

State of Knowledge on Per- and Polyfluoroalkyl Substances (PFASs) at Military Sites

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Project Team

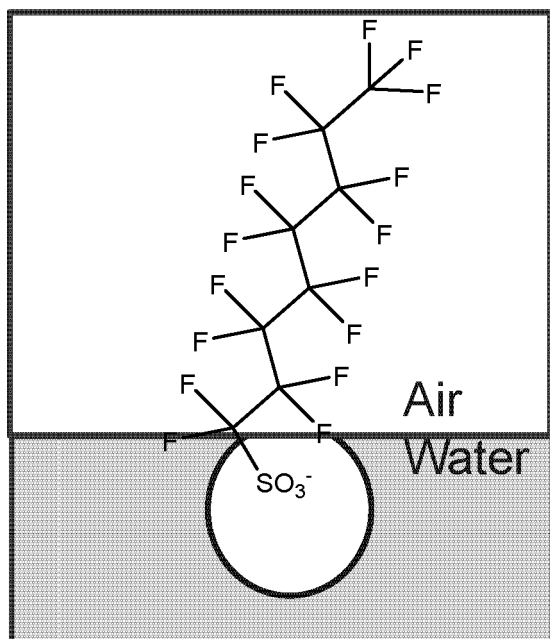
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 - ◆ Soil scientist

Technical Objectives

- Characterize per- and polyfluoroalkyl substances (PFAS) composition of aqueous film-forming foam (AFFF) formulations
- Characterize PFAS and precursor composition of AFFF-contaminated groundwater, sediment and soil
- Characterize PFAS biodegradation under aerobic and anaerobic conditions
- Characterize the sorption of the newly-identified anionic, cationic and zwitterionic PFASs

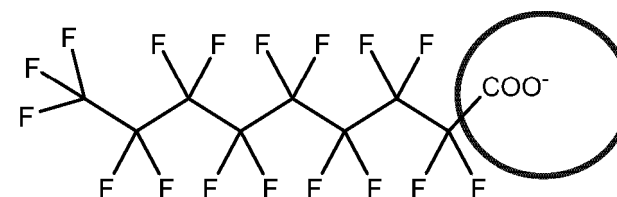
Unique Chemistry of PFASs

- C-F bond is the shortest & strongest in nature
 - ✓ hydrophobic & oleophobic¹
 - ✓ less predictable behavior in laboratory & environmental systems



PFOS (perfluorooctane sulfonate)

- Few engineered/environmental degradation processes, stable in:
 - ✓ heat
 - ✓ acid/base
 - ✓ oxidants
 - ✓ biological systems



PFOA

(perfluorooctanoate)⁴

¹Krafft and Riess 2015 Chemosphere 129:4-19

PFASs vs. ~~PFCs~~

- PFAs = Per and polyfluoroalkyl substances

- Communicate accurately

✓ contract laboratories, regulatory community, the public, internationally¹

- PFC = 'Perfluorinated' = restrictive term

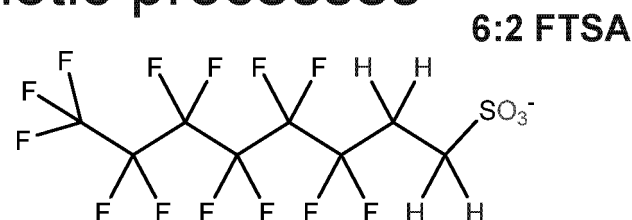
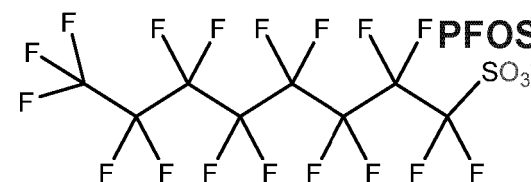
✓ all carbons in aliphatic chain must be bonded **only** to F

✓ no degradation in environment

- Polyfluorinated = not all carbons in chain bonded to F

✓ CH₂ – linkages create 'weakness' in molecule

✓ susceptible to biodegradation, abiotic processes (oxidation)



¹Buck et al. 2011 Integr Environ Assess Manag 7:513-541

Why are PFASs Emerging Now

- Traditional analytical instruments (GC/MS) for priority pollutants are 'blind' to non-volatile PFASs
- PFAS are measured by LC-MS/MS
 - ✓ Commercial LC-MS/MS < 15 yrs ago
 - ✓ Quality standards <10 yrs
 - ✓ Standards for telomer sulfonates = 2015!
- Significance of field reports of foaming groundwater and soil overlooked

