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

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SERDP DOD ▪ EPA ▪ DOE | ESTCP

Project Team

- Dr. Jennifer A. Field, Oregon State University
  - ♦ Environmental analytical chemist
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  - ♦ Advanced oxidation and contaminant fate expert
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  - ♦ Environmental microbiologist/engineer
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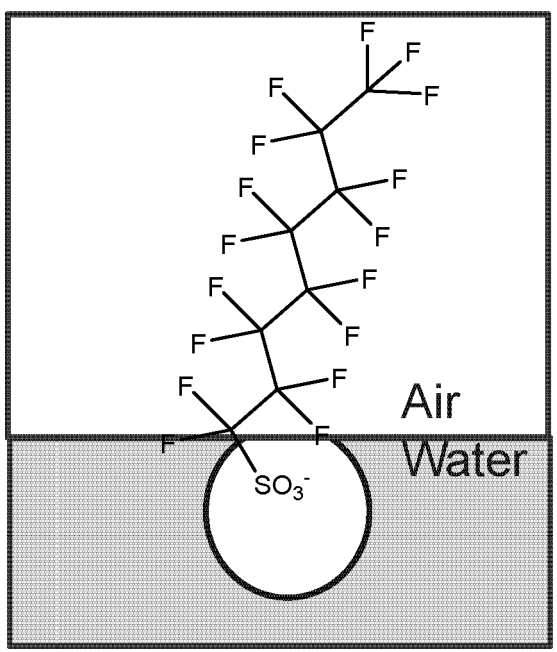
  - ♦ Soil scientist

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

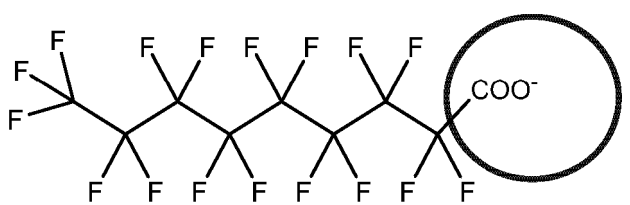
Unique Chemistry of PFASs

- C-F bond is the shortest & strongest in nature
  - ✓ hydrophobic & oleophobic[1]
  - ✓ less predictable behavior in laboratory & environmental systems



PFOS (***per***fluorooctane sulfonate)

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

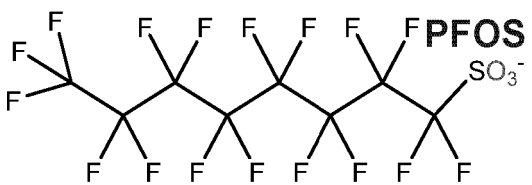


PFOA (***per***fluorooctanoate)

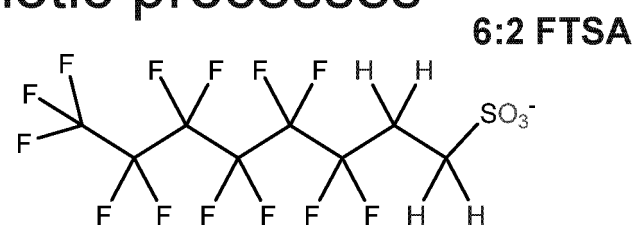
[1]Krafft and Riess 2015 Chemosphere 129:4-19

PFASs vs. ~~PFCs~~

- **PFAs = Per and polyfluoroalkyl substances**
- **Communicate accurately**
  - ✓ contract laboratories, regulatory community, the public, internationally[1]
- **PFC = 'Perfluorinated' = restrictive term**



  - ✓ all carbons in aliphatic chain must be bonded ***only*** to F
  - ✓ no degradation in environment
- **Polyfluorinated = <u>not a</u>ll carbons in chain bonded to F**
  - ✓ CH_2 – linkages create 'weakness' in molecule
  - ✓ susceptible to biodegradation, abiotic processes (oxidation)



