



# Emerging Contaminants: Per- and Polyfluoroalkyl Substances (PFASs)

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## Introductions

### • Jennifer A. Field

- Professor Oregon State University
- Ph.D. in Geochemistry, Colorado School of Mines
- 20+ yrs experience in PFAS analysis, fate, and transport
- 26 peer-reviewed publications on PFASs
- Associate Editor for Environmental Science & Technology

### • John Kornuc

- Biologist, Naval Facilities Engineering Command (NAVFAC) Engineering and Expeditionary Warfare Center (EXWC)
- Ph.D. Biochemistry, UCLA; BS Microbiology, Ohio State
- 30+ years experience in environmental – site investigations, remediation, laboratory establishment

## Presentation Overview

### Overview – Why We Care

- Unique Chemistry, Properties, Toxicity
- Aqueous Film Forming Foam (AFFF)
- Site Characterization & Transport
- Beyond the Fence
- Navy Guidance
- Regulatory Considerations
- Sampling Considerations
- Analytical Methods
- Remediation Methods
- Case Studies Update
- Wrap-Up

You will notice footnote indicators in the presentation slides. They refer to literature cited, in the Wrap-Up section.

## PFASs Overview – Why We Care

- A class of chemicals that are ubiquitous due to
  - Wide variety of uses
  - Persistence
  - High mobility
- They are a concern due to:
  - Known or suspected toxicity, especially for PFOS and PFOA
  - Bioaccumulation
  - Some have very long half lives, especially in humans
- DoD's use of Aqueous Film-Forming Foam (AFFF)
  - Some AFFF formulations contain high levels of PFOS
  - Resulted in elevated levels of these chemicals in the environment up to 106 higher than background
  - State representatives for Warminster area have recently called on Navy to perform a health effects (C8) study

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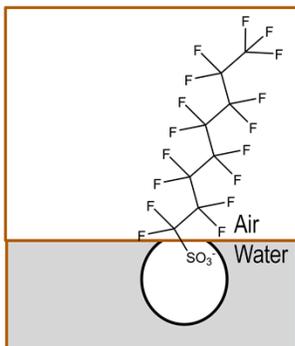
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## Unique Chemistry of PFASs ~~PFCs~~

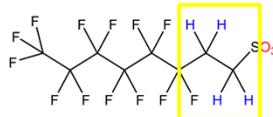
- **C-F bond:** shortest & strongest bond in nature
  - Properties less predictable: hydrophobic and oleophobic<sup>1</sup>
- **Perfluorinated** – all carbons in chain bonded only to F (e.g., PFOS and PFOA)
  - Few engineered or environmental degradation processes degrade perfluorinated forms



- **Polyfluorinated**

- Not all carbons in chain bonded to F
- CH<sub>2</sub> – linkages = ‘weakness’ in molecule, open to chemical and biological degradation

- **Per- and polyfluoroalkyl substances (PFASs)<sup>2</sup>**



**PFOS** (perfluorooctane sulfonate)

**6:2 FTSA** (fluorotelomer sulfonate)

### Literature Cited

<sup>1</sup>Goss and Bronner, 2006, J Phys Chem

<sup>2</sup>Buck et al., 2011 Integr Environ Assess Manag

## Environmentally-Relevant Properties: Anionic PFASs

- **Negatively-charged anions at environmental and physiological pHs (4-10)**
- **Low vapor pressure and Henry's Law so cannot be air-stripped (caution when disposing of 'treated' water from air stripper system)**
- **Water soluble so readily transported in soil/sediment (more on transport later)**

7 Unique Chemistry

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Chemical Abstracts (CAS) Numbers for both protonated (free acid) forms and salts ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ) of PFOS and PFOA

Chemical properties (water solubility, vapor pressure, Henry's Law) depend on form  
Properties in databases (TOXNET)<sup>1</sup> are specific to protonated form  
Properties difficult to predict (e.g., EPISUITE)<sup>2</sup> since PFASs were not in the 'training sets' used to establish predictions

<sup>1</sup>TOXNET (<http://toxnet.nlm.nih.gov/newtoxnet/hsdb.htm>)

HSDB is a toxicology database that focuses on the toxicology of potentially hazardous chemicals. It provides information on human exposure, industrial hygiene, emergency handling procedures, environmental fate, regulatory requirements, nanomaterials, and related areas. The information in HSDB has been assessed by a Scientific Review Panel.

<sup>2</sup>EPISUITE (<http://www2.epa.gov/tsca-screening-tools/epi-suitetm-estimation-program-interface>) The Estimation Programs Interface (EPI) suite TM was developed by the US EPA's Office of Pollution Prevention and Toxics Syracuse Research Corporation.

## Why are PFASs Emerging Now?

- PFASs are non-volatile and cannot be detected using traditional analytical instruments (gas chromatography mass spectrometry or GC/MS)
- Field reports of foaming groundwater and soil were major clues about PFAS occurrence but significance was not recognized
- PFAS are measured by liquid chromatography tandem mass spectrometry (LC-MS/MS), available <15 years ago

## Toxicity

- **Carcinogenicity**
  - **Production workers**
    - PFOA – excess leukemia<sup>3,4</sup> and kidney<sup>4</sup> cancers
    - PFOS – increased prostate cancers<sup>5</sup>
  - **Exposed community studies – 70,000 Ohio & West Virginia residents (C8 Health Project)<sup>6</sup>**
    - Correlations between PFOA and kidney, testicular, prostate, ovarian cancer, & non-Hodgkin lymphoma
- **Immunotoxicity**
  - **Negative associations with antibody levels in children<sup>7</sup> and adults<sup>8</sup>**
- **Many PFASs detected in human blood (US, China, Germany – many classes, not just PFOS and PFOA)<sup>9</sup>**
- **Half lives in humans**
  - PFOA 2.3 to 3.5 – 3.8 yrs<sup>10,11</sup> and PFOS 4.8 - 5.4 yrs<sup>11</sup>
  - PFHxS 7.3 – 8.5 yrs<sup>11</sup> (**longest reported half life of any PFAS**)
  - PFBS 25.8 days<sup>12</sup>

### Literature Cited

<sup>3</sup>O'Berg et al., 1987, J Occup Med

<sup>4</sup>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

<sup>5</sup>Alexander et al., 2003, Occup Environ Med; Lundin et al., 2009, Epidemiology

