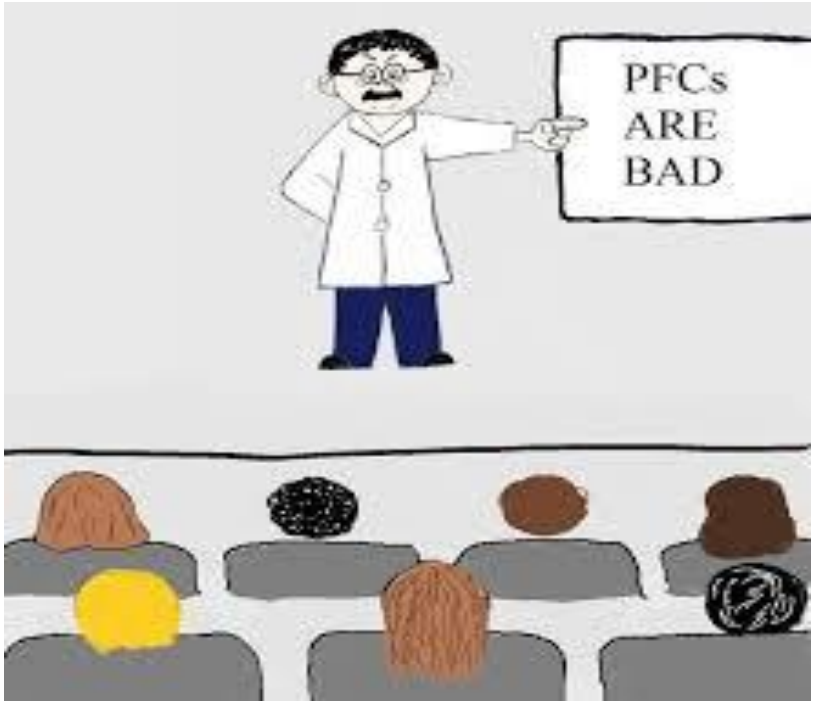



Fingerprint Evaluation of PFAS Source, Identification of Surface Partitioning, and Associated Remedial Implications

Presentation for Battelle
May 2017

Presentation Outline

- Site Background
  - Water Supply Reservoir
  - PFOS Regulations/Guidance
- Response Actions
- AFFF – Finger Printing
- Source Assessment
  - Sampling
  - Fingerprint
  - Remediation
- PFOS – Surfactant Properties
- Surface Partitioning
  - Sampling Implications
  - Remedial Alternatives
- Q&A