[1]Buck 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

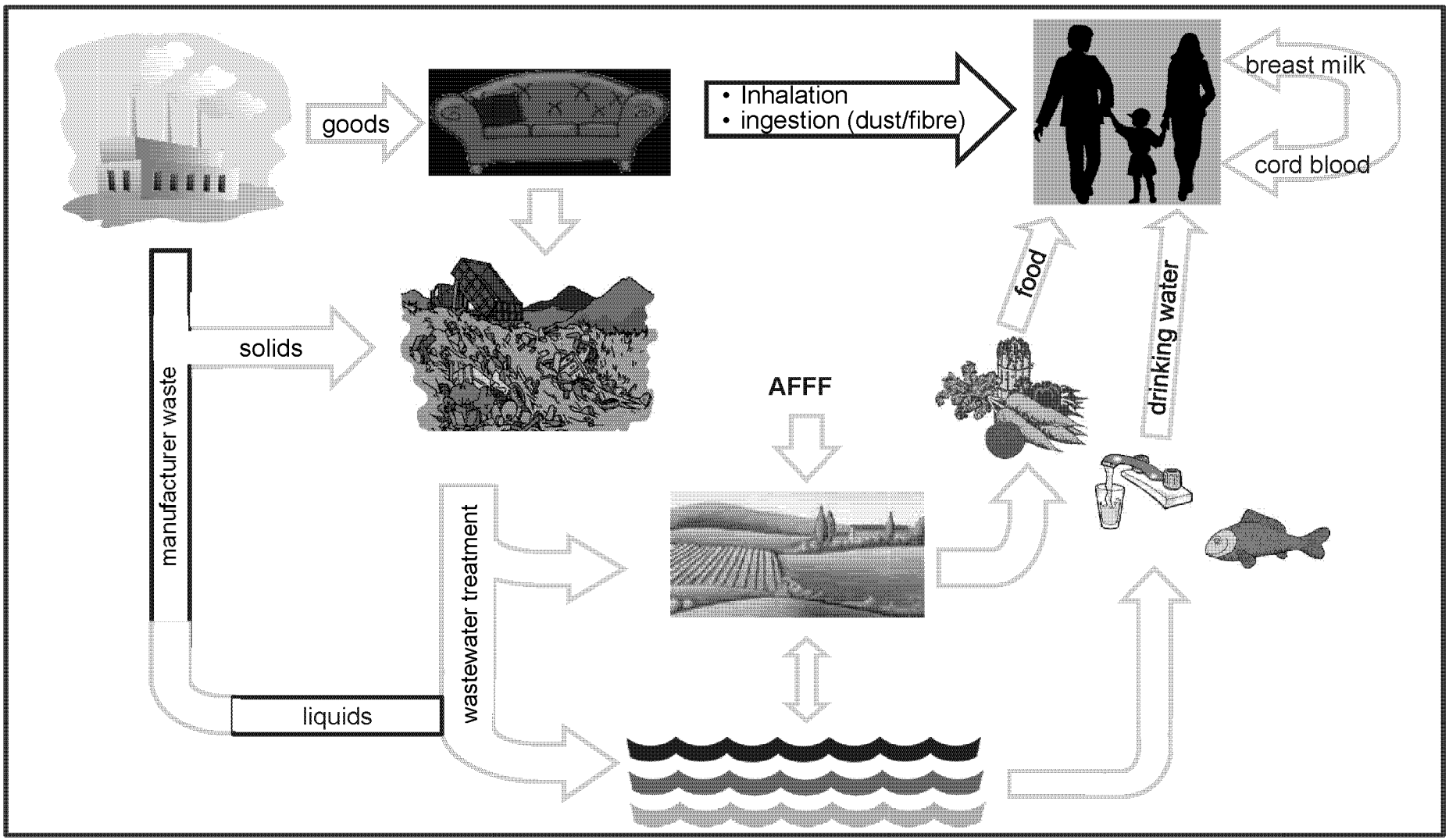
Speculation: we associate foam with fun, not contamination