Speculation: we associate foam with fun, not contamination

PFOA & PFOS Toxicity

- **Carcinogenicity**

- ◆ Production workers¹⁻³ and exposed community studies – 70,000 Ohio & West Virginia residents (C8 Health Project)⁴

- **Immunotoxicity**

- ◆ Negative associations with antibody levels in children⁵ and adults⁶

- **Many PFASs detected in human blood**

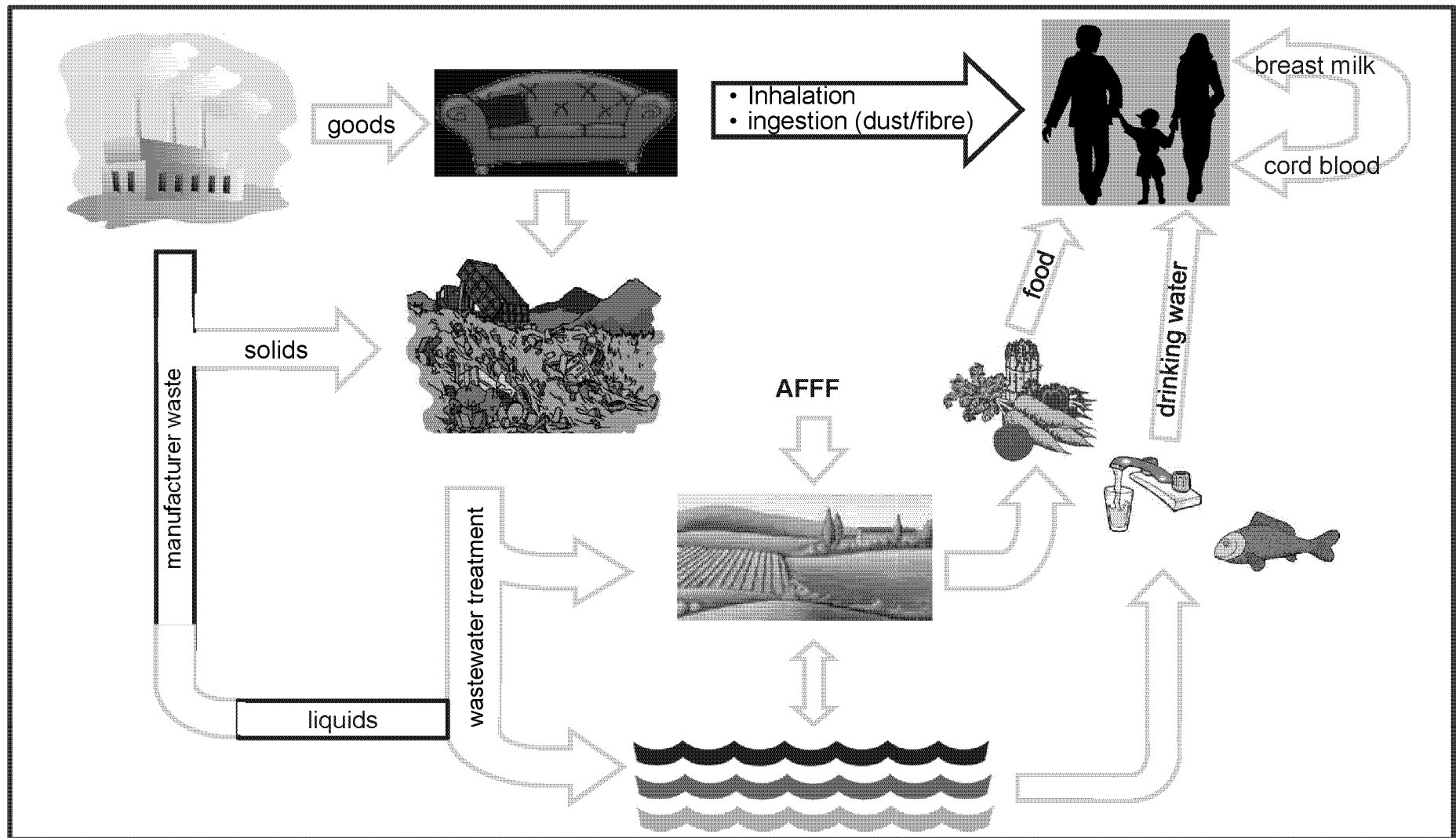
- ◆ US, China, Germany (PFSAs, PFCAs, amides, acetic acids, telomer sulfonates, phosphinates, phosphates)¹