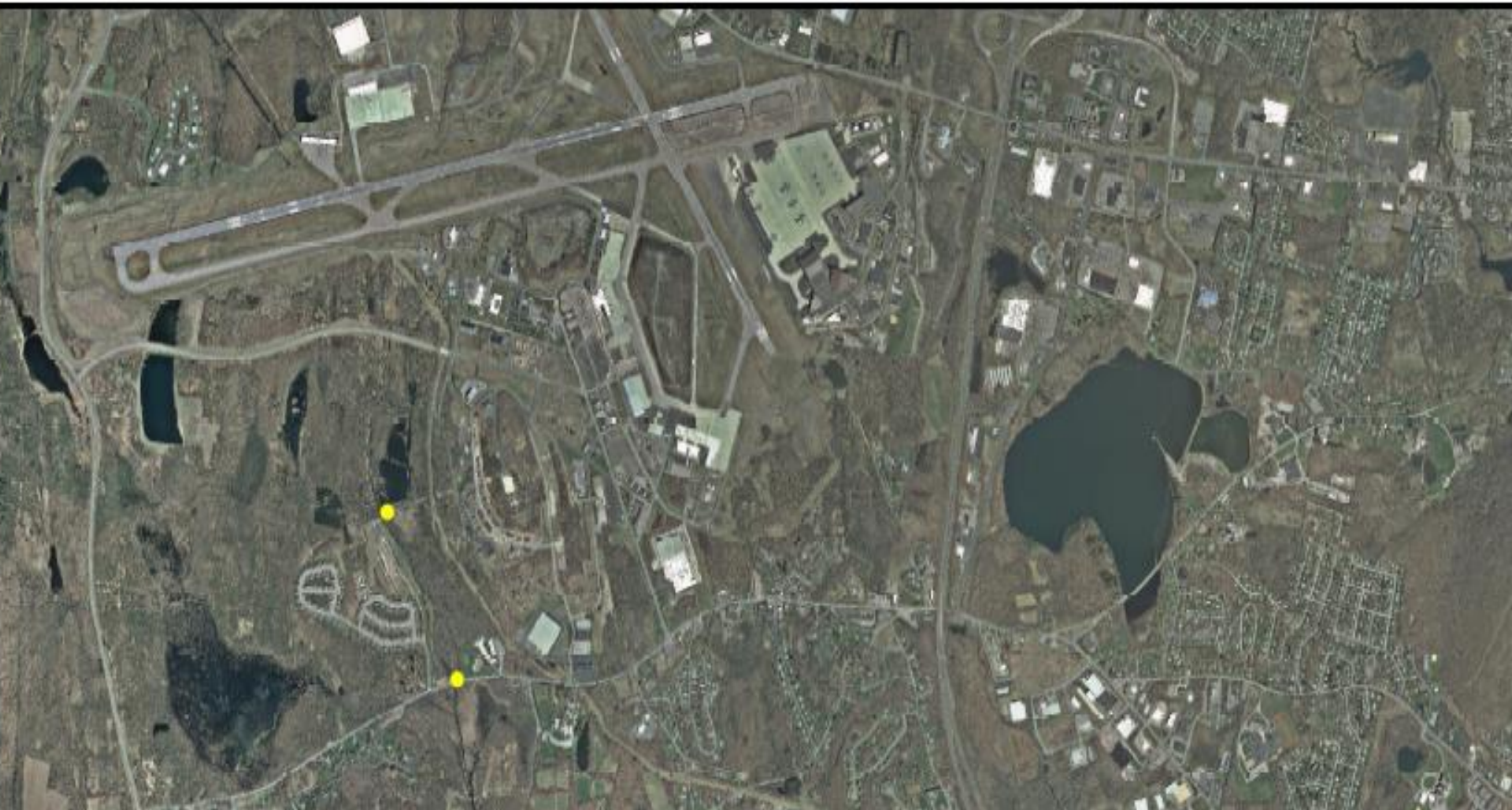





Site Background

Reservoir Description (Confidential Site)

- Water Supply Reservoir since the early 1900s
- Capacity has been expanded by raising dam
- **Rerouted stream that included airport drainage to expand capacity**
- Water Capacity of 1.5 billion gallons
- Currently serves city of 25,000
- Water Treatment System- 1 to 1.5 million gpd



PFOS Identified in Water Supply

- EPA Considers Perfluorooctane Sulfonate (PFOS) an emerging contaminant
- PFOS included in the EPA Third Unregulated Contaminant Monitoring Rule (UMCR -3, May 2012)
- PFOS identified in drinking water at concentrations between 140 to 170 ppt (2013 and 2104)
- At the time EPA Provisional Short Term Health Advisory of 200 ppt
- August 2016 EPA Lifetime Drinking Water Health Advisory set at 70 ppt




Response Actions

Response by City and State

- May 2016 – Transition to new temporary water supply
- State makes commitment to cover transition costs ($2.4 million)
- State commits to fund the design and construction of GAC polishing system
- State installs temporary water treatment system to drain water from reservoir to reduce potential dam integrity issues
- State commits to conducting a comprehensive investigation of Off-Site source
- Off – Site Source Area listed as a State Superfund Site – DOD responsible for cleanup