<sup>6</sup>Steenland and Woskie, 2012, Am J Epidemiol

<sup>7</sup>Grandjean et al., 2012, JAMA

<sup>8</sup>Granum et al., 2013, J Immunotox

<sup>9</sup>Yeung et al., 2016, Env Chem

<sup>10</sup>Bartell et al., 2010, Environ Health Perspect

<sup>11</sup>Olsen et al., 2007, Environ Health Perspect

<sup>12</sup>Olsen et al., 2009, Toxicol

## What's New on the Regulatory Landscape?

- **Sep. 1, 2015: PFOA proposed for addition to Stockholm Convention**
- **Jan. 27, 2016: Gov. Cuomo (NY) declared PFOA as hazardous substance<sup>13</sup> – “unlock state resources and legal remedy to address contamination”**
- **March 2, 2016: State Rep. Stephens and O’Neill request ‘C8 Study’ for Warminster/Horsham area**
- **March 10, 2016: Gov. Cuomo, Shumlin (VT), and Hassan (NH) request EPA to review PFOA**
- **Apr. 3, 2016: EPA Health Advisory levels (short term exposure values) – will announce status if changed**

<sup>13</sup><https://www.governor.ny.gov/news/governor-cuomo-announces-immediate-state-action-plan-address-contamination-hoosick-falls>

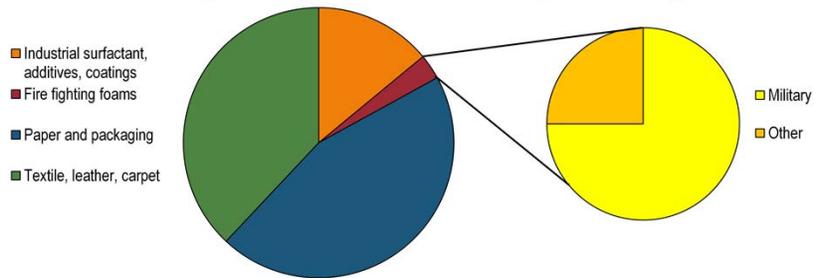
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## Aqueous Film Forming Foam (AFFF)

- **Only 3% of 3M C8-based PFAS production used in AFFFs<sup>14</sup>**
  - Other uses (surfactant, additive, paper, textiles, carpet) become sources including landfill leachate and WWTP effluent and biosolids
- **Military uses ‘lions share’ (75%) of AFFF<sup>15</sup>**
- **‘Other’ = municipal airports, refineries, industry**



12 Aqueous Film Forming Foam (AFFF)

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### Literature Cited

<sup>14</sup>US EPA 2000a

<sup>15</sup>Moody et al., 2000, Environ Sci Technol

## History of AFFF Use

- **Aqueous film forming foam<sup>16</sup>**

- Complex, proprietary mixtures of fluorinated & hydrocarbon surfactants, water, corrosion inhibitors, solvent (e.g., butyl carbitol)
- PFASs only a few% but still **mg/L** levels PFASs in AFFF product
- **Need 10<sup>6</sup> dilution to get below EPA PHAs for PFOS/PFOA**



*Courtesy U.S. Navy*

- **6% (Navy) AFFFs on the Qualified Product List (QPL)<sup>17</sup>**

- 1970-1976 Light Water™ (3M) and Ansulite® (Ansul)
- 1976 Aer-O-Water® (National Foam)
- 1994 Tridol (Angus)
- After 2002 Chemguard (Chemguard), FireAde® (Fire Service Plus)

- **Bottom line: Multiple AFFFs used at most sites**

13 Aqueous Film Forming Foam (AFFF)

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<sup>16</sup>Kevin Matlock, Fire Emergency Services, Air Force, Tyndall AFB

<sup>17</sup>Information and photos courtesy of John Farley, Director, CBD/ex-USS SHADWELL Fire Test Operations, Naval Research Laboratory, Washington DC

## AFFF: Historical Equipment Testing & Training<sup>18</sup>

Test Type	Diluted AFFF (gal)	AFFF (L)	Event/yr	PFOS (kg)	PFOA (kg)	ΣPFAS (kg)	Σ20 yr (kg)
Capacity (2 trucks) <sup>19</sup>	3,000	341	1	3.2	0.032	4.7	93
Nozzle discharge <sup>19</sup>	10	1.1	1	0.01	0.0011	0.015	0.31
Training <sup>20</sup>	20	2.3	4	0.084	0.0084	0.12	2.5
Crash <sup>21</sup>	50,000	5,678				41 kg	

- Navy has not conducted Capacity/Time and Distance tests with AFFF since at least 2003<sup>22</sup>
- Refractometer tests also conducted but frequency & volume variable<sup>22</sup>
- Navy stopped training with 'live' AFFFs late 1980s-1990s but AFFF training activity continues at a limited number of Navy sites, wastes collected for disposal<sup>22</sup>

14 Aqueous Film Forming Foams (AFFF)

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### Literature Cited

<sup>18</sup>Kevin Matlock, Fire Emergency Services, AFCEC/CXF

<sup>19</sup>No fuel used, testing specified in National Fire Association (NFA) Standard 412, annual testing suspended by Air Force in 2015

<sup>20</sup>500-700 gallons fuel used & training varied by base, twice per year required, may have been quarterly depending on personnel training schedule

<sup>21</sup>B2 crash 20,000 gallons fuel & actual AFFF used not known (Ansul used as example)

<sup>22</sup>Carl Glover, Navy CNIC

## Stockpiles: PFAS Sources of Tomorrow

- **Stockpiles can and will be used for emergencies**
  - AFFFs currently on QPL  
<http://qpldocs.dla.mil/search/parts.aspx?qpl=1910>
- **Stockpiles are potentially large!**
  - No official Navy estimate of stockpile volume/type yet
  - Air Force: 356,000 gallons AFFF stockpiled (telomer-based);  
110,000 gallons 3M in containers (not used)
  - Encouraged not to use 3M AFFF (PFOS) since 2002, may incinerate
- **Continued use of fluorotelomer-based AFFF**
  - Does not contain PFOS and precursors do not degrade to PFOS
  - Precursors degrade to PFCAs and FTSA

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### Guidelines

DoD information on AFFF<sup>W</sup>

MN guidelines<sup>X</sup>

German guidelines

### Excerpts from guidelines

Class B fires only (do not use on wood, paper, textiles)

### Common sense

Avoid off-label uses like cleaning

Avoid all unnecessary discharges to water/soil/sediment

Foam has high BOD, depletes oxygen from water

Foam has the potential to remove oils from birds (hypothermia)

<sup>W</sup><http://www.denix.osd.mil/cmrmd/upload/Chemical-&-Material-Emerging-Risk-Alert-for-AFFF.pdf>

<sup>X</sup><http://www.pca.state.mn.us/index.php/view-document.html?gid=17926>

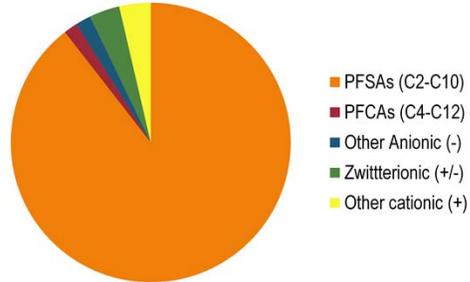
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## 3M AFFF: Military Wide Use Began in 1970