- **Based on 3M (industrially-exposed) workers**

- ◆ PFOA 2.3 yrs² -3.8 yrs³; PFOS 4.8-5.4 yrs³
- ◆ PFHxS 7.3–8.5 yrs³ (longest reported half life of PFASs)
- ◆ PFBS 25.8 days⁴

¹O'Berg et al. 1987 J Occup Med; ²Deposition: Hearing before Leach et I vs. El DuPont de Nemours Company. Civil Action No 01-C-608, Circuit Court of Wood County, West VA, June 25, 2004; ³Alexander et al. 2003 Occup Environ Med; Lundin et al. 2009 Epidemiology; ⁴Steenland and Woskie, 2012, Am J Epidemiol; ⁵Grandjean et al 2012, JAMA; ⁶Granum et al. 2013 J Immunotox; ⁷Yeung et al. 2016 Env Chem; ⁸Bartell et al. 2010, Environ Health Perspec; ⁹Olsen et al. 2007 Environ Health Perspect; ¹⁰Olsen et al. 2009, Toxicol

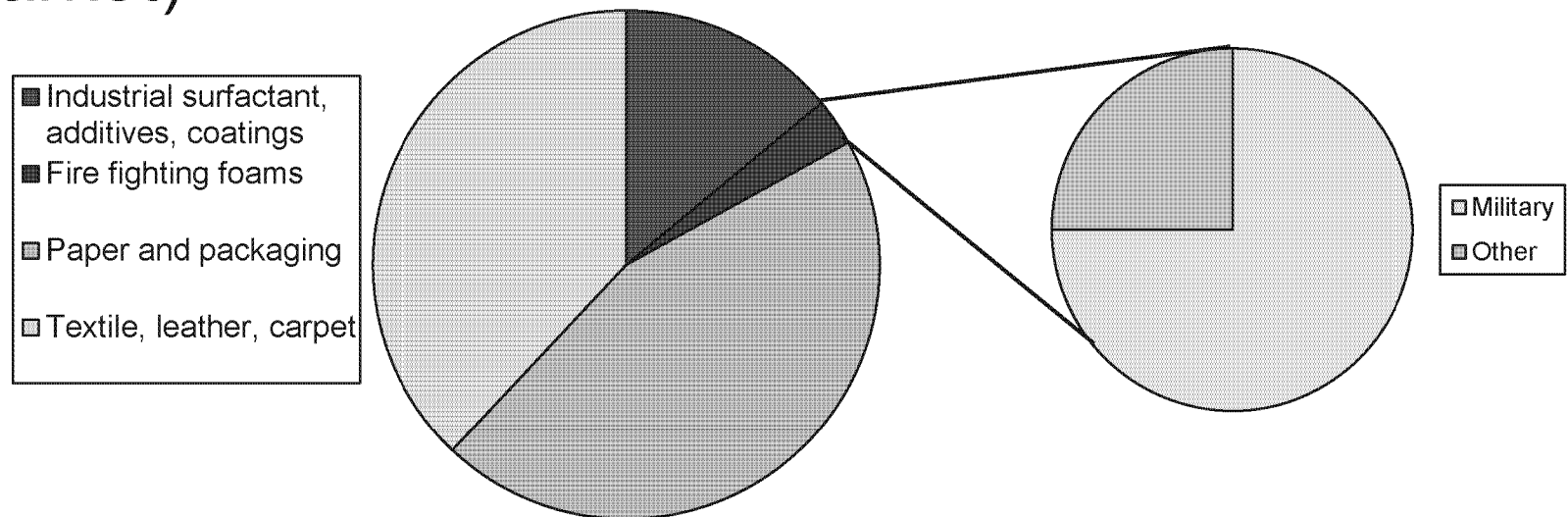
Sources & Exposure Pathways



Adapted from Oliaei 2013 Environ Pollut Res 20:1977-1992

Total 3M PFAS Production and AFFF

- Only 3% of 3M's C8-based PFASs used in AFFF¹
- Military uses 'lions share' of AFFF (75% of AFFF market)²



