This has poisoned everything’ — pollution casts shadow over New Mexico’s booming dairy industry

For the past 20 years, dairy farmers have been battling a pollution crisis in New Mexico.

With a second farm shuttered due to massive PFAS contamination, Maine legislators weigh easing access to the courts


https://www.iatp.org/blog/202007/second-farm-shuttered-due-massive-pfas-contamination-maine-legislators-weigh-easing
PFAS Treatment Technologies for Water

Stage of Development

Mature
- Optimization Research
- Development Research

Experimental
- In Situ Foam Fractionation
- Injected Activated Carbon
- Enzymes

Practicability
- Not Viable
- Feasible

Technologies:
- AOP/ARP*
- Flocculation/Electrocoagulation
- Sonolysis
- Plasma
- Electrochemical Treatment
- RO/NF**
- Activated Carbon
- Ion Exchange
- Ozofractionation
- Polymeric Adsorbents
- Incineration
- Photolysis

* AOP/ARP: Advanced oxidation processes/advanced reduction processes
** RO/NF: Reverse Osmosis/Nanofiltration
PFAS Treatment Technologies for Soil/Sediment

Stage of Development

Mature
- Fixation/Separation
  - Optimization Research
  - Development Research
- Destruction

Experimental
- AOP/ARP*
  - Ball Milling

Practicability
- Not Viable
- Feasible

AOP/ARP: Advanced oxidation processes/advanced reduction processes

*Note: AOP/ARP: Advanced oxidation processes/advanced reduction processes.
PFAS Foams being Replaced

- C8 (PFOS) generally phased-out, replaced with foams containing C6 and C8 (20% PFOA precursors)
- C6-pure foams with shorter (C6) perfluorinated chains, still contain PFOA and precursors
- C4, C6 PFAS are less bioaccumulative, but extremely persistent and more mobile in aquifer systems vs C8 - more difficult and expensive to treat in water.
- Regulations addressing multiple chain length PFAS (long and short) are evolving globally – PFHxA restrictions coming
- Fluorine free (F3) foams contain no persistent pollutants
- F3 foams pass ICAO tests with highest ratings for extinguishment times and burn-back resistance and are widely available as replacements to AFFF
- Lastfire Independent Large Scale Storage Tank Test Program Results 2018: “It is not possible to state, for example, that all C6 foams demonstrate better performance than all FF foams and vice versa”
Research Work – Rational Progression - more than 200 tests

Small scale
Simulated tank fire
Critical application rates

Larger scale
“Real life” Application
NFPA rates

Phases have included
- Different foams
- Different nozzles
- Different application methods
- Different rates
- Different fuels (including crude)
- Different preburns
- Fresh/Salt water

Subsurface tests

Spill fire
Critical application rates

Longer flow
“Real life” Application
NFPA rates

Self expanding
foam

Vapour
suppression

Hybrid
Medium
Expansion

Further obstructed
spill fire testing
Decontamination of Fire Suppression Systems

• Fire suppression systems remain significant ongoing source of PFAS to F3 foams
• g/L PFAS appear in F3 foams if suppression system not decontaminated properly
• Fluorosurfactants self assembled on surfaces
• Water flushing not effective
• Requires specialist decontamination
• Solutions developed in UK and used globally

Denmark just became the first country to ban a toxic lining common in food containers.

Fighting fire with fluorine-free foams
Fluororganic compounds are common in firefighting foams due to their performance boosting effects. Some par-fluorinated substances are recognised as having adverse effects on our health and the environment. As a result, the manufacturers of firefighting foams are investing in the development of new, improved fluorine-free foam concentrates. A serious challenge since high-risk areas such as the chemical and petrochemical industry require foams with the highest possible performance.

Today, European manufacturers offer a new generation of high performing fluorine-free foams for various applications.

Two of these companies share their experience in replacing fluorine-based foams with safer substances.

From the beginning of our existence, we were convinced of the negative impact of fluorine and focused our research into finding a good alternative without fluorinated derivatives,” says Ms Audrey Rossard, Technical Manager from the French company BIO-EX.

BIO-EX sold their first fluorine-free foam in 2002. Their environmental challenge has been to convince their customers to choose their new generation of green products, which are 100% fluorine-free, and have proven to be effective.

“We haven’t just made a simple substitution of the fluorinated surfactant, but have worked with all the constituents of the formula to develop the best product,” says Ms Rossard.
The Cost of Inaction

• Non-health costs, e.g., treatment of contaminated drinking water, are estimated to range between 16.9 and 170.8 billion EUR over the next 20 years. The estimates are based on actual costs of PFAS contamination incurred by communities and industries in the U.S. and Sweden.

• Health-related costs may be even higher. Epidemiological research on PFAS exposures of workers and communities with contaminated drinking water indicates that annual health-related costs range between 52 and 85 billion EUR each year.
Summary

Challenges

• PFAS diversity - short chains and ethers replacing long chains
• Proprietary precursors form PFAAs
• Uncertain toxicology of broader group of PFAS
• A significant mass of PFASs in source areas can bleed PFASs to form plumes for decades

Solutions

• Total PFAS can be detected – TOP assay
• Rapid In Vitro toxicological screening started
• Evaluation of exposure pathways and development of site specific CSMs essential for PFAS management
• Multiple remediation technologies evolving
• Effective and green substitutions for PFAS often available
PFAS Publications

3 Per- and Polyfluoroalkyl Substances

EMERGING CONTAMINANTS HANDBOOK

A review of the precursors, environmental fate, monitoring, and policy implications of PFAS (perfluoroalkyl substances) and other emerging contaminants. This handbook provides an overview of the latest research and developments in the field of emerging contaminants, including PFAS, and offers insights into future directions for study and policy development.

This handbook is a valuable resource for researchers, policymakers, and practitioners who are interested in understanding the challenges posed by emerging contaminants, including PFAS, and in developing effective strategies for addressing these challenges.