- 89% PFSAs (e.g., PFOS) in 3M AFFF
- Only 1.6% of 3M AFFFs are PFCAs (e.g., PFOA)
- All contribute to total fluorine

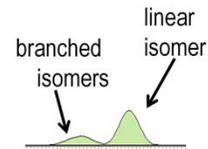


### Transport

- Anions > zwitterions > cations
- Anions, shorter chain lengths generally migrate faster (less retardation)
- Weak acids/bases, transport will depend on pH and molecule's charged state (ionic or neutral)

## PFSAs and PFCAs in 3M AFFF

- When produced 3M's electrofluorination (ECF) process<sup>27</sup>
  - 'Crude' synthesis, many side products
  - Odd & even<sup>23,24</sup> chain lengths (C2-C14)<sup>25,26</sup>
  - **Since 2015 RITS, C2 & C3 sulfonates found in AFFF and groundwater**
  - Branched & linear isomers (30:70)<sup>23,27,28</sup>
    - **If exclude branched isomers, concentrations underestimated (biased low) by 25%**
- PFOA also made by telomerization = only linear chain lengths



### Literature Cited

<sup>23</sup>Alexander et al., 2009, ES&T

<sup>24</sup>3M 1999, EPA docket No. OPPT-2002-0043-0006

<sup>25</sup>Barzen-Hensen et al., 2015, ES&T Letters

<sup>26</sup>Backe et al., 2013, ES&T

<sup>27</sup>Benskin, Rev Environ Contam Toxicol, 2010

<sup>28</sup>Prevedouros et al., 2006, ES&T

## What We Know and Don't Know About 3M AFFF

- **A lot of PFOS!**
- **No 3M AFFF (yet) explains high PFOA in groundwater**
  - See fluorotelomer precursors in AFFF
- **Ultra short-chain C2 & C3 PFSA in AFFF & groundwater<sup>29</sup>**
  - No toxicity data
  - Closest analog: PFBS MN health risk limit (7 µg/L)
  - Highly mobile/leading edge of plumes
  - Challenging to remove by GAC<sup>30,31</sup>

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### Literature Cited

<sup>29</sup>Barzen-Hanson et al., 2015, Environ Sci Technol

<sup>30</sup>Rahman et al., 2014, Water Res

<sup>31</sup>Appleman et al., 2014, Water Res

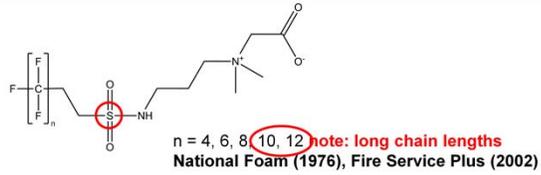
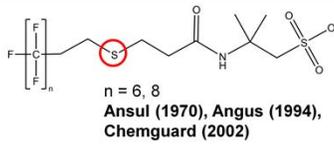
## 3M Degradation Pathways

- None for PFOS/PFOA
- N-EtFOSE<sup>32</sup> degradation products identified
  - Little if any data on N-EtFOSE in AFFF
  - Degradation products
    - Sulfonamide acetic acids (N-EtFOSAA and FOSAA)
    - Sulfonamide (FOSA)
    - PFOS and PFOA

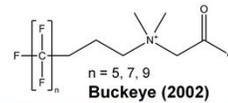
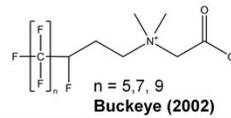
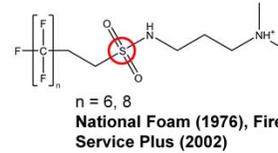
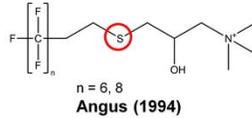
### Literature Cited

<sup>32</sup>Rhoads et al., Environ Sci Technol, 2008

## Fluorotelomer-Based AFFFs



- Add to total mass of F
- None on UMCR3 & Method 537 lists
- Potential to degrade to 6:2 & 8:2 fluorotelomer sulfonates & PFCAs
- 6:2 & 8:2 fluorotelomer sulfonates not major components in AFFF

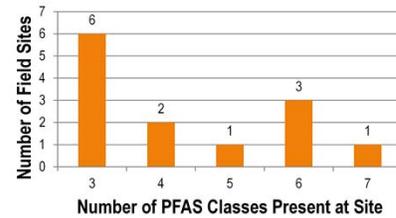
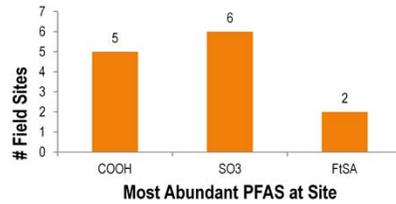


### Transport

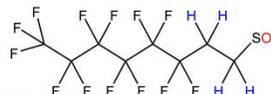
- Anions > zwitterions > cations
- Anions: shorter chain lengths generally migrate faster (less retardation)
- Weak acids/bases: transport will depend on pH and molecule's charged state (ionic or neutral)

## Occurrence of Most Abundant PFASs in Groundwater at Navy and Air Force Bases

- 13 Air Force & Navy bases
- PFASs and PFCAs not always the most abundant
- All sites have PFASs & PFCAs >>EPA PHAs
- No site has just PFASs & PFCAs
- **Highest concentrations in groundwater measured**
  - PFOS = 1,000 µg/L
  - PFOA = 6,600 µg/L
  - 6:2FTSA = 14,600 µg/L



## More on FTSAs



6:2 FTSA (fluorotelomer sulfonate)

- **Most sites have  $\mu\text{g/L}$  to  $\text{mg/L}$  levels of FTSA**

- **Australia: human health screening criteria  $5 \mu\text{g/L}$ <sup>36</sup>**

FTSA ( $\mu\text{g/L}$ )	Proposed Action	# DoD Sites
Not detected	None	1
<5	No further action	2
5 – 290	Monitor, confirm exposure pathways	6
<290	Remediate	1

- **Aquatic organisms**

- *D. magna* 48-h  $\text{EC}_{50}$ <sup>37</sup> (>112  $\text{mg/L}$ ) may be within same order of magnitude as PFOS (58  $\text{mg/L}$ )<sup>38</sup> and PFOA (>100  $\text{mg/L}$ )<sup>39</sup>
- Algae most sensitive species (compare to *Daphnia* and fish)<sup>37</sup>