PFOA & PFOS Toxicity

- **Carcinogenicity**
  - Production workers[1-3] and exposed community studies – 70,000 Ohio & West Virginia residents (C8 Health Project)[4]
- **Immunotoxicity**
  - Negative associations with antibody levels in children[5] and adults[6]
- **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 yrs[2] -3.8 yrs[3] ; PFOS 4.8-5.4 yrs[3]
  - PFHxS 7.3–8.5 yrs[3] (longest reported half life of PFASs)
  - PFBS 25.8 days[4]

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

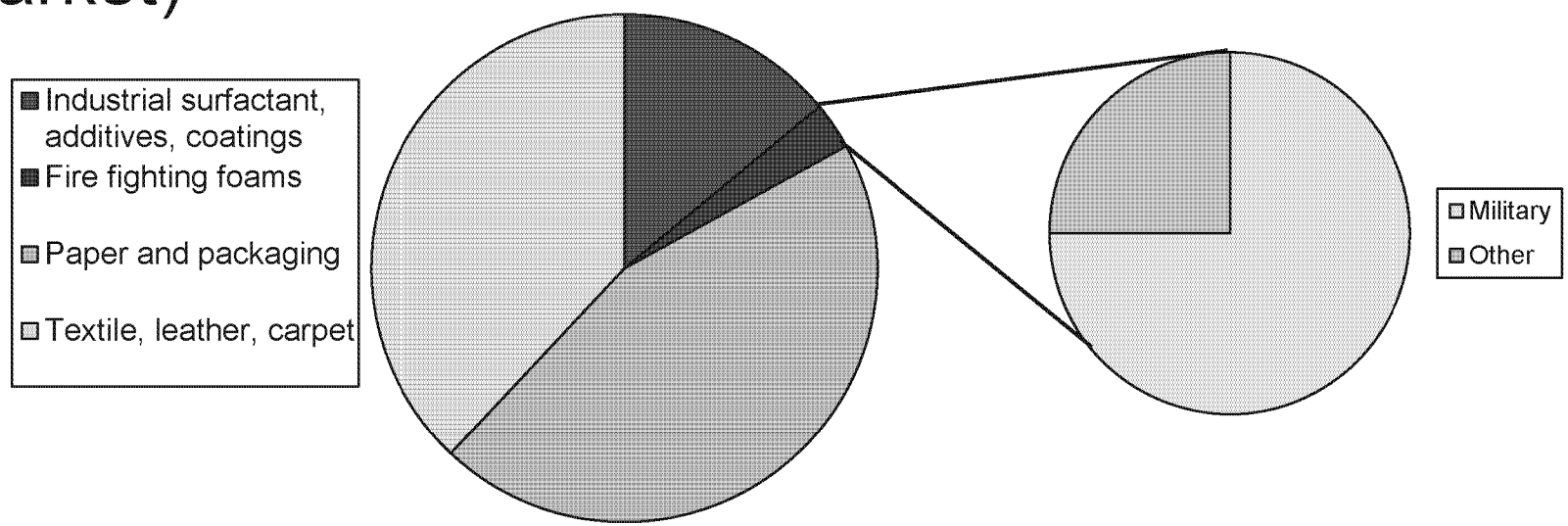
Sources & Exposure Pathways



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

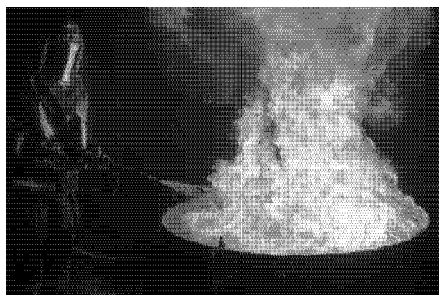
Total 3M PFAS Production and AFFF

- Only 3% of 3M's C8-based PFASs used in AFFF[1]
- Military uses 'lions share' of AFFF (75% of AFFF market)[2]



