PFASs — Emerging Contaminants

Sponsored by
Moderator: Melissa Helton, PG, Senior Project Manager, AMEC E&I

Speakers:
• Hud Heaton, P.E., Program Manager, MMRP, AMEC E&I
• Shalene Thomas, Associate Assessor, AMEC E&I
• Robert Delaney, DSMOA Coordinator, Michigan Department of Environmental Quality
• Harry Behzadi, Vice President, Operations, Accutest
Environmental Committee
Environmental Committee Mission

The Mission of the Environmental Committee is to **enhance professionalism, create value** for the civil service and military members, and **provide true training** and a **forum for interchange of ideas**.

The Environmental Committee seeks to achieve this mission through several avenues, including:

– Guest speakers on relevant topics during monthly conference calls,
– Supporting conferences that promote environmental awareness and Committee objectives, and
– Special membership meetings at the annual **SAME Joint Engineer Training Conference & Expo (JETC)** to recruit new members and promote the Environmental Committee's mission.
Committee Areas of Interest

- BRAC/Privatization
- Munitions Response and Operational Range Sustainment (subcommittee)
- Environmental Management Systems (EMS)
- Community Involvement
- Analytical Environmental Testing/Data Quality
- Environmental Information Systems/Geospatial
Committee Organization

• Chair: Hud Heaton, P.E. (MAJ, EN Ret) AMEC
  Environment and Infrastructure
• Vice Chair, Munitions Response: Nelline Kowbell, P.E. CH2MHiIl
• About 250 Committee Members on SAME Roster
• 20-40 attend monthly calls
Accomplishments

• JETC 2013
  – Held a Committee Meeting and had educational presentation on PBRs
  – Sponsored two educational sessions
    • Munitions Response - Advanced Geophysics for Munitions Response
    • Range Sustainment

• Hosted numerous Monthly Calls (3rd Wednesday of each month)
  – April 2014: MMRP, Including the UPF-QAPP
  – March 2014: The Future of the Range Sustainment Program
  – February 2014: Emerging Contaminants
  – January 2014: Three Aspects of Quality: Field; Data; and Report
  – September 2013: Radiological Remediation of Soils Contaminated by the Fukushima Daichii Nuclear Disaster
  – August 2013: FUSRAP Overview
  – June 2013: An Overview of the Army NGB Environmental Programs and Structure

• Moderating 2 Seminars at JETC 2014
  – PFASs – Emerging Contaminants
  – Low Level Radiological Contamination
2014 Committee Goals

• Continue Monthly Educational Seminars
• Get more people actively engaged
• Consider hosting a paid Educational Webinar
• Learn Spyder-phone!
PROBLEM SOLVING
There are few of life's problems that cannot be solved with the proper application of a high explosive projectile.
PFASs
(Perfluoroalkyl and Polyfluoroalkyl Substances)
Introduction and Background

Shalene Thomas, PMP
AMEC Environment & Infrastructure • shalene.thomas@amec.com
General Overview

• What are Emerging Contaminants?
• What are PFASs?
• Nomenclature and Why It Is Important
• History and Sources
• Fate and Transport
• Toxicity
• Regulatory Overview
• Research and Development Trends
What is an Emerging Contaminant?

- DoD and EPA definitions generally state:
  - Presents potential unacceptable risk
  - Has no published standard
  - New science, detection, or pathway available\(^1,2\)

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\(^2\) EPA Federal Facilities Restoration and Reuse Office:

http://www.epa.gov/fedfac/documents/emerging_contaminants.htm#additional_ec
PFASs - what’s in a name?

PFNA  PFAS  PFOA  PFCs  PFOS

Fluorocarbons

PFAC

PolyFluoroalkyl substance

PerFluoroalkyl substance

FTOH
PFASs - what's in a name?

Polyfluoroalkyl substance

**i.e. FTOH**

**i.E 8:2 FTOH**

Perfluoroalkyl substance

**PFAC**

**PFAS**

**i.e. PFOA**

**i.e. PFNA**

**i.e. PFOS**

Fluorocarbons

**i.E 8:2 FTOH**
PFASs

Polyfluoroalkyl substance (Precursors)

Perfluoroalkyl substance (PFCS)

PFAC

i.e. PFOA

i.e. PFNA

PFAS

i.e. PFOS

Fluorocarbons
What are Perfluorochemicals (PFCs)?

- PFCs are *perfluorinated* compounds
- Fully fluorinated (i.e. no hydrogen atoms)
- Are human-made compounds
- Shortest and strongest bond in nature
- Stable in acids, bases, oxidants, heat
- Lipid and water repellent
- Persistent in environment

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What are Perfluorochemicals (PFCs)?