### Literature Cited

<sup>36</sup>Jarman et al., A Human Health Screening Criteria, Abstract E017

<sup>37</sup>Hoke et al., Chemosphere, 2015

<sup>38</sup>Beach et al., Rev Environ Contam Toxicol, 2006

<sup>39</sup>Colombo et al., Ecotox Environ Safety, 2008

## Why should RPMs care about the 'other' fluorine?

- Many PFASs used in AFFF and identified in groundwater, sediment/soil but won't be on 'lists' any time soon
  - Toxicity data and analytical standards don't exist
- Treating of drinking water sources requires knowledge of target contaminants to identify appropriate technology
  - Short-chain PFASs exhibit early breakthrough on GAC, limited removal by conventional ion exchange<sup>40,41</sup>
- Oxidation may increase *in-situ* production of persistent PFCAs and fluorotelomer sulfonates
  - Source areas may contain bound precursors
- Increasing regulator and public awareness regarding presence of precursors and 'other' PFASs

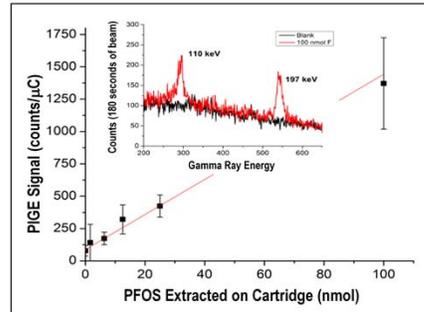
### Literature Cited

<sup>40</sup>Rahman et al., 2014, Water Res

<sup>41</sup>Appleman et al., 2014, Water Res

## Precursors and Total Fluorine: Alternative Methods

- Total oxidizable precursor (TOP) assay<sup>42</sup>
  - Polyfluorinated chemicals react with hydroxyl radicals but *perfluorinated* do not (e.g., PFOS and PFOA)
  - Net increase in PFCAs after oxidation of sample = precursors
- Total fluorine by PIGE<sup>43</sup>
  - PFAS sorbed onto media to create 'target'
  - 10 nA of 3.4 MeV protons for 180 s
  - Quantitative, high-throughput, inexpensive



### Literature Cited

<sup>42</sup>Houtz et al., ES&T, 2013

<sup>43</sup>Lunderberg et al., 2015, Fluoros, Golden, CO

## Transport: General Concepts

- **Transport related to chemical structure**
  - **Anions > zwitterions > cations**
  - **Shorter chain lengths generally migrate faster (less retardation, lower K<sub>oc</sub>)**
    - Likely to impact surface waters
    - Challenging to remove by GAC
  - **For many precursors, transport will depend on pH and molecule's charged state**
- **Cationic & zwitterionic PFASs may be cation exchanged onto source-zone sediments**
- **pH impacts ionization and transport of ionizable substances**

## Sorption of PFAAs – Chain length and head group

Analyte	Carbons in Tail	$K_{oc}^{44}$	$R_f$
PFBA	3	76	5
PFPeA	4	23	1.4
PFHxA	5	20	1.1
PFHpA	6	43	3
PFOA	7	78	5
PFNA	8	229	14
PFDA	9	912	57
PFUnA	10	3,600	225
PFBS	4	62	4
PFHxS	6	112	7
PFOS	8	631	39

- Affinity for sediment organic carbon ( $K_{oc}$  &  $K_d$ ) ~ # carbons in tail
- Short-chain PFCAs = greater  $K_{oc}$  than expected
  - Sorption not explained by only  $f_{oc}$  of sediment
- Compare retardation factors ( $R_f$ ) to groundwater velocity to predict arrival time at a groundwater well

$$R_f = 1 + K_d \frac{\text{Bulk density}}{\text{Porosity}}$$

where  $K_d = K_{oc} * f_{oc}$   
and  $f_{oc}$  = fraction of organic carbon

### Literature Cited

<sup>44</sup> Guelfo and Higgins, 2013, *ES&T*

## Solution Chemistry & Transport

- Decreasing pH (more acidic), increases retardation
- Increasing ionic strength increases retardation – may be relevant for sites near estuaries/ocean
- Remedial approaches that change pH or introduces polyvalent cations (i.e., ISCO) potentially impacts anionic PFAS transport
- Sorption generally increases in the presence NAPLs

### Literature Cited

<sup>1</sup> Guelfo and Higgins, 2013, *ES&T*

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## Drinking Water Contamination linked to Military & Civilian Airports (AFFF)

- **Sweden: Military airport origin of km-long plume<sup>45</sup>**
  - Spatial distribution related to drinking water delivery, occurring in or before 1990s
  - **PFBS in blood even though short chained**
- **Leaky landfill<sup>2</sup>, military<sup>46</sup>, and civilian airports<sup>47</sup> sources of human exposure to PFASs through drinking water**

