Per- and polyfluoroalkyl substances (PFAS) - Overview of Technical and Regulatory Issues Resulting from AFFF Use at Military and Industrial Facilities

Jason Conder, PhD

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Aqueous Film Forming Foam (AFFF)
Not snow!
Aqueous Film Forming Foam (AFFF) Not snow!

Perfluoroalkyl and polyfluoroalkyl substances (PFAS)
Jason Conder

- PhD Environmental Toxicologist and Chemist
- PFAS site investigation and risk assessment
- Various PFAS projects since ~2005
  - 3 peer-reviewed papers on PFAS (chemistry, ecotoxicology, risk assessment)
  - US Department of Defense Frequently Asked Questions (FAQ) PFAS
  - Several ongoing risk assessments for PFAS

Critical Review
Are PFASs Bioaccumulative? A Critical Review and Comparison with Regulatory Criteria and Persistent Lipophilic Compounds

JASON M. CONDER,* ROBERT A. HORE,† § WATTS EL WOLE,* MARC H. RUSSELL,‡ AND ROBERT C. BUCK* (PFOA) and perfluorooctanoic acid (PFOA) is a long chain, biologically persistent, toxic perfluorinated organic compound. PFASs are present in the environment at low concentrations. There is concern that these compounds may accumulate in the food chain and cause adverse biological effects. Several recent reports have documented the bioaccumulation of PFASs in wildlife and humans. Recent studies have also shown that PFASs can affect the development of embryos and fetuses. The US Environmental Protection Agency (EPA) has issued a draft guidance document for the ecological risk assessment of PFASs. This document provides a framework for assessing the ecological risk of PFASs, including the bioaccumulation potential of these compounds. The guidance document is based on a review of the latest scientific literature and data on PFASs. The guidance document also includes a risk assessment model that can be used to estimate the potential risks associated with PFASs. The model incorporates data on the bioaccumulation potential of PFASs and is designed to be used in conjunction with other risk assessment tools. The guidance document is intended to help EPA and other environmental regulatory agencies make informed decisions about the management of PFASs.
Overview

• Key issues for assessing and managing Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS)
  – It’s not just a drinking water issue
• Topics
  – Brief review of PFAS organic chemistry, sources, and AFFF
  – PFAS fate and exposures
  – Toxicology and risk assessment
  – Regulations
What are PFAS?

- **PFAS:** Perfluoroalkyl and Polyfluoroalkyl Substances
- A family of synthetic organic compounds that contain multiple fluorine (F) atoms

- Incorrectly referred to as "PFCs"
  - Greenhouse gases regulated by the Kyoto Protocol
  - PFCs are one of the families of PFAS (all PFCs are PFAS, not all PFAS are PFCs)
PFAS

- Hundreds-thousands of compounds

Lindstrom et al. (2011); Barzen-Hanson et al. (2017)
Uses and Sources

- Excellent surfactants
- High production volumes, variety of applications since the 1940s-1960s
  - Aqueous Film Forming Foam (AFFF)
  - metal plating (mist suppression)
  - fluoropolymer manufacture
  - polymeric/surfactant products in leather, paper, textiles, sealants, paint, cleaning products
  - pesticides (Sulfuramid)
  - photographic applications / photolithography
  - semiconductors
  - aviation hydraulic fluids
**AFFF History**

- **AFFF = Aqueous Film Forming Foam**
  - Complex, proprietary mixtures of fluorinated and hydrocarbon surfactants, water, corrosion inhibitors, solvent
  - ~1-10% PFAS by weight
  - 10s to 1000s of liters per use

- **History**
  - Mid 1960s – 1970: 3M sole source supplier of AFFF
  - 1973: National Foam
  - 1976: Ansul
  - 1994: present: Angus, Chemguard, Fire Service Plus

- **Multiple AFFFs used at most sites, and PFAS composition varies by manufacturer**
75% of AFFF produced was used by military

Other AFFF users

- Oil and gas industry
- Bulk fuel storage
- Chemical manufacturers
- Airports
- Municipalities
- Landfills
- Misc. (metal working industries, print industries, communities)
PFAS Fate and Exposures
Abiotic Environmental Fate

- Moderate-high water solubility/mobility
  - Groundwater plumes from contaminated areas many miles long
- Extremely persistent or transform to persistent PFAS
- Persistent PFAS at contaminated sites not volatile
- Can also partition to soils and sediment (organic matter)

Minnesota 3M PFAS plumes in groundwater 10+ miles long, cover over 100 miles² (MDH, 2012)
• Range of behaviors
  = variety of compartments to track
Biological Fate