- Only two PFCs are considered Emerging Contaminants:
  - Perfluorooctane sulfonate (PFOS)
  - Perfluorooctanoic acid (PFOA)

- Why are these most common?
  - Largest amount manufactured within the US\(^3\)
  - Most research and development to date specific to PFOS/PFOA
  - Approximately 20 PFC species (including PFOS and PFOA) have approved analytical standards. Over 90 species known

History

- First produced in the 1950’s by 3M
- Have been used and produced until 2000 when 3M and seven other companies agreed to cease production
- 2010/2015 PFOA Stewardship Program developed by EPA cooperatively with major manufacturers

No longer produced after 2002
Sources

- Non-stick cookware (Teflon - PFOA)
- Stain-proof carpeting/furniture (Scotchgard - PFOS)
- GORE-TEX clothing
Sources

- Fast-food containers (microwave popcorn bags)
- Aqueous film-forming foams (AFFF) that were commonly used as fire suppressants
- Semiconductors (photo-acid generators and anti-reflective coatings)
Fate and Transport

- Readily absorbed following ingestion
- No transformation of PFOS or PFOA has been observed in soil, sediment, sludge, water or biota systems (USEPA)
- As a result of the chemical stability of PFOS and PFOA and the low volatility of these substances in ionic form, these substances are persistent in water and soil³
Fate and Transport

- PFOS exhibits a higher tendency to bind to organic matter compared to PFOA, due to its longer perfluoroalkyl chain length (Conder et al. 2008)
- Washington State found WWTP effluent ranging from 0.061 to 0.418 ug/l

Toxicity

• Studies have shown small quantities of PFOS and PFOA in blood of general human population\(^3\)

• Fish and fishery products seem to be one of the primary sources of human exposure to PFOS\(^2\)

• PFOS and PFOA have a half-life of approximately 4 years in humans. The long half-life could lead to adverse health effects\(^2\)
Toxicity

- PFOA is a confirmed carcinogen in animals and is defined as “likely to be carcinogenic to human” by the EPA

- Epidemiological studies have shown an association between PFOS exposure and bladder cancer. Associations to other cancers have also been identified
Currently no legally enforceable Federal standards

In 2009, EPA set a “provisional health advisory” limit of 0.4 ppb for PFOA in drinking water. A criteria of 0.2 ppb was set for PFOS

Several states have developed “guidelines” for screening in water (ug/l) including but not limited to:

<table>
<thead>
<tr>
<th>State</th>
<th>PFOA</th>
<th>PFOS</th>
<th>Other PFCs</th>
<th>Source</th>
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Note:
Grey Highlight= Based on EPA Standard

Michigan -0.011 ug/L for surface water classified as drinking water, 0.012 ug/L for surface water classified as non-drinking water, 0.10 ug/L for Groundwater
Research and Development

• ESTCP and SERDP – two research projects wrapping up in 2014
  – ER-2128 Characterization of the fate and biotransformation of fluorochemicals in AFFF-contaminated groundwater
  – ER-2126 Behavior of perfluoroalkyl chemicals in contaminated groundwater
Research and Development

• Four more projects funded and kicked off in 2014 for evaluation of In-situ Treatment of perfluoralkyl substances
  – ER-2423
  – ER-2424
  – ER-2425
  – ER-2426

• Broad Agency Announcements (No selections made- 31 total submissions)
Questions?
References

1 DoD Instruction 4715.18, Emerging Contaminants, June 11, 2009. DUSD (I&E) is Deputy Under Secretary of Defense for Installation and Environment

2 EPA Federal Facilities Restoration and Reuse Office: http://www.epa.gov/fedfac/documents/emerging_contaminants.htm#additional_ec


Perfluoroalkyl and Polyfluoroalkyl Chemicals
A Regulator’s Perspective

Robert Delaney
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Objectives

• An understanding of the potential magnitude of the problem
• Regulatory challenges that must be addressed
• Future direction of the regulatory environment for addressing PFAS
Case Study

Former

Wurtsmith Air Force Base
Former Wurtsmith Air Force Base
Fire Training Pad – Site FT02
Site Wide – Total PFCs in ppt
Extent of Contamination from Wurtsmith
Drinking Water Supply for 10,000 People
Industrial Area Plumes

Legend

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<td>&gt; 1,000,000</td>
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Clean Up Criteria

- **PFOS**
  - Residential drinking water: 0.220 parts per billion (ppb) (estimated)
  - **GSI: 0.012 ppb (published)**
- **PFOA**
  - Residential drinking water: 0.150 ppb
New Installation Restoration Projects

• Screening level effort only for groundwater and surface water contamination

• Detected so far:
  – Approximately 30 sites above some criteria
  – Between 40 and 50 different plumes detected
  – Expect more plumes will be detected
Why Should We Care?