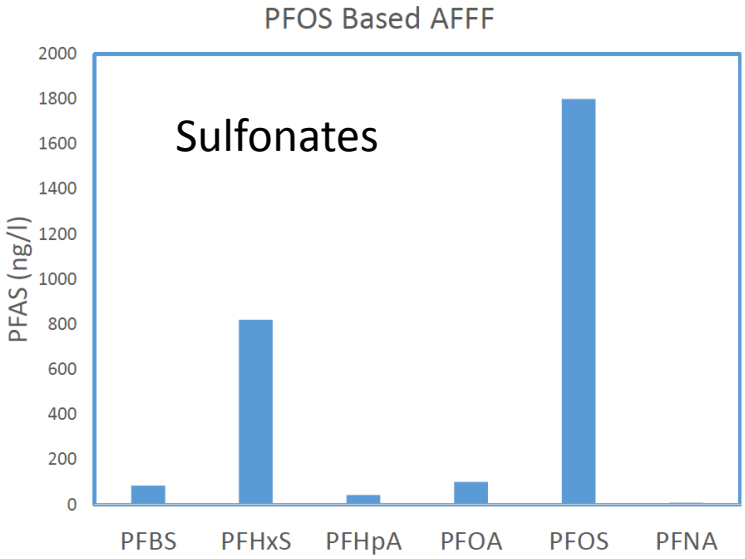



AFFF Fingerprinting and PFC Mixtures

Forensic Evaluation PFAS Finger Printing

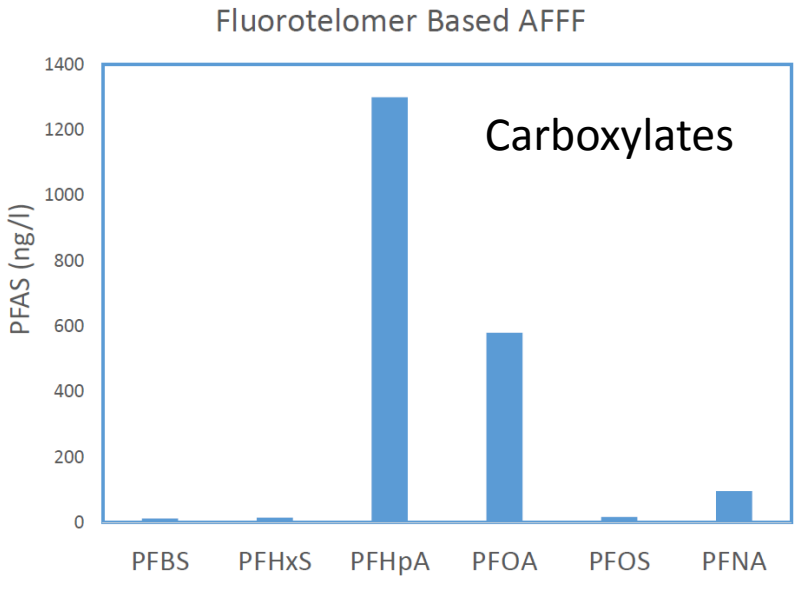
- Compare chromatograms of PFAS compounds identified
  - Fluorinated chain length
  - Specific mixtures of carboxylates and sulfonate compounds
- Distinguish electrochemical fluorination products from fluorotelomerization products
- Evaluate PFOS isomers to distinguish AFFF manufactured with similar technologies
- Compound Specific Isotope Analysis (CSIA)?