¹US EPA 2000; ²Moody et al. 2000 ES&T 34:3864-3870

AFFF History

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¹Stev
Direc

AFFF: Equipment Testing & Training¹

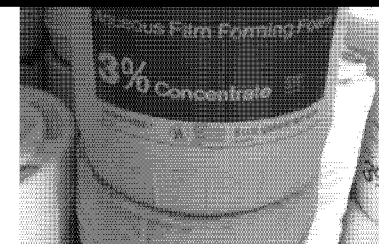
Test type	Diluted AFFF (gal)	AFFF (L)	Event/ yr	PFOS (kg)	PFOA (kg)	ΣPFAS (kg)	Σ20 yr (kg)
Capacity ²							
Nozzle discharge ²							
Training ³							
Crash ⁴							

- Annual equipment testing NFPA 412 stopped by Air Force in 2015
- Most personnel training with 'live' AFFFs (all formulas) stopped 1990s-2000s

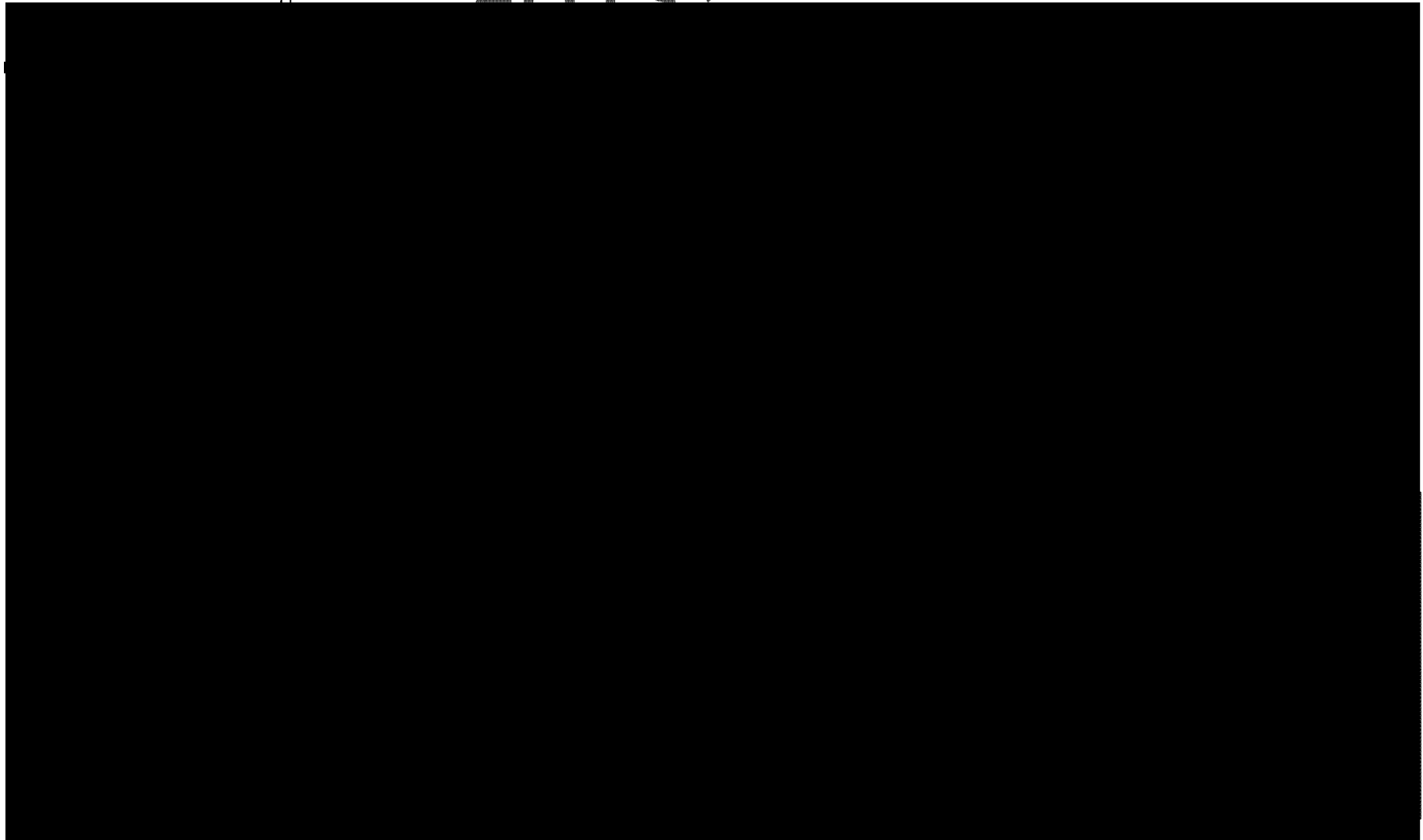
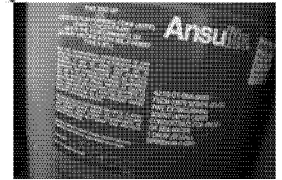
¹Kevin Matlock, Fire Emergency Services, AFCEC/CXF; ²No fuel used, testing specified in National Fire Association (NFA) Standard 412, annual testing suspended by Air Force in 2015; ³500-700 gallons fuel used & training varied by base, twice per year required, may have been quarterly depending on personnel training schedule

