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
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
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
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

PFOS Based AFFF

PFAS (ng/l)

Sulfonates

PFBS PFHxS PFHpA PFOA PFOS PFNA

Fluorotelomer Based AFFF

PFAS (ng/l)

Carboxylates

PFBS PFHxS PFHpA PFOA PFOS PFNA
Total Ion Chromatograph of Technical Grade PFOS

3M AFFF: Branched and linear isomers (30:70)
If exclude branched isomers, concentrations underestimated and biased low

Peak for Linear isomer of PFOS
PFOS Sources and Reservoir Source ID
Sources of PFAS Contamination

“Isn’t that Hanger ___”
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 2
Outfall Upstream of Reservoir
5,300, 1,300, 600, & 5,900

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

Potential Source 4
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

Parallel Planar Configuration Created by Hydrogen Bonds

Weak Hydrogen Bonding to Conjugated P-Orbitals of Aromatic Hydrocarbons
PFOS Surface Chemistry

AIR

SO$_3^-$

low

WATER

high

SO$_3$SO$_3$SO$_3$SO$_3$SO$_3^-$
Outfall 10

Ponded Outfall

Manhole

Drainage Area
Includes a Former Training Area
Biased High “Invisible Sheen”
## PFAS Concentrated on Stagnant Surface

<table>
<thead>
<tr>
<th>PFAS (ng/l)</th>
<th>Guidance</th>
<th>Manhole</th>
<th>Pond</th>
<th>Invisible Sheen Factor</th>
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<tbody>
<tr>
<td>PFOA</td>
<td>70</td>
<td>100</td>
<td>490</td>
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<tr>
<td>PFOS</td>
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<td>1800</td>
<td>8900</td>
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<td>PFHxS</td>
<td>820</td>
<td>3100</td>
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<td>PFBS</td>
<td>84</td>
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<td>PFHpA</td>
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<td>180</td>
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<tr>
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<td>PFOS/PFOA</td>
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<td>PFOA/PHpA</td>
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<tr>
<td>PFOS/PFBS</td>
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Outfall 10 Fingerprints

Moving Water - Manhole

Stagnant Water Pond
PFOS Surface Partitioning – Potential Sampling Bias
# Potential Invisible Sheen Sampling Bias

<table>
<thead>
<tr>
<th>PFAS (ng/l)</th>
<th>MW7 8/4/2014</th>
<th>MW7 3/14/2016</th>
<th>Invisible Sheen Factor</th>
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<tr>
<td>PFBA</td>
<td>230</td>
<td>120</td>
<td>1.9</td>
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<tr>
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<td>5,000</td>
<td>4.2</td>
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<tr>
<td>PFOA</td>
<td>3,500</td>
<td>1,200</td>
<td>2.9</td>
</tr>
<tr>
<td>PFBS</td>
<td>230</td>
<td>120</td>
<td>1.9</td>
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<tr>
<td>PFHxS</td>
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<td>3,200</td>
<td>2.0</td>
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<td>PFDA</td>
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<td>PFPeA</td>
<td>290</td>
<td>190</td>
<td>1.5</td>
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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
Questions?

Michael Eberle
P: (484) 213-3973  |  E: MEberle@trcsolutions.com
www.trcsolutions.com

Elizabeth Denly
P: (978) 656-3577  |  E: EDenly@trcsolutions.com
www.trcsolutions.com