AFFF Finger Historic Fire and Recent Spill

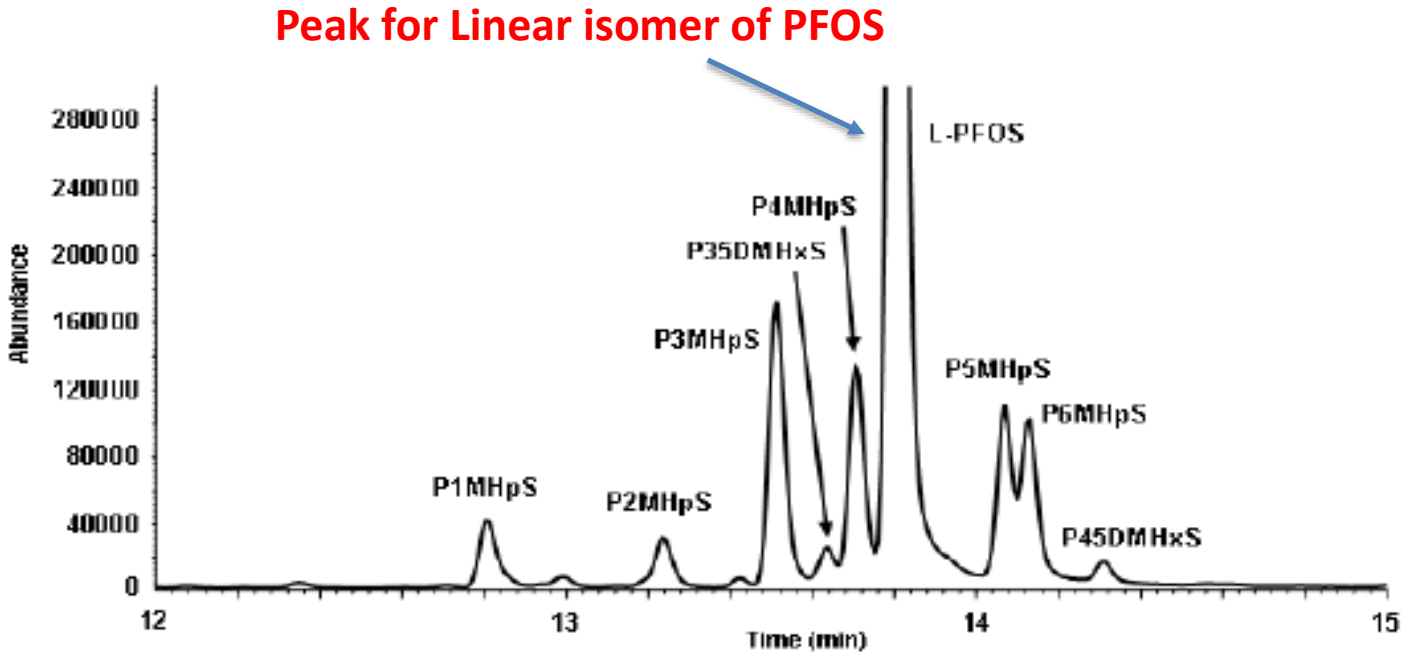


1990 Fire Extinguished with AFFF – Surface Water

Recent Limited Release Impacting Perched Water



Total Ion Chromatograph of Technical Grade PFOS



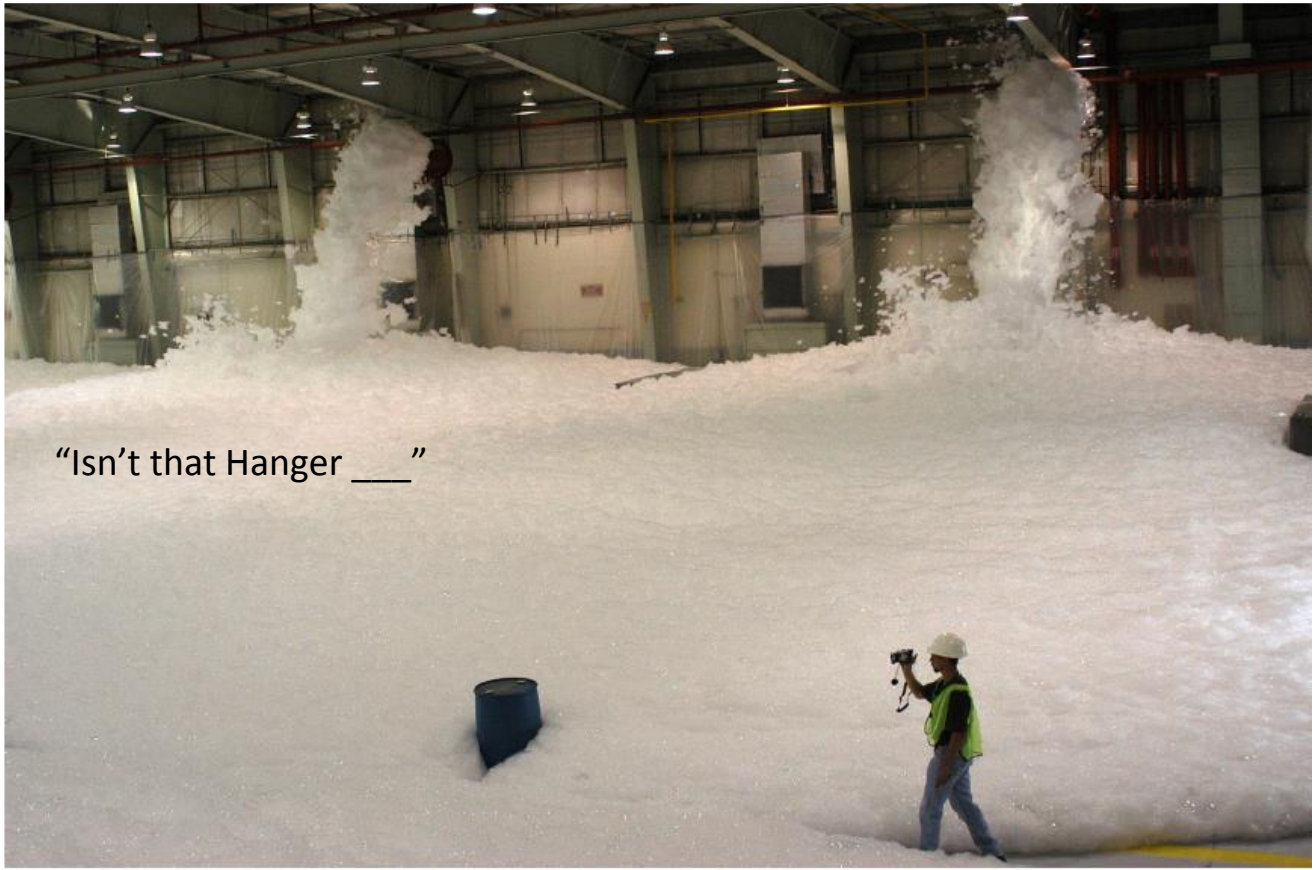
3M AFFF: Branched and linear isomers (30:70)