- Detectable in nearly any biological tissue
- Partitions to protein (proteinophilic), not fat/lipid
  - Blood, liver, kidney, muscle are primary repositories
  - Traditional models not useful for understanding or predicting bioaccumulation and toxicity
- Not metabolized, or metabolizes to persistent PFAS (precursors)

99% of California teachers with detectable PFAS

Source: Open source graphics from USFWS, Cal EPA DTSC
Chemical Size Affects Bioaccumulation

Short PFAS

Long PFAS
Chemical Size Affects Bioaccumulation

Short PFAS  ⬅️ Less bioaccumulative ⬆️ Long PFAS

Animals

Chemical Size Affects Bioaccumulation

Short PFAS

More bioaccumulative

Plants

Long PFAS

Less bioaccumulative

water evaporation leaves PFAS behind

water and PFAS uptake
Human Exposure Pathways

• **Major**
  – Diet (bioaccumulation)
    • Fish and seafood
    • Homegrown produce
  – Drinking water
  – Incidental soil/dust ingestion

• **Usually insignificant or minor**
  – Dermal absorption
  – Inhalation
PFAS in Municipal Drinking Water Supplies

• PFAS detected above drinking water health criteria
  > 60 drinking water systems
  – EPA Unregulated Contaminants Monitoring program (UCMR3)

Ecological Exposure Pathways

• **Major**
  
  – Incidental soil/sediment ingestion
  
  – Diet (biomagnification)
    
    • Aquatic food webs particularly susceptible to longer PFAS
    
    • Plants readily accumulate shorter PFAS

• **Dermal absorption** (aquatic life)

• **Insignificant/minor**
  
  – Inhalation
Conceptual Site Model for AFFF Risk

On-Site (AFFF Area)

Source → Soil → Groundwater
Conceptual Site Model for AFFF Risk

Source → Soil → Groundwater

On-Site (AFFF Area)
Conceptual Site Model for AFFF Risk

Source → Soil

Eco: Little/no Natural Habitat = Little/no exposure

Human: Industrial

On-Site (AFFF Area)
Conceptual Site Model for AFFF Risk

Source → Soil → Groundwater → Aquatic Ecosystems → Offsite Groundwater

Eco: Little/no Natural Habitat = Little/no exposure
Human: Industrial

On-Site (AFFF Area) → Off-Site
Conceptual Site Model for AFFF Risk

On-Site (AFFF Area)

- Source
  - Eco: Little/no Natural Habitat = Little/no exposure
  - Human: Industrial

Soil

Groundwater

Off-Site

- Highest Risk Potential
  - Aquatic Ecosystems
  - Offsite Groundwater

Off-Site
Toxicology of PFOA and PFOS

- **Most toxicology studies have focused on PFOA and PFOS**
  - Non-cancer effects in mammals are primarily focused on developmental effects
  - Immunotoxicity potential
  - Potential carcinogenic properties
    - “Suggestive” for both (USEPA) and “Possibly” for PFOA (International Agency for Research on Cancer)

- **Human health reference doses for PFOS and PFOA currently both 20 ng/kg body weight*day (USEPA)**
  - Some states have alternate values

- **Ecological**
  - Wildlife effects
    - Effects on liver and kidney
    - Reproduction
  - Aquatic toxicity data (fish, invertebrates) for some compounds
  - Plants and soil invertebrates not as sensitive
Toxicology of Other PFAS

• Some information in peer-reviewed literature and chemical registration information
• Most focused on the PFCAs and PFSAs, the perfluoroalkyl acid “families” to which PFOA and PFOS belong
• Effects generally similar (developmental, liver, kidney, etc.)
• Dozens to thousands of compounds
Example PFOS Risk-based Screening Criteria in Water

- Residential (Drinking Water)
- Consumption of Fish by Fishermen (Surface Water)
- Aquatic Toxicity (Surface Water)
- Consumption of Aquatic Organisms by Birds (Surface Water)
Example PFOS Risk-based Screening Criteria in Water

- [PFOS Water] (ng/L)
- Method Detection Limits

- Residential (Drinking Water)
- Consumption of Fish by Fishermen (Surface Water)
- Aquatic Toxicity (Surface Water)
- Consumption of Aquatic Organisms by Birds (Surface Water)
Example PFOS Risk-based Screening Criteria in Water

Ambient/Background
Method Detection Limits

PFOS Water (ng/L)

- Residential (Drinking Water)
- Consumption of Fish by Fishermen (Surface Water)
- Aquatic Toxicity (Surface Water)
- Consumption of Aquatic Organisms by Birds (Surface Water)

Ambient in groundwater/surface waters: D’Agostino and Mabury, 2017; Li et al., 2011; Sinclair et al., 2004; Konwick et al., 2008; Eschauzier et al., 2012; ATSDR, 2015
Example PFOS Risk-based Screening Criteria in Water