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

AFFF History



- **Proprietary mixtures**
  - ✓ Complex mixtures with ***g/L*** PFASs
- AFFFs (MilSpec) on Qualified Product List[1]
  - ✓ 1965-1976 Light Water (3M)
  - ✓ 1976 Ansulite (Ansul) and Aer-O-Water (National Foam)
  - ✓ 1994 Tridol (Angus)
  - ✓ After 2002 Chemguard (Chemguard), Buckeye (Buckeye), Fireaide (Fire Service Plus)
- **Bottom line**: Multiple AFFFs used at most sites
- **Detection frequencies**:[2] testing/maintenance > hangars/buildings > emergency response
- **Other:** pipes, storage container areas, oil-water separators, waste disposal sites

[1]Steve Fletcher, Fire Protection Engineer, NAVSEA HQ, SEA 05P5; [2]Anderson et al. 2016 Chemosphere;Photo courtesy of John Farley, Director, CBD/ex-USS SHADWELL Fire Test Operations, Naval Research Laboratory, Washington DC

AFFF: Equipment Testing & Training[1]

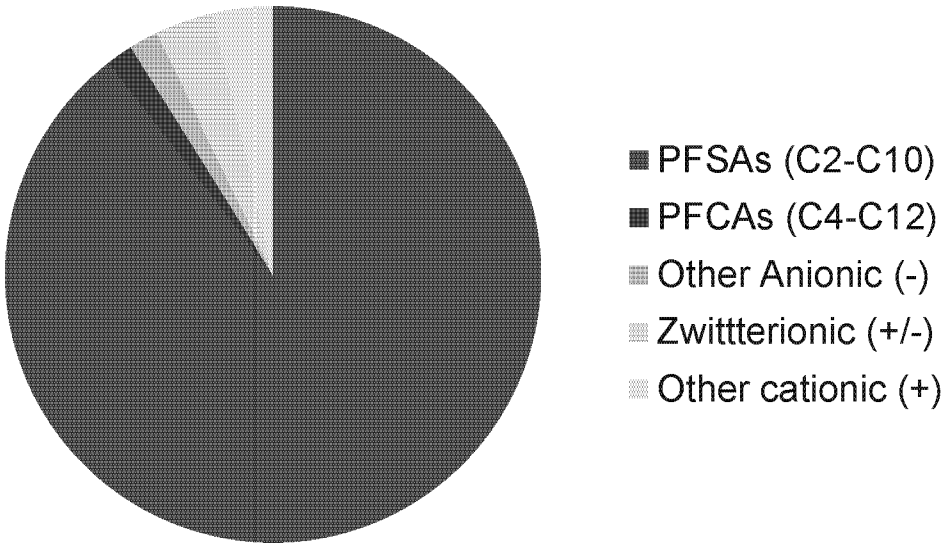
Test type	Diluted AFFF (gal)	AFFF (L)	Event/ yr	PFOS (kg)	PFOA (kg)	ΣPFAS (kg)	Σ20 yr (kg)
Capacity[2]	3,000	341	1	**3.2**	0.032	4.7	**93**
Nozzle discharge[2]	10	1.1	1	0.01	0.0011	0.015	**0.31**
Training[3]	20	2.3	4	~~0.084~~	0.0084	~~0.12~~	**2.5**
Crash[4]	50,000	5,678		**53**	5.3	**77**	

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

[1]Kevin Matlock, Fire Emergency Services, AFCEC/CXF;[2]No fuel used, testing specified in National Fire Association (NFA) Standard 412, annual testing suspended by Air Force in 2015;[3]500-700 gallons fuel used & training varied by base, twice per year required, may have been quarterly depending on personnel training schedule