If exclude branched isomers, concentrations underestimated and biased low




PFOS Sources and Reservoir Source ID

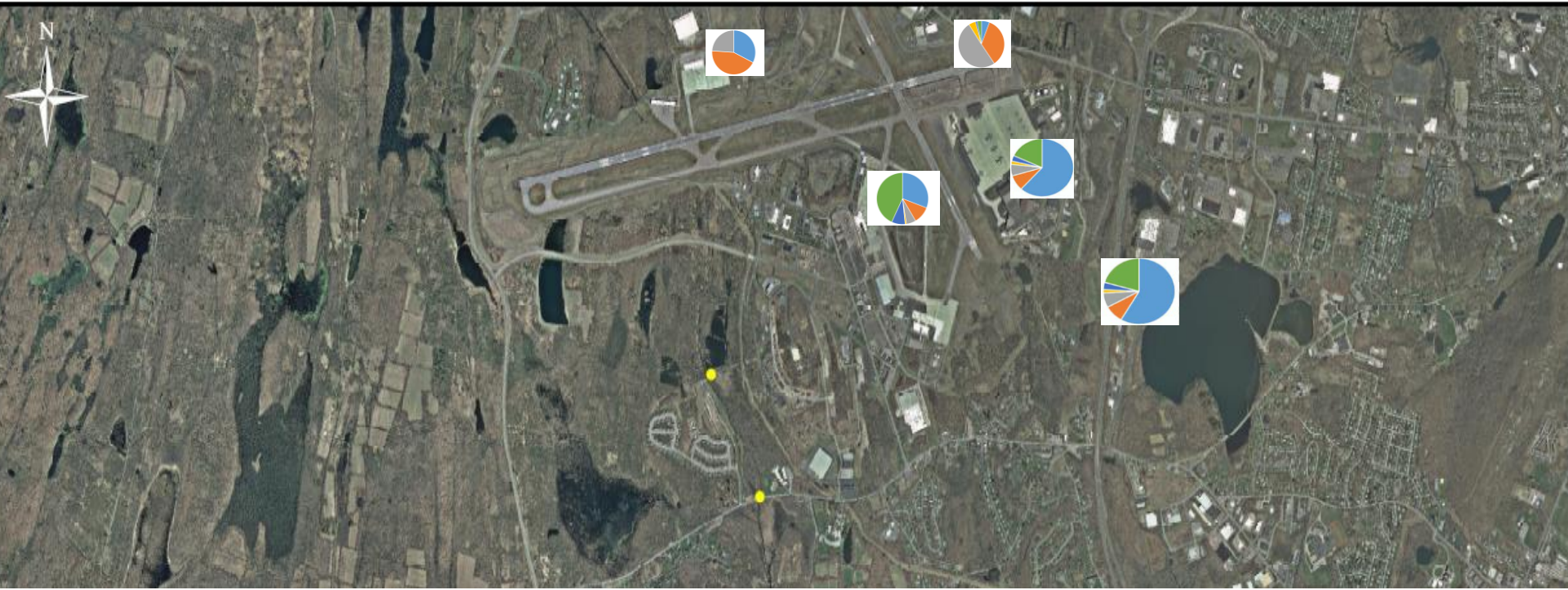
Sources of PFAS Contamination



Known AFFF Discharge Locations

Area 2
Drainage is not a tributary to Reservoir

Source Characterization



Off – Site Source Identification

Potential Source 1
Upgradient Outfall
10, 5, 58, & **68**

Potential Source 4
Outfall Upstream of Reservoir
5,300, 1,300, 600, & **5,900**

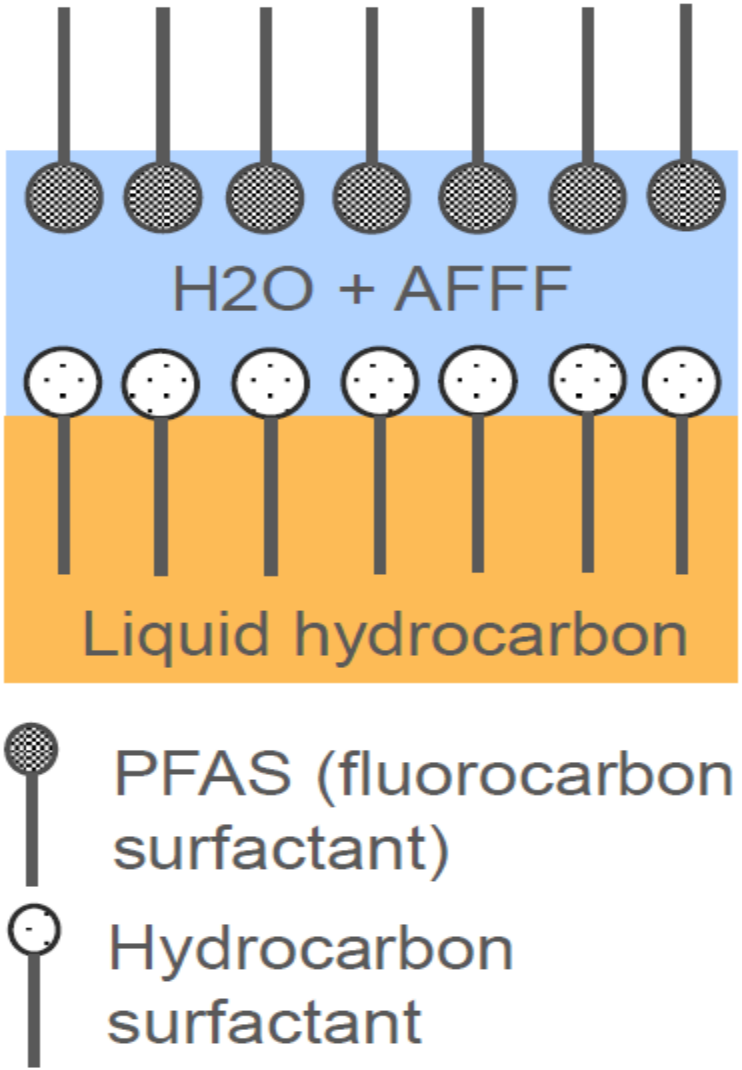
Potential Source 3
Fire Training Area
150, 210, 52, & **202**

Reservoir
Feeder Stream to Reservoir
600, 140, 55, & **655**

PFOS, PFHxS, PFOA, and **PFOS+PFOA**
concentration ppt EPA Guidance **70 ppt**
PFHpA