3M AFFF: Sole Source 1965-1975

¹Place et al. 2012, ES&T 46:7120-7127;²Backe et al. 2012 ES&T 47:5226-523;³Barzen-Hansen and Field 2015 ES&T Letters 2: 95-99



Polyfluorinated forms in Fluorotelomer AFFEs^{1,2}



Alt. 2010-EG&T-10-7000-707-1

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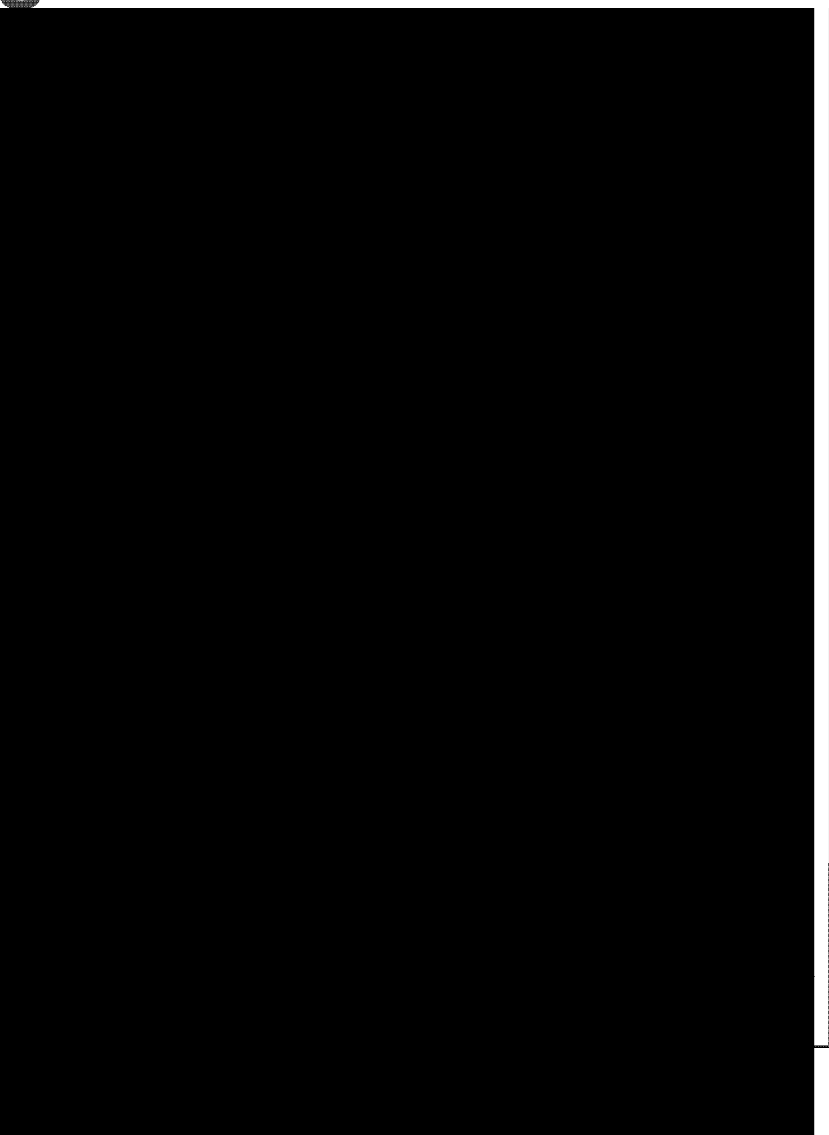
Aerobic Biode