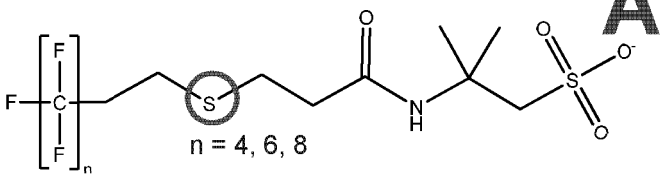
3M AFFF: Sole Source 1965-1975

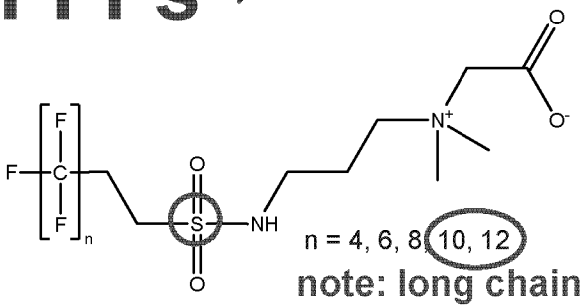
- 89% PFSAs (e.g., PFOS) in 3M AFFF[1-3]
- *Only* 1.6% PFCAs(e.g., PFOA)
- *All* contribute to total fluorine



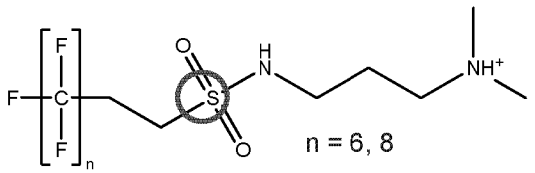
[1]Place et al. 2012, ES&T 46:7120-7127;[2]Backe et al. 2012 ES&T 47:5226-523;[3]Barzen-Hansen and Field 2015 ES&T Letters 2: 95-99

Polyfluorinated forms in Fluorotelomer AFFFs[1,2]

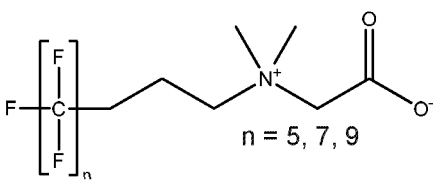


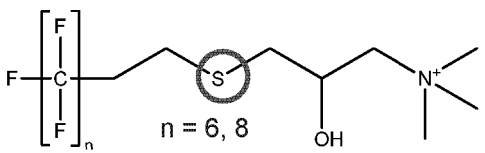


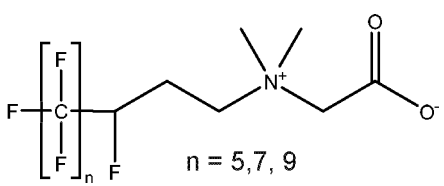
note: long chain lengths!

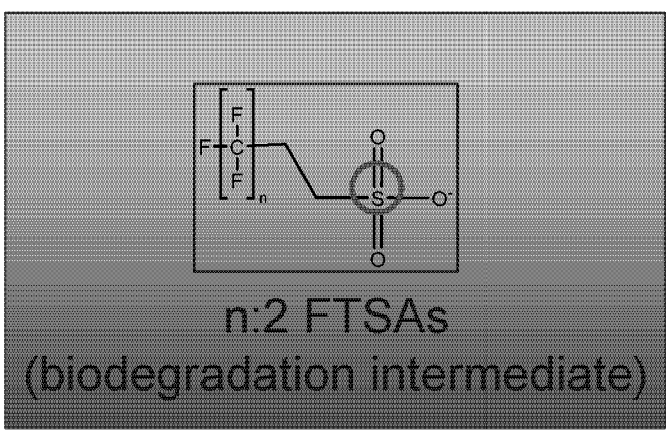


- none listed on UMCR3 & Method 537 lists
- *all* contribute to total F
- –S- forms degrade to FTSAs & short-chain PFCAs[3,4]
- 6:2 & 8:2 FTSAs = major degradation products in groundwater[2] (only trace levels in AFFF)