Top Ten Toxic Chemicals Suspected to Cause Autism and Learning Disabilities¹

1. Lead
2. Methylmercury
3. Polychlorinated Biphenyls
4. Organophosphate pesticides
5. Organochlorine pesticides
6. Endocrine disruptors
7. Automotive exhaust
8. Polycyclic aromatic hydrocarbons
9. Brominated flame retardants
10. Perfluorinated compounds

Eating these fish may harm your health.
Characteristics of PFCs

- Ubiquitous in the environment
- Virtually indestructible
- Mobile
- Highly toxic
- At least 98% of Americans with detectable levels in their blood\(^2,3\)
- Bioaccumulate & Biomagnify
State Wide Issue

- PFAS are being found in surface water and fish around the State

- Flint River, Saginaw River and Kalamazoo River, in limited testing, show ambient water concentrations of PFAS above or near the Surface Water criteria\(^4\)
Implications

- Wide spread contamination in the state
- Potential for highly concentrated contamination in localized areas
- Landfills, waste water treatment plants, metal plating, car washes, accident scenes, fire training locations, farm fields, airports, etc.
Regulatory Path Forward

- Draft RfD likely to be challenged
  - Did not use human data
  - Did not use what many consider the best study findings to base RfD upon
  - Trend in literature seems to indicate levels in humans too high already
  - RfD more likely to go down
Waste Water Treatment Issues

- New NPDES permits will be impacted
  (many waste water treatment plants are discharging above the 12 ppt level)\textsuperscript{5,6}
- Non-attainment waters
- Treatment is expensive
Forces Shaping Future of PFAS Regulation

- Eventual national drinking water standard
- Increasing state regulation of PFAS
- Standards for more PFAS than just PFOS and PFOA
- Push back from industry
- Substitutions for currently used PFAS by industry
How Important is the PFAS Issue?

Questions?
Contact Information

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(517) 284-5085
References


Emerging Contaminants:
PFOA and PFOS

Harry Behzadi, Ph.D
VP of Operation, Corporate Technical Director, Accutest Laboratories
What is an Emerging Contaminant?

• Chemicals and materials with:
  – Perceived or real threat to human health or environment
  – Either no peer reviewed health standard or an evolving standard

• May have:
  – Insufficient human health data/science
  – New detection limits
  – New exposure pathways
Why are ECs Important?

**Proactive**

Early EC Actions

**versus**

**Reactive**

Readiness Impacts
Clean up Cost
Compliance costs
Health Claims
Life Cycle costs

$$$
Small Investment

$$$
Large Impact

Potential Large Payback
What are PFOA and PFOS?

- PFOA and PFOS are fully fluorinated organic compounds and are the most common perfluorinated chemicals (PFCs).
- PFOA is a perfluoralkyl carboxylate that is produced synthetically as its’ salts. Ammonium salt is the most widely produced form.

- Name: pentadecafluorooctanoic acid
- Other names: PFOA, perfluorooctanoate, perfluorocaprylic acid
- CAS number: 335-67-1
- Molecular formula: C8HF15O2
- Molar mass: 414.07 g/mol

- C-F bond is the shortest and strongest bond in nature.
What are PFOA and PFOS?

- PFOS is a perfluoralkyl sulfonate that is commonly used as a simple salt (such as potassium, sodium, or ammonium) or incorporated into larger polymers

![Chemical Structure of PFOS](image)

- Systematic name: Heptadecafluoro-1-octanesulfonic acid
- Other names: PFOS, Perfluorooctane sulfonic acid
- CAS number: 1763-23-1
- Molecular formula: C8HF17O3S
- Molar mass: 500.13 g/mol

- They are man-made compounds and do not occur naturally in the environment
Other Perfluorinated Organic Compounds (PFCs)

• Perfluoroalkylsulfonic acids
  – Perfluorobutanesulfonic acid (PFBS)
  – Perfluorohexanesulfonic acid (PFHxS)
  – Perfluorooctanesulfonic acid (PFOS)
  – Perfluorodecanesulfonic acid (PFDS)

• Perfluoroalkylcarboxylic acids
  – Perfluorohexanoic acid (PFHxA)
  – Perfluoroheptanoic acid (PFHpA)
  – Perfluorooctanoic acid (PFOA)
  – Perfluorononanoic acid (PFNA)
  – Perfluorodecanoic acid (PFDA)
Other Perfluorinated Organic Compounds (PFCs)

• Perfluoroalkylcarboxylic acids
  – Perfluoroundecanoic acid (PFUnA)
  – Perfluorododecanoic acid (PFDoA)
  – Perfluorotridecanoic acid (PFTrDA)
  – Perfluorotetradecanoic acid (PFTeDA)