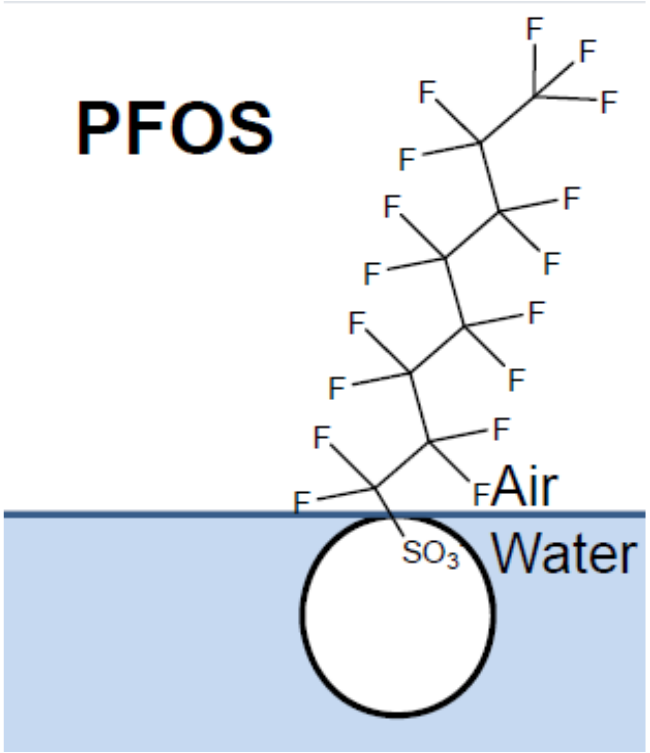



PFOS Surfactant Properties



Typical AFFF contained PFOS prior to 2002 Concentrations Decreasing in the Environment with the Exception of Some Historic Releases

PFOS Surface Properties



Hydrophobic and Oleophilic Tail

Hydrophilic Head



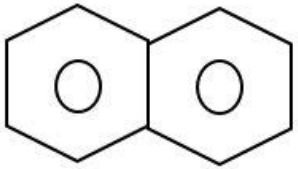

PFOS Surface Partitioning – Invisible Sheen

Invisible Sheen Properties / Chemistries

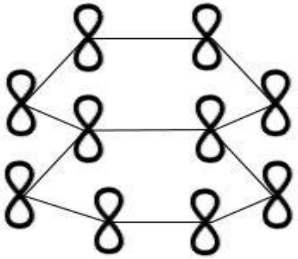
- Review of typical PAH hydrocarbon sheen
- Configuration of PFAS Sheen
- Environmental implications
  - Accumulation of water air interface
  - Biased high sampling results