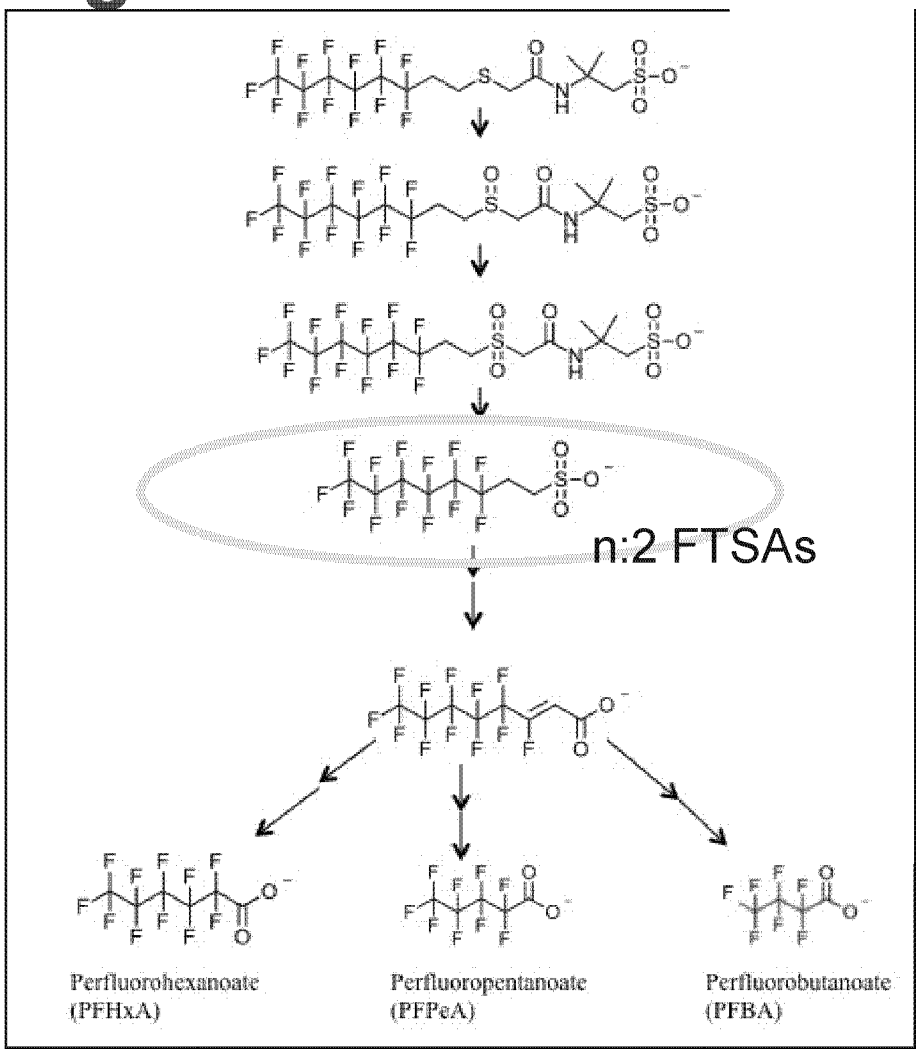




[1]Place et al. 2012, ES&T 46:7120-7127;[2]Backe et al. 2012 ES&T 47:5226-5234;[3]Weiner et al. 2013 Environ Chem 10:486-493; [4]Harding-Marjanovic et al. 2015 ES&T 49:7666-7674