• Other PFCs and Fluorinated Telomers
  – Perfluoroctanesulfonamide (PFOSA)
  – N-ethyl-perfluoroctanesulfonamidoacetic acid (N-EtFOSAA)
  – N-methyl-perfluoroctanesulfonamidoacetic acid (N-MeFOSAA)
  – 1H,1H,2H,2H-perfluorohexanesulfonic acid (4:2 FTS)
  – 1H,1H,2H,2H-perfluoroctanesulfonic acid (6:2 FTS)
  – 1H,1H,2H,2H-perfluorodecanesulfonic acid (8:2 FTS)
Common Uses of PFOA and PFOS

• They are used in a wide variety of industrial and commercial products, such as textiles and leathers, fire fighting foams, metal plating, photo lithography, semi-conductors, paper and packaging, coating additives, cleaning products, and pesticides

• The presence of strong C-F bonds makes them chemically and thermally very stable, resistant to hydrolysis, photolysis, microbial degradation or metabolism

• PFOS chemicals are no longer manufactured in United States. However, they can be imported and used for specific limited uses

• The 3M Company, the primary manufacturer of PFOS, completed a voluntary phase-out of PFOS production in 2002
Environmental Impacts of PFOA and PFOS

- During past manufacturing processes, large amounts of PFOS and PFOA were released into the air, water and soil in and around fluorochemical facilities.

- Because of the chemical stability of PFOS and PFOA and the low volatility of these substances in ionic form, they are persistent in water and soil.

- Studies have found small quantities of PFOS and PFOA in blood samples of humans and wildlife worldwide, indicating that exposure to the chemicals is widespread.

- Source of Exposure: food and food packaging, DW, dust and ambient air.
# Federal and State Standards for PFOA and PFOS

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* in water (ug/L)
Sample Containers/ Preservative/ Holding Time

- **Sample Container**
  - Samples should be collected in 125-250ml wide-mouth polyethylene (HDPE) bottles fitted with unlined (no Teflon) polyethylene screw caps

- **Preservative**
  - Samples must be shipped at <10ºC

- **Holding time**
  - 14 days from collection to extraction; 28 days from extraction to analysis

- **Additional Info**
  - All sources of Teflon should be avoided during collection and storage. These are potential sources of PFC interference. Also, sampler should avoid contact with fluoropolymers, aluminum foil, blue ice, pre-wrapped foods or snacks, and should not use Post-It Notes

- **Method**
  - EPA DW 537 and 537 Modified
Challenges

• High cost of analysis, due to expertise, instrumentation, and standards cost

• Contamination OR loss due to filtration/sample concentration; PTFE in seals, o-rings, tubing, septa

• Limited number of authentic standards for PFAS other than carboxylates, sulfonates, and telomer sulfonates

• Caution when field sampling, avoid PFTE (e.g., Teflon bailers), and Tyvek
Detection and Site Characterization for PFOA and PFOS

• HPLC-MS/MS has allowed for more sensitive determination of individual PFOS and PFOA in soil, water, and air

• Sample Analysis: LC/MS/MS
  – LC
  Unlike gas chromatography, which is unsuitable for nonvolatile and thermally fragile molecules, liquid chromatography can safely separate a very wide range of organic compounds

  – MS
  Mass spectrometers generate three dimensional data. In addition to signal strength, they generate MS data that can provide valuable information about the molecular weight, structure, identity, quantity, and purity of a sample.
LC/ MS/ MS Specifications

Ion Sources: Electrospray Ionization

Diagram showing the process of electrospray ionization with labels for spraying nozzle, Taylor cone, charged parent droplet, solvent evaporation, Coulomb fission, charged droplet at the Rayleigh limit, charged progeny droplets, and power supply.
LC/ MS/ MS Specifications

Mass Analyzer: Triple Quadrupole
LC/ MS/ MS Specifications

Mass Analyzer: Collision-Induced Dissociation
To obtain structural information, analyte ions are fragmented by colliding them with neutral molecules, in a process known as collision induced dissociation (CID). Voltages are applied to the analyte ions to add energy to the collisions and create more fragmentation.
LC/ MS/ MS Specifications
Extracted Ion Chromatogram
Extracted Ion Chromatogram
## Reported Parameters

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<th>LOD AQ ng/l</th>
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* not recoverable by SPE
References


United States Fact Sheet Solid Waste and EPA 505-F-11-002

Environmental Protection Agency Emergency Response (5106P), May 2012

DoD’s Emerging Contaminants Program Carole LeBlanc, Ph.D. Special Expert, Emerging Contaminants, Office of the Deputy Under Secretary of Defense

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