Typical PAH Hydrocarbon Sheen Chemistry

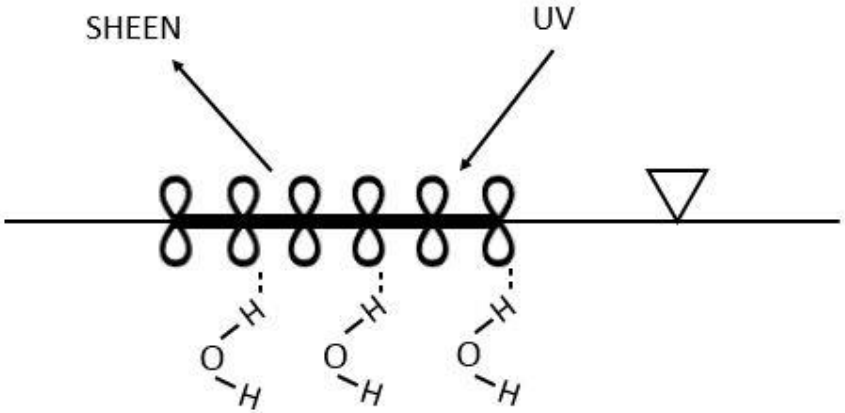
Naphthalene



Conjugated P-Orbitals

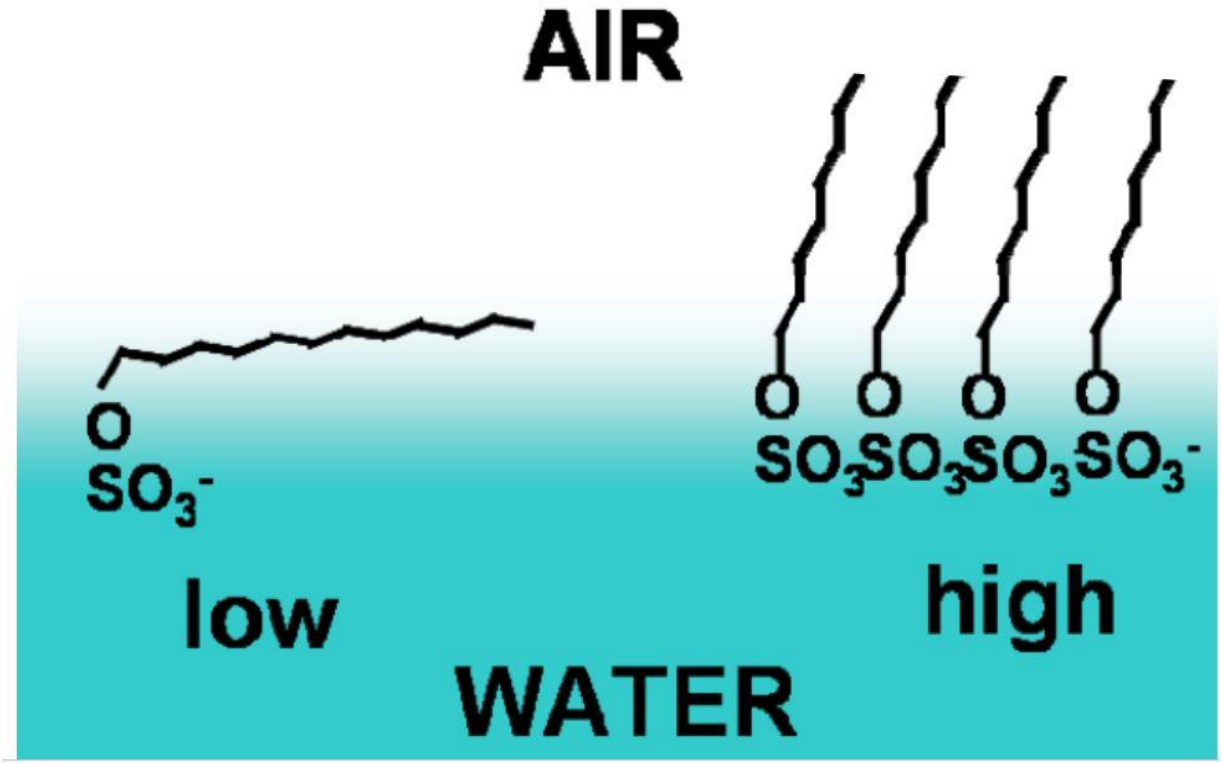


Weak Hydrogen Bonding to Conjugated P-Orbitals of Aromatic Hydrocarbons



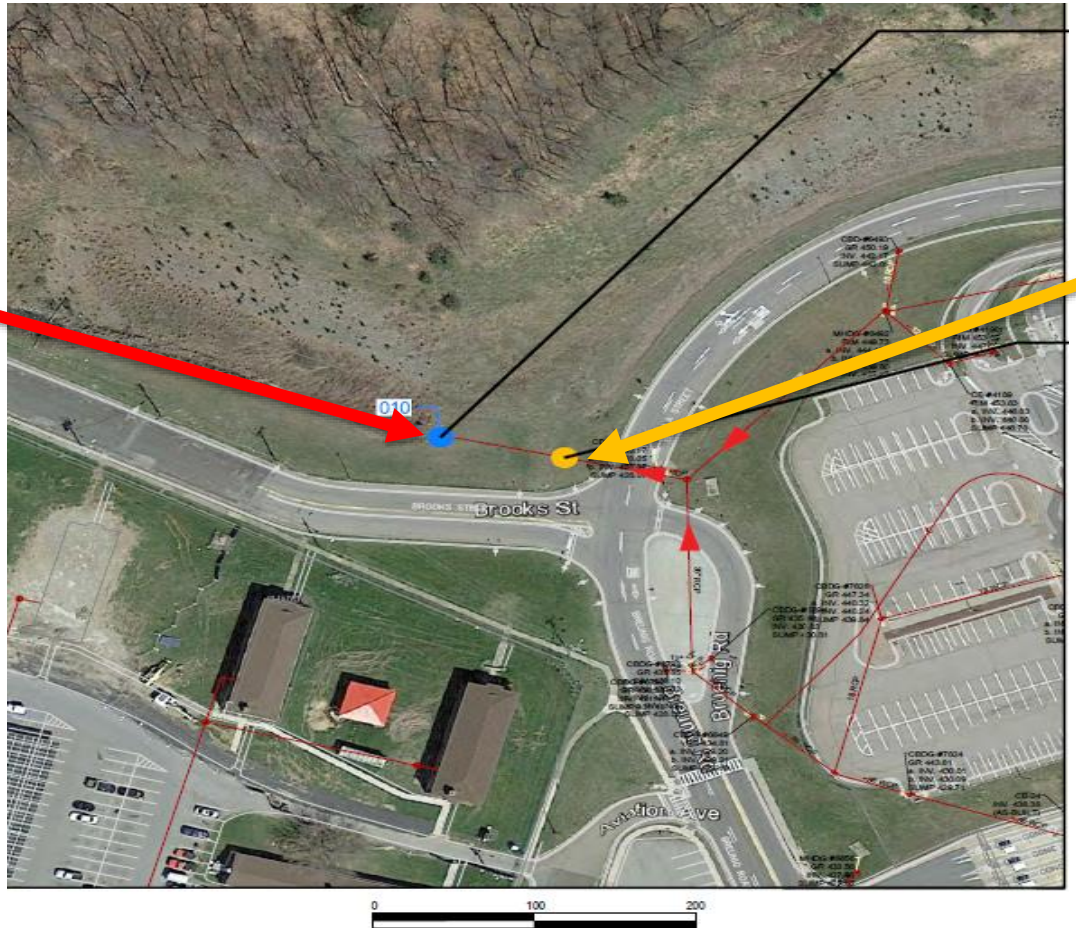
Parallel Planar Configuration Created by Hydrogen Bonds