Aerobic Biodegradation

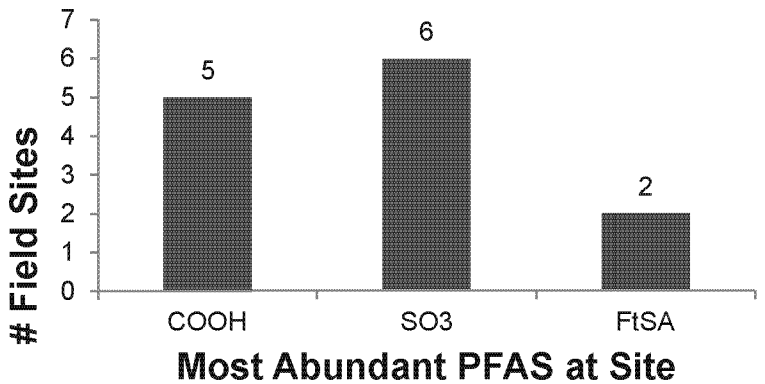
- Ansul precursor degrades to FTSAs & short-chain (≤ C6) PFCAs[1,2]
- FTSAs >> precursors in site groundwater[3]
- FTSAs stable under anoxic conditions ~ decade
- -SO- and -SO_2- intermediates in groundwater

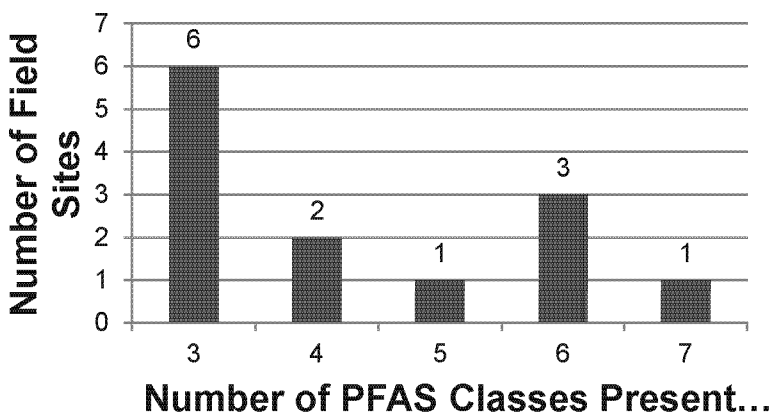


[1]Weiner et al. 2013 Environ Chem 10:486-493; [2]Harding-Marjanovic et al. 2015 ES&T 49:7666-7674;[3]Backe et al. 2012 ES&T 47:5226-5234

PFASs in Groundwater at Military Bases

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





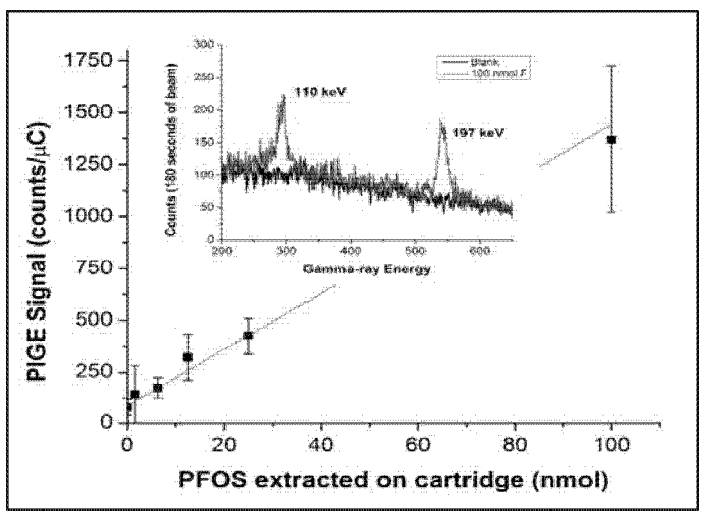
[1]Schultz et al. 2004 ES&T 38:1828-1835