¹Wein
Marjan
ES&T

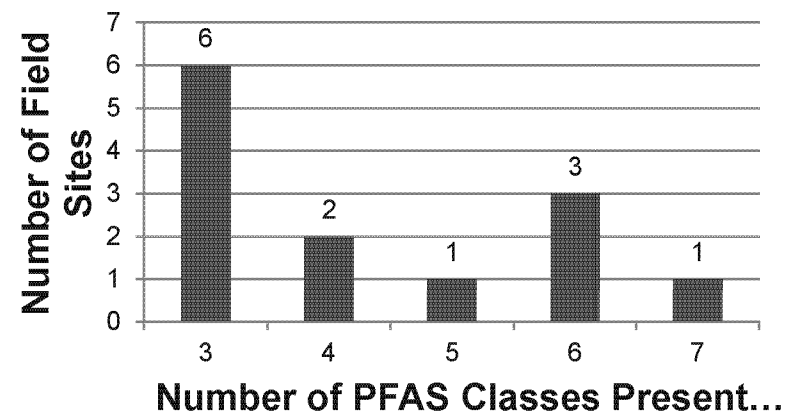
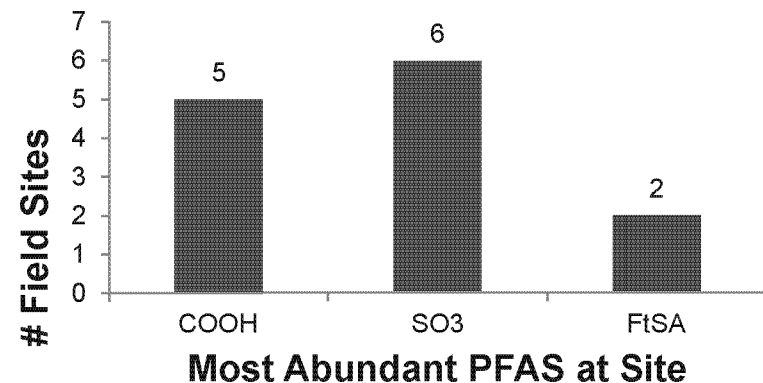


gradation



PFASs in Groundwater at Military Bases

- 13 Air Force & Navy bases
- PFASs and PFCAs not always the most abundant
- PFASs & PFCAs concentrations >> EPA's HAs
- No site has just PFASs & PFCAs
- Groundwater concentrations greater than any other aqueous media¹
 - ✓ PFOS = 1 mg/L
 - ✓ PFOA = 6.6mg/L
 - ✓ 6:2FTSA = 14 mg/L



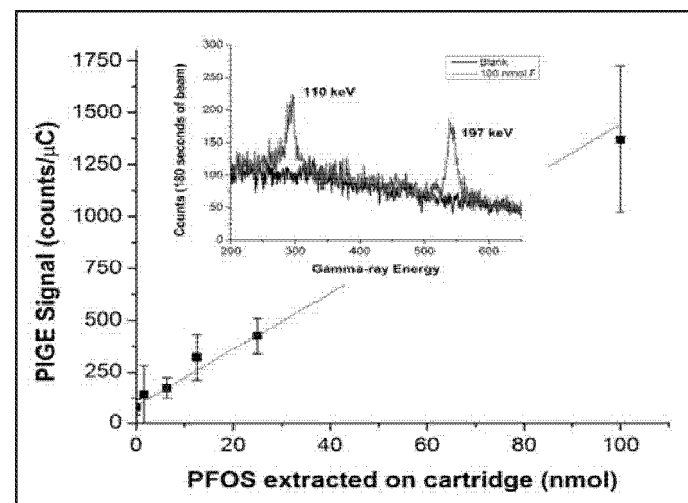
¹Schultz et al. 2004 ES&T 38:1828-1835

Closing the Mass Balance: Why Care?