PFOS Surface Chemistry



Outfall 10

Ponded Outfall



Manhole

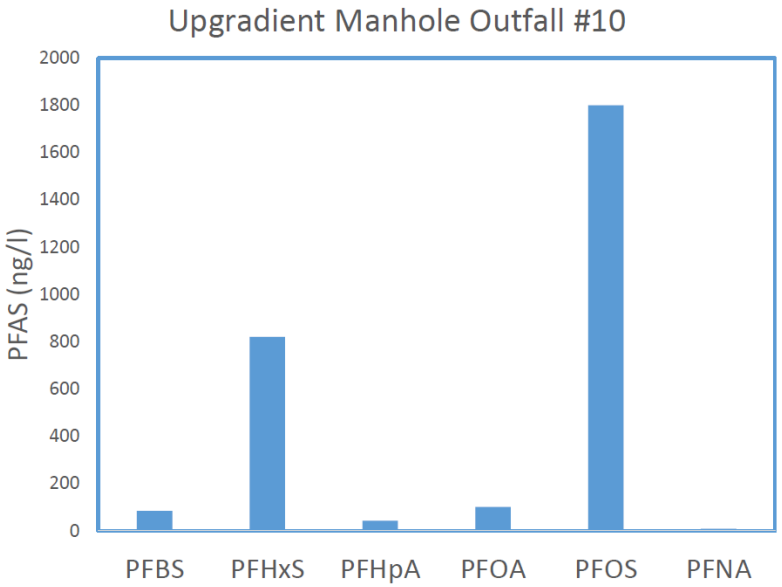
Drainage Area Includes a Former Training Area

Biased High “Invisible Sheen”

PFAS Concentrated on Stagnant Surface

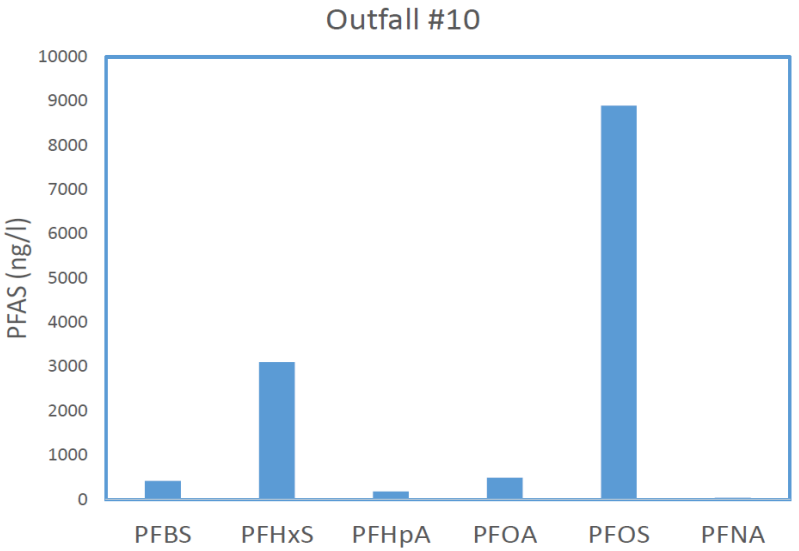
PFAS (ng/l)	Guidance	Manhole	Pond	Invisible Sheen Factor
PFOA	70	100	490	4.9
PFOS	70	1800	8900	4.9
PFHxS		820	3100	3.8
PFBS		84	420	5.0
PFHpA		42	180	4.3
PFNA		8.2	40	4.9
PFOA & PFOS	70	1900	9390	4.9
PFOS/PFOA		18	18	
PFOS/PFHxS		2.2	2.9	
PFOA/PHpA		2.4	2.7	
PFOS/PFBS		21.4	21.2	

Outfall 10 Fingerprints



Moving Water - Manhole

Stagnant Water Pond






PFOS Surface Partitioning – Potential Sampling Bias

Potential Invisible Sheen Sampling Bias

PFAS (ng/l)	MW7		Invisible Sheen Factor
	8/4/2014	3/14/2016	
PFBA	230	120	1.9
PFOS	21,000	5,000	4.2
PFOA	3,500	1,200	2.9
PFBS	230	120	1.9
PFHxS	6,500	3,200	2.0
PFDA	88	200	0.4
PFHpA	580	170	3.4
PFHxA	1,600	780	2.1
PFNA	220	99	2.2
PFPeA	290	190	1.5

Invisible Sheen Sampling Implications

- Surface samples collected from static water bodies could be biased high
- Static surface samples collected from wells may be biased high
- Biased sheen sampling in wells may account for the large variability noted in some groundwater sampling results




Invisible Sheen - Potential Remedial Options

Potential Remedial Alternatives Derived from Sheen Properties

- Evaluate surface adsorbents similar to sheen booms
- Analyze wave action foams and collect if PFAS rich
- Bioconcentrate PFAS in aquatic surface plants or algae and harvest

Unresolved PFAS Reported Properties vs Observed

- PFAS solubility's reported in the 100 to 1,000 mg/l range
- But normally not reported greater than 0.100 mg/l and typically less than 0.010 mg/l
- Two to three orders of magnitude below solubility limits

Thank you

Questions?

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