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

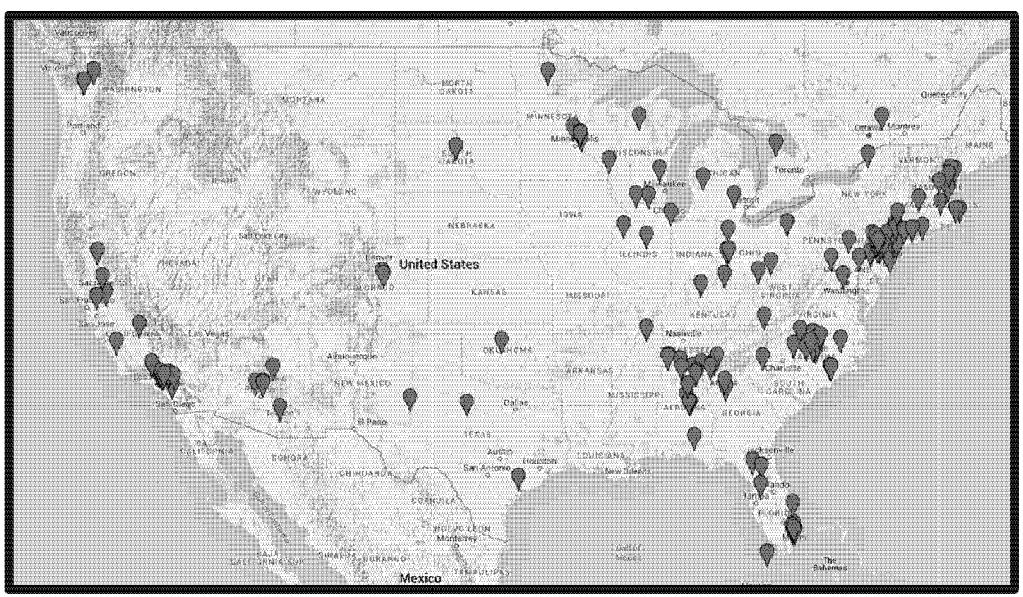
- Additional analytical tools for closing the mass balance on fluorine:
- Total oxidizable precursor (TOP) assay
  - ✓ Quantifies precursor (total PFASs) in groundwater, sediment, soil[1]
  - ✓ Closes mass balance in microcosm studies[2]
- Total fluorine by PIGE[3]
  - ✓ PFAS in groundwater sorbed onto media to create 'target'
  - ✓ 10 nA of 3.4 MeV protons for 180 s
  - ✓ Quantitative, high-throughput
  - ✓ Inexpensive screening tool



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

UCMR3 Data: Public Water Supply

- UCMR3: public water systems serving > 10,000 people
- 3 PFSAs & 3 PFCAs analyzed
- Positive hits (>MRL) for one or more PFASs (June 2015 database)
- Drinking water important source of short-chain PFASs[1-3]



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

Sources & Fingerprinting

- **Landfill Leachate (municipal refuse/consumer products)**
  - ✓ 2nd place (μg/L)[1-3]
  - ✓ short-chain PFCAs & fluorotelomer acids[3]
- **Municipal wastewater effluent**
  - ✓ 3rd place (< 0.1 μg/L)[4-6]
- **Chromium electroplating (mist suppression)**[7,8]
- **Industrial (plastics/polymer) manufacturing**
  - ✓ PFNA in NJ[9] & PFOA in NY[10]
- **Other:** municipal airports & fire departments, oil refineries

[1]Allred et al. 2014 J Chrom A 1359: 202-211;[2]Allred et al. 2015 ES&T 49:7648–7656;[3]Benskins et al. 2012 ES&T 46:11532-11540; [4]Schultz et al. 2006 ES&T 40:289-295l;[5]Sinclair and Kannan 2006 ES&T 40:1408-1414 ;[6]Logananthan et al 2007 Water Res 41:4611-4620;[7]EPA Region 5 PFOS Chromium Electroplater Study, 2009; [8]Yang 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 Koc)[1-3]
    - likely to impact surface waters
    - challenging to remove by GAC[4]
  - ✓ 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 forms[5-9] that are most difficult to remove

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