- Many PFASs used in AFFF & identified in groundwater, sediment/soil that won't be 'lists' any time soon
- Selection of remedial treatments and treatment of drinking water sources requires knowledge of 'targets'
- Increasing regulator and public awareness regarding presence of precursors and 'other' PFASs
- **Bottom line:** Minimizing/preventing future liabilities

Towards Mass Balance on Fluorine

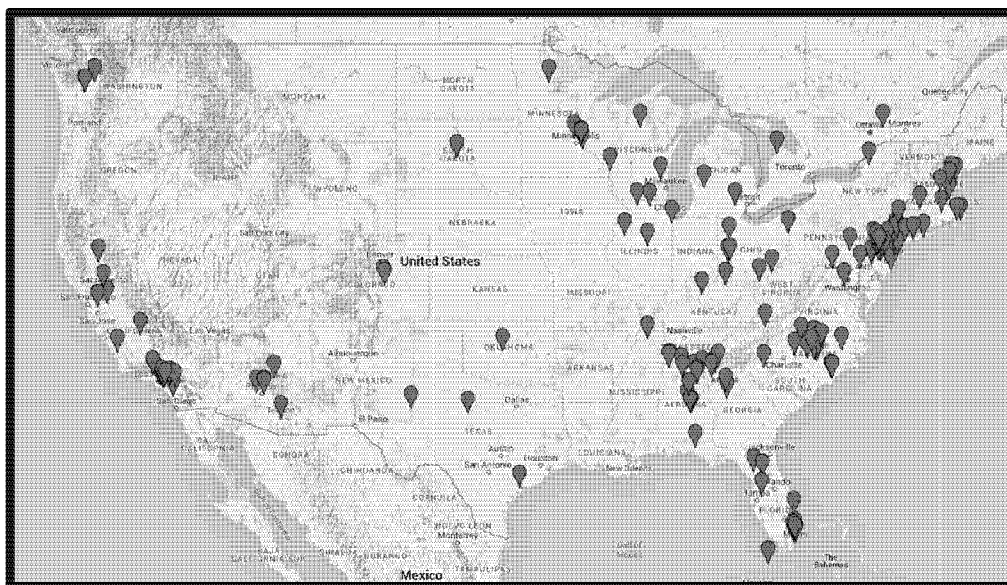
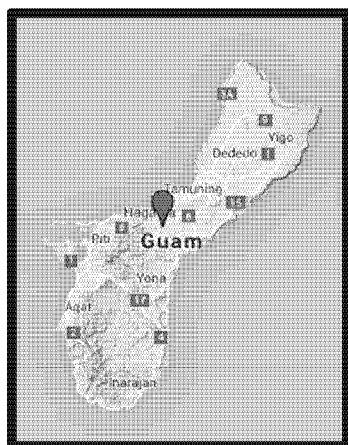
- Additional analytical tools for closing the mass balance on fluorine:
- Total oxidizable precursor (TOP) assay
 - ✓ Quantifies precursor (total PFASs) in groundwater, sediment, soil¹
 - ✓ Closes mass balance in microcosm studies²
- Total fluorine by PIGE³
 - ✓ PFAS in groundwater sorbed onto media to create 'target'
 - ✓ 10 nA of 3.4 MeV protons for 180 s
 - ✓ Quantitative, high-throughput
 - ✓ Inexpensive screening tool



¹Houtz et al. 2013 ES&T 47:9342-9349; ²Harding-Marjanovic et al. 2015 ES&T 49:7666-7674; ³Lunderberg et al. 2015 Fluoros, Golden, CO;

UCMR3 Data: Public Water Supply

- UCMR3: public water systems serving > 10,000 people
- 3 PFSA's & 3 PFCAs analyzed
- Positive hits (>MRL) for one or more PFASs (June 2015 database)
- Drinking water important source of short-chain PFASs¹⁻³



¹Gyllenhammar et al. 2015 Environ Res 140:673-683;²Eschauzier et al. 2013 Sci Tot Environ 458:477-485;³Weiss et al. 2012 Intl Hyg Environ Health 215:212-215

Sources & Fingerprinting

- **Landfill Leachate (municipal refuse/consumer products)**
 - ✓ 2nd place ($\mu\text{g/L}$)¹⁻³
 - ✓ short-chain PFCAs & fluorotelomer acids³
- **Municipal wastewater effluent**
 - ✓ 3rd place ($< 0.1 \mu\text{g/L}$)⁴⁻⁶
- **Chromium electroplating (mist suppression)**^{7,8}
- **Industrial (plastics/polymer) manufacturing**
 - ✓ PFNA in NJ⁹ & PFOA in NY¹⁰
- **Other:** municipal airports & fire departments, oil refineries