### Literature Cited

<sup>45</sup>Gyllenhammar et al., 2015, Environ Res

<sup>46</sup>Eschauzier et al., Sci, 2013, Tot Environ

<sup>47</sup>Weiss et al., 2012, Intl J Hygiene Environ Health

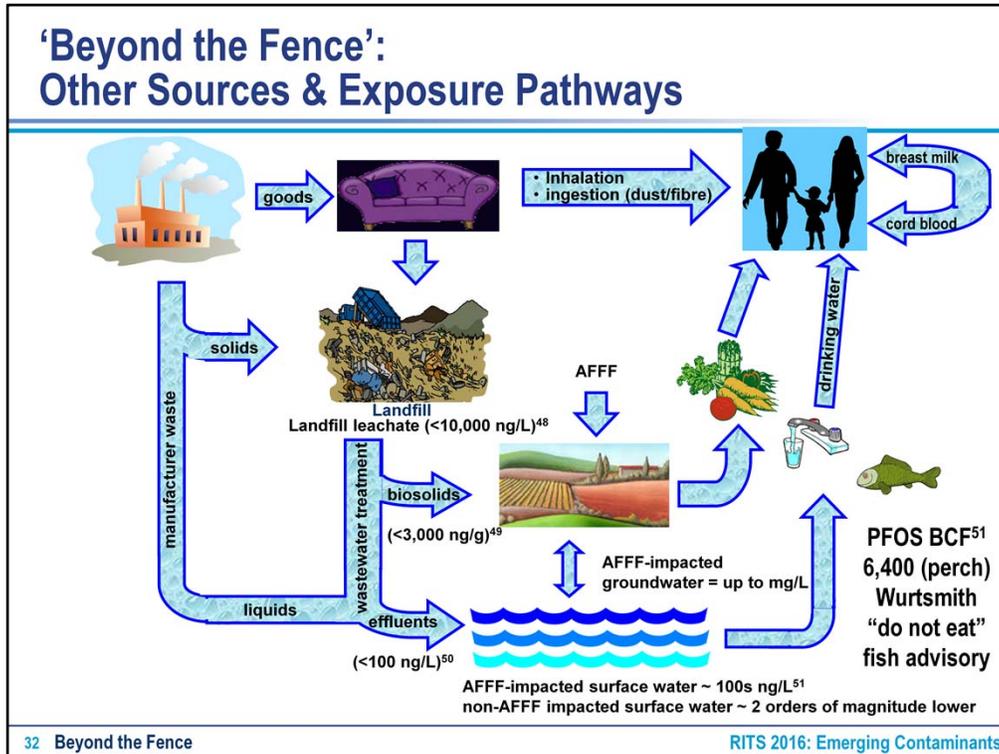


Figure adapted from Oliaei 2013, Environ Pollut Res

<sup>48</sup>Allred et al., 2014, J Chrom

<sup>49</sup>Schultz et al., 2006; Higgins ES&T, 2005

<sup>50</sup>Schultz et al., 2006, a&b ES&T

<sup>51</sup>Ahrens et al., 2015, Chemosphere

## Beyond the Fence: Wastewater Treatment

- **Municipal and industrial wastewater treatment plant (WWTP) effluent**
  - 3<sup>rd</sup> highest source (<0.1 µg/L levels) after landfill leachates and AFFF-impacted sites<sup>52-54</sup>
  - No significant removal of PFOA & 6:2 fluorotelomer sulfonate<sup>52</sup>
  - *Net increase* in PFOS mass flow during WWTP<sup>52</sup>
- **Impacted drinking water due to**
  - Land application of WWTP biosolids<sup>55</sup> in US
  - Other organic solid waste in Germany<sup>56</sup>

### Literature Cited

<sup>52</sup>Schultz et al., 2006, Environ Sci Technol

<sup>53</sup>Sinclair and Kannan, 2006, Environ Sci Technol

<sup>54</sup>Loganathan et al., 2007, Water Res

<sup>55</sup>Lindstrom et al., 2011, Environ Sci Technol

<sup>56</sup>Skutlarek et al., 2006, Environ Sci Pollut Res

## Beyond the Fence: Landfills

- **Landfill Leachate**

- 2nd most concentrated (tens of  $\mu\text{g/L}$ )<sup>57-59</sup> point source of many PFAS classes after AFFF-impacted groundwater
- Most abundant short-chain PFCAs & fluorotelomer acids (unique signature to landfill leachate)<sup>59</sup>

- **Cautionary tale**

- Pump and treat system installed (N) to treat VOCs in landfill leachate impacted groundwater<sup>60</sup>
  - ‘Spray air stripper system’ sprayed into water containing PFASs into air to strip out VOCs
  - PFASs penetrated soil profile

### Literature Cited

<sup>57</sup>Allred et al., 2014, J Chrom A

<sup>58</sup>Allred et al., 2015, Environ Sci Technol

<sup>59</sup>Benskins et al., 2012, Environ Sci Technol

<sup>60</sup>EPA Region 5 PFOS Chromium Electroplater Study, 2009

<sup>x</sup>Yang et al., 2014, Environ Sci Pollut Res

<sup>y</sup>Oliaei et al., 2013, Environ Sci Pollut Res

## Beyond the Fence: Electroplating and Plastics/Polymer Manufacturing

- **Chromium electroplating – PFSA's used for mist suppression**
  - PFCAs and PFSA's ( $\mu\text{g/L}$ ) in discharge water<sup>57</sup>
  - 6:2 FTSA 'alternative' mist suppression agent<sup>58</sup>
- **Industrial (plastics/polymer) manufacturing sources**
  - PFNA: West Deptford, NJ Solvay Specialty Polymers<sup>60</sup>
  - PFOA: Saint Gobain Performance Plastics and Honeywell polymer manufacturing in Hoosick Falls, NY<sup>61</sup>
- **Limited public data: municipal airports, AFFF production/formulation sites, oil refineries**

35 Beyond the Fence

RITS 2016: Emerging Contaminants

### Literature Cited

<sup>57</sup>Allred et al., 2014, J Chrom A

<sup>58</sup>Allred et al., 2015, Environ Sci Technol

<sup>59</sup>Benskins et al., 2012, Environ Sci Technol

<sup>60</sup>EPA Region 5 PFOS Chromium Electroplater Study, 2009

<sup>61</sup>Yang et al., 2014, Environ Sci Pollut Res

YOliaei et al., 2013, Environ Sci Pollut Res

## Mid-Talk Key Points and Take-Away Messages

- Hundreds of fire/crash testing (mixed waste) sites
- PFOS and PFOA are important but not the only major PFASs at AFFF-contaminated sites
- Full characterization of PFAS contamination needed
  - More accurate conceptual site models, identify remedial approaches that save time and cost
  - Optimized monitoring
  - Fingerprinting PFAS sources and source zones
  - Accurate predictions of transport & indicators of in-situ biotransformation
- Mobility in groundwater anions > zwitterions > cations and anion mobility depends on chain length, influenced by sediment, soil, and water geochemistry
- 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

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### Navy Guidance

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- Sampling Considerations
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# DoD Instruction – ECs

## Emerging Contaminants Department of Defense INSTRUCTION June 11, 2009

As identified by the DUSD(I&E),  
a contaminant that has:

- Possible pathway to enter environment
- Potential unacceptable human health or environmental risk
- Developing regulatory standards, new detection capabilities, or pathways



Department of Defense  
**INSTRUCTION**

NUMBER 4715.18  
June 11, 2009  
*Certified Current Through June 11, 2016*

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US(RA)TBL

SUBJECT: Emerging Contaminants (ECs)

References: See Enclosure 1

1. **PURPOSE.** This instruction establishes policy and assigns responsibilities for the identification, assessment, and risk management of ECs that have the potential to impact the Department of Defense (DoD) in accordance with the authority in DoD Directive (DoDD) 5134.01 (Reference (a)) and the guidance in DoDD 4715.1E, DoD Instruction 5000.02, and Defense Acquisition University Risk Management Guide (Reference (b), (c), and (d)).

2. **APPLICABILITY.** This instruction:

- Applies to OSD, the Military Departments, the Office of the Chairman of the Joint Chiefs of Staff and the Joint Staff, the Combatant Commands, the Office of the Inspector General of the Department of Defense, the Defense Agencies, the DoD Field Activities, and all other organizational entities within the Department of Defense (DoD) (hereinafter referred to collectively as the "DoD Components").
- Applies to the DoD activities and programs involving the development, production, use, storage, or release of chemicals and materials that can be considered ECs at DoD operations, activities, and installations in the United States.
- Applies to the DoD managed response actions at formerly used defense sites.
- Does not apply to:
  - Contractor-owned or contractor-operated facilities.
  - Radioisotopic data collected under the Naval Nuclear Propulsion Program or other DoD radiological programs.
  - Chemical, biological, radiological, nuclear, and explosive incident training or response programs.