USEPA Drinking Water Health Advisory (70 ng/L) (applied to sum of PFOA and PFOS in drinking water)
PFAS Regulatory Drivers

• 2016 drinking water lifetime health advisory level for PFOS and PFOA (70 ng/L, PFOA+PFOS)
  – Advisory level, not a legally enforceable Federal standard
  – Supersedes the 2009 interim health advisory levels of 200 ng/L PFOS and 400 ng/L PFOA

• CERCLA
  – PFAS not yet CERCLA hazardous substances, so no cost recovery for Superfund (although they are considered a CERCLA pollutant or contaminant and can be investigated)

• Others
  – Site investigations and management driven by other forces, including: voluntary action (regulatory and public perception pressure), litigation, Clean Water Act (TMDL), variable approaches at state-level

• Risk assessment for PFOA and PFOS can be used as regulatory drivers

• Consult legal counsel – PFAS regulatory landscape will continue to evolve
PFAS Regulations and Guidance

- **USEPA path forward**
  - 2018 PFAS National Leadership Summit
    - Recognized PFAS as a national priority
    - “PFAS National Management Plan” will provide a roadmap
    - USEPA has initiated steps to evaluate the need for an MCL for PFOS and PFOA

- **US States are taking the lead…**
PFAS Regulations and Guidance

**US States**

- Multiple (14) states currently have standards and guidance for PFOS and PFOA following EPA health advisory level

- Several states have standards and guidance that are more protective
  - New Jersey MCLs: 14 ng/L PFOA, 13 ng/L PFOS
  - Vermont primary groundwater enforcement standard: 20 ng/L PFOA, PFOS

- California
  - Interim notification levels: 14 ng/L PFOA, 13 ng/L PFOS
  - Response levels (recommend taking source offline): USEPA drinking water health advisory
PFAS Regulations and Guidance

• **US States**
  – Nine states have assessment criteria for additional PFAS beyond PFOS, PFOA and PFHxS, including:
    • PFNA, PFBA, PFBS, PFHxA, PFPeA, PFHpA, PFOSA, PFDA, PFDS, PFUnA, PFDoA, PFTrDA, PFTeDA
    • One state (North Carolina) has an assessment criterion for GenX, a replacement for PFOA
PFAS Ban in AFFF

• **Washington State banning PFAS in AFFF**
  – Bans the sale starting in July 2020 unless its use is required by federal law or if AFFF will be used by an oil refinery, oil terminal, or chemical plant for fire fighting

• **No room for scientific discourse?**
  – Non-PFAS foams don’t work as well in putting out fires
  – What’s in the non-PFAS foams?
  – Re-formulated AFFF (short-chain PFAS) not as harmful as original AFFF
  – Now that we know to control AFFF use carefully, can Best Management Practices be part of the answer?
Remediation

• Remediation extremely challenging because most PFAS not bio- or chemically-degradable

• Current default/best approaches very expensive
  – Soil
    • Excavation and disposal (landfill)
  – Water
    • Pump & treat with activated carbon
    • Large volumes of carbon needed due to high water solubility of PFAS
    • Order of magnitude more expensive than pump & treat for VOCs
    • Systems optimized for VOCs not likely addressing PFAS
Conclusions

- A lot left to learn about PFAS
- Not just a human health drinking water issue
- Not just PFOS and PFOA
- Off-site issues are important
- Concentrations of PFAS at many sites can trigger concerns
- A lot of uncertainties and unanswered questions
- Site-specific risk assessment possible
For More Information…
ITRC Fact Sheets (draft/in development):

- Naming Conventions and Physical and Chemical Properties
- Regulations, Guidance, and Advisories
- History and Use
- Environmental Fate and Transport
- Site Characterization Considerations, Sampling Precautions, and Laboratory Analytical Methods
- Remediation Technologies and Methods
- Aqueous Film Forming Foam

▶ https://pfas-1.itrcweb.org/
4-hour Symposium, Nov 4, Sacramento, CA

ITRC Symposium on Characterizing and Managing PFAS at Impacted Sites

November 4, 2018
1:00 PM to 5:00 PM
Led by ITRC PFAS Experts

Location:
Sacramento Convention Center
1400 J St, Room 202
Sacramento, CA 95814

Travel Scholarships:
Available for state employees from OR, NV, UT, ID, & AZ attending this training. Please contact Tadbir Singh at tsingh@ecos.org or 202-849-4980 for details.

Who Should Attend?
State and federal environmental and health agencies, tribes, local governments, communities and others interested in learning about PFAS.

FREE for state and federal employees, academics, and public stakeholders!

Registration Fee for Private Sector: $10

Register HERE

• Other 4- or 8-hour sessions being offered in other locations in the US over the next 4-6 months (contact me for details)