¹Allred et al. 2014 J Chrom A 1359: 202-211; ²Allred et al. 2015 ES&T 49:7648–7656; ³Benskins et al. 2012 ES&T 46:11532-11540; ⁴Schultz et al. 2006 ES&T 40:289-295; ⁵Sinclair and Kannan 2006 ES&T 40:1408-1414 ; ⁶Logananthan et al 2007 Water Res 41:4611-4620; ⁷EPA Region 5 PFOS Chromium Electroplater Study, 2009; ⁸Yang et al. 2014 Env Sci Pollut 21:4634-4642Res; ⁹<http://www.njspotlight.com/stories/15/04/06/drinking-water-panel-calls-for-stricter-standard-on-potential-carcinogen/>; ¹⁰<http://www.villageofhoosickfalls.com/news.html>

Transport Generalizations

- Transport related to chemical structure & charge/ionization
 - ✓ For anions, shorter chain lengths generally migrate faster (less retardation, lower K_{oc})¹⁻³
 - likely to impact surface waters
 - challenging to remove by GAC⁴
 - ✓ Transport potential: anions > zwitterions > cations
 - ✓ For many polyfluorinated forms, transport will depend on pH and molecule's charged state (ionic or neutral), ionic strength, ion exchange capacity
- Cationic forms potentially cation exchanged onto source-zone sediments
 - ✓ Mobile or immobile under what conditions?
 - ✓ Caution when applying oxidants to source-zone sediments, potential to liberate PFASs as water soluble, short-chain forms⁵⁻⁹ that are most difficult to remove

¹Higgins et al. 2006 ES&T, 40:7251-7256; ²Higgins and Luthy, 2007 ES&T 41:3254-3261; ³Guelfo and Higgins 2013 ES&T 47:4164-4171; ⁴Appleman et al. 2014 Wat Res 51:246-255; ⁵Houtz and Sedlak, 2012 ES&T 46: 9342-9349; ⁶Houtz and Sedlak, 2013 ES&T 47: 8187-8195; ⁷Yang et al. 2014, Environ Sci Pollut 21: 4634-4642; ⁸Fang et al. 2015 Environ Tox Chem 34: 2625-2628; ⁹Park et al. 2016 Chemosphere 145: 376-383

New SERDP/ESTCP Projects

- ESTCP Project ER-201574-T2
“Catalyzing Rapid Information Transfer Among Key Stakeholders on Per- and Polyfluoroalkyl Substances (PFASs) at Contaminated Military Sites” OSU lead (J. Field)
- SERDP Project ER-2627
“Advancing the Understanding of the Ecological Risk of Per- and Polyfluoroalkyl Substances” Townson University lead (C. Salice)
- ESTCP Project ER-201633
“Characterization of the Nature and Extent of Per- and Polyfluoroalkyl Substance (PFASs) in Environmental Media at DoD Sites for Informed Decision-Making” Navy lead (J. Kornuc)

Conclusions

- PFOS and PFOA are important but not the only major PFASs at AFFF-contaminated sites
- Fluorotelomer-based substances partially biodegrade to metastable intermediates, including short-chain PFCAs, but not to PFOS
- Mobility in groundwater anions > zwitterions > cations
- Anion mobility depends on chain length
- Mobility of many substances influenced by sediment, soil and water geochemistry

Benefits of Future SERDP/ESTCP Projects to DoD

- Hundreds of fire/crash testing (mixed waste) sites
- Full characterization of PFAS contamination
 - ✓ More accurate conceptual site models
 - ✓ Identify remedial approaches that decrease time and cost
 - ✓ Optimized monitoring
 - ✓ Fingerprinting to differentiate AFFF from other sources
 - ✓ Source zone identification
 - ✓ Accurate predictions of transport
 - ✓ Indicators of in situ biotransformation
- Groundwater contaminated by PFAS used as drinking water source is a potential exposure pathway for humans and wildlife
 - ✓ Attention to short-chain PFAS highly mobile, difficult to remove from water

**For additional information, please visit
<https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Emerging-Issues/ER-2128>**

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