# NAVFAC PFC Interim Guidance/FAQs

- **Finalized/Issued: January 29, 2015**
- **Objective: Assist RPMs with issues related to PFCs (PFASs) at ER sites to promote a consistent approach across Navy installations**
- **Issues Addressed:**
  - Funding responsibilities: BRAC, ERN\*
  - Investigation and sampling methodology
  - Remediation considerations
- **Focus on Drinking Water (DW)**
  - \*Past release as substantiated by the CSM



[http://navfac.navy.mil/content/dam/navfac/Specialty%20Centers/Engineering%20and%20Expeditionary%20Warfare%20Center/Environmental/Restoration/er\\_pdfs/gpr/don-ev-guid-pfc-faq-20150129i.pdf](http://navfac.navy.mil/content/dam/navfac/Specialty%20Centers/Engineering%20and%20Expeditionary%20Warfare%20Center/Environmental/Restoration/er_pdfs/gpr/don-ev-guid-pfc-faq-20150129i.pdf)

## NAVFAC PFC Interim Guidance – Highlights

- **If CSM indicates:**
  - Past use of AFFF or other PFAS-containing material
    - And a potential route of exposure exists
  - Then investigate for presence of PFOS, PFOA, and PFBS
- **If detections exceed PHAs in a drinking water source:**
  - Immediately provide alternate drinking water, report and determine further action (plume control, TCRA, treatment, etc.)
- **If detections exceeding screening levels:**
  - Delineate and perform quantitative RA; if no chance for exposure and migration delay further action until state of science advances; if potential for exposure, at a minimum delineate and possibly take further action (LUCs, plume control, TCRA, remediation, etc.)
- **Consult HQ, LANT, Risk Assessment Workgroup (RAW)**

## What/Where to Sample

- **Investigation Considerations**

- **CSM Substantiates Investigation; Generally 2 Categories in DON:**

Historical release and/or use of AFFF; Examples	Historical activities that may have released PFC; Examples
Fire Training Areas (FTAs) Using AFFF	Mist Suppression in Plating Facilities
Crash or Fire Sites Where AFFF Was Used	Oil-water Separators
Fuel Spills Treated With AFFF	Other Piping Systems
Hangars, Runways, and Flight Line Areas	
Storage Areas, Piping, and Equipment Cleanout Areas	
Runoff Areas	

- **The CSM should be used to make decisions on whether an area should be investigated particularly with regard to potential exposure pathways, especially drinking water**
- **Media may include one or all media potentially impacted, depending on CSM**

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- Remediation Methods
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- Wrap-Up

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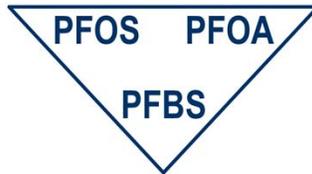
## Which PFAS Compounds to Analyze?

### LET'S REVIEW:

- **PFAS comprise a large group of compounds**
- **AFFF formulations differ in which compounds are present**
- **PFOS, PFOA, and PFBS are not transformed in the environment**
  - **3M produced AFFF containing high levels of PFOS until 2002**
    - Also contains a variety of other perfluorinated PFASs (including PFBS)
  - **The other manufacturers produce(d) AFFF with polyfluorinated PFASs**
    - No PFOS, PFOA, or PFBS
    - However, some compounds may degrade to PFOA and other PFCAs
  - **A variety of AFFF products were used over time at FTAs, so sites likely contain many PFASs, and transformation products**

## Regulatory Considerations

- **Only PFOS, PFOA and PFBS have EPA toxicity values...**
  - **PFOS and PFOA: Have Tier III toxicity values (Provisional Health Advisories [PHAs])**
    - These are not promulgated and not ARARS, but can be used for risk determination
  - **PFBS: Has a Tier II toxicity value (EPA Superfund Reference Dose [RfD])**
- **SO, per NAVFAC Interim Guidance (January 2015) only PFOS, PFOA (and PFBS) should be used to initially assess site**



## Regulatory Values

- The PHAs are currently under review and revisions (likely downward) are expected soon; at that time, the revised values will be applicable

Current (as of April 3, 2016):

- PFOS: 0.2 µg/L (PHA)
- PFOA: 0.4 µg/L (PHA)
- PFBS: 7 µg/L (RfD)

- Per NAVFAC Guidance:

- 1) If DW levels of PFOS, PFOA or PFBS are Greater Than (GT) Regulatory Values, provide alternative DW and take further action per Interim Guidance on PFCs
- 2) If DW levels are GT 25% of Regulatory Value but Less Than (LT) Regulatory Value, continue sampling and monitoring
- 3) If DW levels are LT 25% of Regulatory Value only monitor plume migration

## Regulatory Values (cont.)

- **States, in some cases have also set their own regulatory values**
  - If an installation is located in that state, and the value is promulgated, the more stringent value will apply
  - If the value is not promulgated, the EPA PHA will be used
  - Example: New Jersey, PFOA and PFNA
- **Check with LANT, RAW, or HQ before using values other than the EPA PHAs (for PFOS and PFOA) and the Superfund RfD (for PFBS)**

## Regulatory Values, States

Authority	Media	PFOS (µg/L)	PFOA (µg/L)	PFBS (µg/L)	PFBA (µg/L)
EPA	Drinking Water	0.2 (PHA)	0.4 (PHA)	7 (RfD)	
MI	Drinking Water	0.012	0.42		
MN	Drinking Water	0.3	0.3	7	7
NJ	Drinking Water		0.04 (not promulgated)		
NC	Groundwater		PFNA: 0.013 (µg/L) (promulgated MCL) 1		
IL	Provisional groundwater remediation objectives	0.2 (Class I and II)	0.4 (Class I) 2 (Class II)		
ME	Remedial Action Guidelines: groundwater residential	0.06	0.1		
OH	Amended US/DuPont consent agreement		0.4		

## Screening Levels

### • Human Health Risk Assessment

#### – Screening Levels

- Developed between RPM and regulators
- Ordinarily begin with EPA Regional Screening Level (RSL) tables; but these are not yet developed for PFOS and PFOA
- EPA Provisional Health Advisories (PHAs are Tier III – least confident):

Media	PFC	Residential Exposure*	Industrial Exposure*
Groundwater (µg/L)	PFOA	4.0	NA
	PFOS	1.6	NA
Soil (mg/kg)	PFOA	12	165
	PFOS	4.9	66

\* Values calculated using RfD derived by EPA in their short term provisional HAL (2009) and the exposure assumptions used to calculate EPA RSLs in May 2014)

## Screening Levels (cont.)

### Other PFAS Screening Levels:

- **PFBS:**

- 1,230 mg/kg residential soil
- 16,500 mg/kg industrial soil
- 383 µg/L residential groundwater
- Calculated using EPA's Online RSL Calculator, December 2014
- [http://epa-prgs.ornl.gov/cgi-bin/chemicals/csl\\_search](http://epa-prgs.ornl.gov/cgi-bin/chemicals/csl_search)

- **6:2 FTSA (6:2 Fluorotelomer Sulfonate):**

- 5 µg/L groundwater screening level in Australia (Jarman, 2014)

- **EPA Region 4 calculated residential soil screening values of 6 mg/kg for PFOS and 16 mg/kg for PFOA**

## Ecological Risk

- Include ecological risk if CSM substantiates
- Screening Levels:
  - Ecological screening levels for PFAS do not exist at this time though some States have guidance for surface water (MN example below)
  - If regulators recommend values, they should be vetted by a Navy ecorisk assessor (10-50 µg/L are typical effects levels)
  - PFOS bioaccumulates in fish; PFOA does not
  - Vegetation: Studies of biosolids containing PFASs applied to land have shown uptake by plants to varying degrees
    - Screening levels or health advisory levels not yet established by EPA

Minnesota Criteria	PFOA Lake (µg/L)	PFOA River (µg/L)	PFOS Lake (µg/L)	PFOS River (µg/L)
Fish Consumption	1.6	2.7	0.012	0.006
DW plus Fish Consumption	0.61	0.72	0.012	0.006
Ecological Acute	15,000	15,000	85	85
Ecological Chronic	1,700	1,700	19	19

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## Sampling for PFAS

- **Many common materials and sampling equipment contain PFAS**
- **Dealing with ultra-low detection levels**

AVOID	OK
Tyvek®	Plastic containers (polypropylene, no lined caps)
Teflon™	Nitrile gloves (change often)
Waterproof clothing	HDPE tubing and bailers
New clothing	Alconox® or Liquinox® soaps
Blue Ice®	PFC-free laboratory certified water
Handling food packaging	
Non-stick or water/grease/stain-resistant	
Glass containers	

## Sampling for PFAS (cont.)

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- **PFAS Stratification**

- PFAS accumulates on water surface
- Do not collect water at the very surface
- Bailers work well

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## PFAS Analytical Methods

- **Only PFOS, PFOA and PFBS have vetted toxicity values at this time, therefore, for initial investigations these would be the primary contaminants of concern**
  - **Drinking Water: EPA Method 537 Version 1.1; labs may include additional PFAS in addition to the standard list**
  - **Groundwater, Soil, Sediment (any media other than drinking water): Each lab has their own method (most are based on EPA 537) since a standard (HW) method does not exist; QA issues have been identified in some labs – check with Navy Chemist or EDQW**
  - **Must be ELAP-Certified for ER project, currently there are 9 labs that analyze PFAS using various analyte lists in various medias**

## EPA Method 537

- **Determines 14 PFASs in drinking water by liquid chromatography/tandem mass spectrometry (LC/MS/MS):**
  - 9 perfluoroalkyl carboxylates: C6-C14 (where C8 = PFOA)
  - 3 perfluoroalkyl sulfonates (C4, C6, C8 where C8 = PFOS)
  - 2 sulfonamidoacetic acids (N-MeFOSAA, N-EtFOSAA)
- **Method does not allow modification to:**
  - Sample collection/preservation (Section 8)
  - Sample extraction (Section 11)
  - Quality control requirements (Section 9)

EPA Method 537 is for drinking water samples only, for a defined list of analytes. This is a promulgated method that must be followed verbatim when analyzing drinking water.

This method clearly states certain sections of the method that are not allowed to be modified.

## Modified 537 or In-House Methods

- **Can modify the method in any way, including ways prohibited in the method**
- **No EPA guidance on hold times, thermal preservation requirements**
- **EPA published methods are sorely needed**
- **In the meantime, DoD ELAP addressing these issues through modification to DoD QSM requirements**

When a method is identified as a “Modified” method or in-house method, it is not required to meet all of the requirements of the referenced method, in this case, Method 537.

There is also no guidance published by the EPA for critical parts of these methods including hold times and thermal preservation requirements. As a result, each laboratory has come up with their own requirements.

As a result of this, methods for matrices other than drinking water greatly vary from laboratory to laboratory. These differences may or may not have a significant impact on your data. The bottom line is a validated published EPA method(s) [for matrices other than DW] is greatly needed to help projects achieve comparable results from laboratory to laboratory and ensure a minimum of precision and accuracy is achieved.

In the meantime, the Environmental Data Quality Workgroup (EDQW) is addressing the situation by including additional specific requirements for PFAS analysis by these methods in the DoD Quality Systems Manual (DoD QSM).

## DoD-ELAP Labs for PFAS Analysis

- **Current as of Jan. 27, 2016 (See DENIX website for current listings):**

- Accutest Laboratories SE (PFAAs in DW, GW, soil)
- ALS Environmental Kelso (PFAAs in DW, GW, soil, tissue)
- Eurofins Lancaster Laboratories (PFAAs and 8:2 FTS in DW, GW, soil)
- Maxxam Analytics Intl. (PFAAs and FTS in DW, GW, soil)
- TestAmerica Denver (PFAAs in GW, soil)
- TestAmerica West Sacramento (PFAAs and FTS in GW, soil)
- Vista Analytical (PFAAs and FTS in GW, soil, tissue)
- Weck Laboratories (PFAAs 6 compounds)
- Axys Analytical – BC Canada (PFAAs and FTS, in DW, GW, soil, tissue)

## What About the Other PFASs?

- Over 200 PFASs have been identified in AFFF and groundwater
- 6:2 Fluorotelomer Sulfonate found at high levels in DoD GW at FTA
- Some compounds at levels greater than PFOS/PFOA (which can be in ppm range)

## Analyzing Other PFASs After the Initial Assessment

- **Useful when:**

- Additional toxicity data or regulatory values become available
- States require other PFASs (if promulgated)
- For delineation (shorter compounds C4 and C2 move faster)
- Treatment feasibility (e.g., GAC may not adsorb short chain compounds)
- Biotic and abiotic transformation / mass balance
- Tracing sources in mixed plumes
- Source zones may contain cations and zwitterions not normally analyzed; these may be mobilized by being transformed by ISCO, for example
- Fluorotelomer AFFF formulations are being delineated

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## Treatments

### Ineffective

- Riverbank Filtration
- Coagulation
- Sedimentation
- Granular Filtration
- Aeration
- Dissolved Air Flotation
- Microfiltration
- Ultrafiltration
- Ozone
- Aeration Packed Tower
- Chlorine
- Ultraviolet Photolysis
- Advanced Oxidation Process
- Chlorine Dioxide
- Chloramination

### Partially Effective

- Anion Exchange
- Granular Activated Carbon

### Effective

- Reverse Osmosis

## Treatment Options for PFAS by Media

- **Groundwater: GAC**
- **Drinking Water: GAC, RO, Nano Filtration, Anion Exchange**
- **Concentrates, Solids, etc.: High Temp Thermal Oxidation**
  - **New Technologies: Plasma-based, Sonochemical, Permanganate/Persulfate**

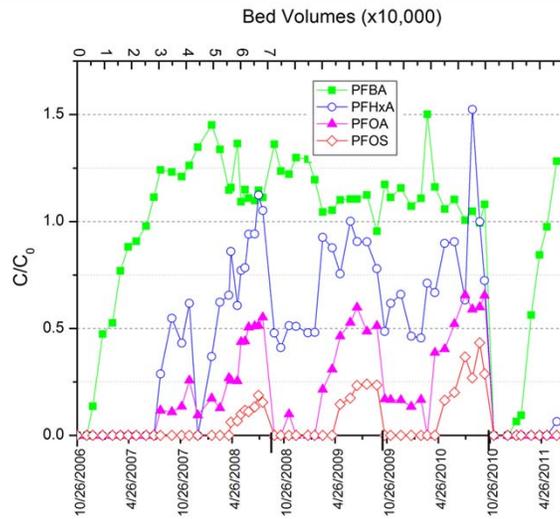
## GAC Treatment

- Only practical treatment for groundwater so far (RO can be used in drinking water)
- Treatment may not effectively remove other PFASs which may be a future concern
  - Longer chain compounds more effectively removed
  - Sulfonates removed better vs. carboxylates
- Various GACs perform differently
- Elevated DOC decreases performance
- Other treatment units (e.g., advanced oxidation) can change PFAS composition, alter GAC performance
- Chars and other biomaterials being studied

Calgon's "PFC" carbon, F600, at Warminster \$\$\$ vs. Coconut Shell Carbon at Brunswick

## GAC Treatment (cont.)

- Calgon® F600
  - Calgon recommends this carbon for PFAS
- 380 – 400 gpm
- ~13 min. EBCT
- Almost 2X cost of other carbons, benefit still being determined at Brunswick and Warminster
- F300 worked just as well in lab testing



## **GAC Treatment Currently in Use for PFAS**

**GAC treatment is currently being used at:**

- **NAS Brunswick, ME – two 5k lb GAC units (in series) sampled monthly coconut shell (lead) and F600 (lag)**
- **NAWC Warminster, PA – two 18k lb GAC units; started with reactivated bituminous carbon, changed out to F600**
  - Sites are being monitored at influent, mid-point and effluent
  - Data being collected will allow for estimates of frequency of carbon changes and projections of cost
  - Some samples will be analyzed for full suite of 100+ PFAS

## Oxidation in Field: Potential to Increase PFCAs and FTSA

- Thermally-activated persulfate oxidized precursors to PFCAs, including PFOA<sup>42</sup>
- Fluorotelomer sulfonates (FTSAs) oxidized by UV/H<sub>2</sub>O<sub>2</sub> to ≤ C7 PFCAs<sup>61</sup>
- Telomer-based AFFFs oxidized by KMnO<sub>4</sub> to 6:2 and 8:2 fluorotelomer sulfonates (FTSAs)<sup>62</sup>

### KEY POINT

Bottom line: Sites that undergo advanced oxidation as remedial strategies run the risk of increasing PFCA and FTSA concentrations.

<sup>42</sup>Houtz et al., ES&T, 2013;<sup>61</sup>Yang et al., 2014, Environ Sci Pollut Res, <sup>62</sup>Fang et al., 2015, Environ Toxicol Chem

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## Case Study: NAWC Warminster, PA Summary

- FTA sampled found to contain PFAS exceeding PHAs in 2011-2012
- Found PFAS in public supply well (less than PHAs in 2013)
- Initiated Potential Sources Evaluation Report
- Warminster Municipal Authority (WMA) samples and posts UCMR3 data to EPA database 2014
- Navy develops RI SAP, completes Potential Source Evaluation report
- WMA Wells 10, 13 and 26 shut down due to PFAS levels
- The next month EPA issues SDWA Administrative Order to provide treatment of WMA wells and provide permanent safe DW for private wells at or above PHAs
- 200 attend NMCPHC supported public meeting, ATSDR and EPA drinking water and Federal Facilities RPM's participated
- Navy awards \$3.9M ESCA grant for GAC treatment of 3 WMA wells, as well as covering other costs

## NAWC Warminster, PA Update

- Of 107 wells tested around Warminster, 13 at\* or exceed PHA, 15 are between 25% of the PHA and the PHA
- 12 of the 13 wells exceeding the PHA at Warminster are now hooked up to PWS
- 15 wells were less than the PHA but exceeded 25% of PHA – will continue to be sampled/monitored
- Cost per hookup \$15-20k, and about \$200/foot of main installed
- Cost for treatment of on-site Navy PWS estimated to be \$1M

\*Since PHAs are published to 1 significant figure (e.g., 0.2 µg/L for PFOS), the DW rounding rule applies for laboratory results; i.e., any result equal to or greater than 0.15 will result in an exceedance because the result must be rounded up to 0.2)

## NAWS Willow Grove, PA Update

- Of 272 wells sampled around Willow Grove 51 are at\* or above PHA
- 52 wells require continued monitoring (i.e., levels are between 25% of PHA but less than the PHA)
- Will require 30-40 hookups to PWS

\*Since PHAs are published to 1 significant figure (e.g., 0.2 µg/L for PFOS), the DW rounding rule applies for laboratory results; i.e., any result equal to or greater than 0.15 will result in an exceedance because the result must be rounded up to 0.2)

## **Inter-Agency Partnering, Public Outreach Key**

**Lessons learned by BRAC PMO from handling of Warminster and other sites:**

- **Existing partnerships between Federal, State, and local government were enhanced to provide concerned citizens with coordinated information**
- **Engage the NMCPHC; they are a valuable resource**
- **Involve the PAO**
- **Community meetings have been well-attended and are useful; follow-on meetings tend to decline in attendance if objectives in communication are being met**
- **A proactive approach is needed, otherwise an Order could be issued; PHAs are being enforced as if an MCL**

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## Conclusions

- **Nearly 300 sites have been identified by the Navy as potential PFAS sites based on their use – of these, FTAs are by far of greatest concern**
- **PFASs should be included as a COPC if the CSM indicates (i.e., past use)**
- **PFAS plumes have unique properties that can cause them to behave differently than most other “conventional” contaminants such as VOCs**
- **Initially PFOS, PFOA and PFBS should be assessed, but:**
  - **The total mass of PFASs is likely much larger and comprised of numerous other compounds; this can:**
    - Have human health and ecological risk implications
    - Impact site investigations and treatment of PFASs and commingled contaminants
- **Treatment options are limited and largely restricted to GAC but new technologies are being developed, as are F&T information for improved CSMs**

## Footnotes

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