Characterization and Treatment of Perfluorinated Compounds: *The Next Big Emerging Class of Contaminants*

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NEWMOA

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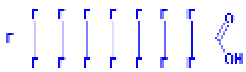
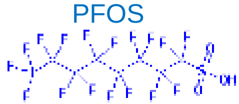
Presentation Outline

- Background/Overview
- Regulatory Status/Considerations
- Site Characterization
- Risk Assessment
- Remedial Action Implications
- Summary
- Q&A and Discussion

PFOA



PFOS



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Background/Overview – Mfg. and Uses

- Synthetic chemicals used in manufacturing fluoro-polymers
  - PFOA – perfluorooctanoic acid and it's principle salts, manufactured from 1947-present[1], 8 manufacturers phased out production by 2010
  - PFOS – perfluorooctane sulfonate, manufactured from 1949-2002
- Typically only a fraction of final product/not an end product
- Used in making surface treatments
  - Non-stick cookware (Teflon®)
  - Breathable, all weather clothing (Gore-tex®)
  - Fluoro-elastomers (gaskets, O-rings, Hoses)
  - Paper and packaging protectors
- Used in making performance chemicals
  - Aqueous Film Forming Fire fighting foam (AFFF)
  - Mining and oil surfactants
  - Metal plating baths (chromium)
  - Insecticides

[1] Prevedouros ES&T, 2006
[2] Paul et al. ES&T, 2009

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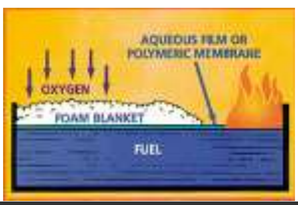
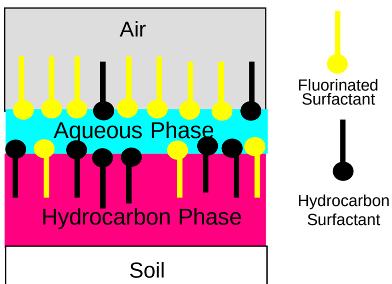
Aqueous Film Forming Foams (AFFF)

- PFCs are used in AFFFs that were routinely used for fire fighter training at municipal and military fire training areas
- AFFF blankets fuel, cools the fuel surface, prevents re-ignition by suppressing release of flammable vapors
- Until 2000, AFFF effluent from fire-fighting activities were allowed to discharge to the environment
- C6 and Fluorine free AFFF developed as alternatives
- C8 AFFF still on DOD and other facilities
- At least 9 different formulations





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Background/Overview – AFFF & Fire/Crash Sites

Estimated Quantity of AFFF in U.S.[1]

AFFF Use Sector	Estimated Quantity AFFF Concentrate (Gallons)	Possible Margin of Error ± %	Likely Range of Actual Quantity (Gallons)
U.S. Military	2,838,500	± 5%	2,696,575 – 2,980,425
Other Federal	18,500	-0 + 25%	19,500 – 24,375
Aviation (ARFF)	729,016	-5 + 20%	692,565 – 874,819
Aviation (Hangars)	850,000	± 25%	637,500 – 1,062,500
Merchant Ships/Offshore	80,000	± 25%	60,000 – 100,000
Fire Depts (non-aviation)	1,360,000	± 35%	884,000 – 1,836,000
Oil Refineries	1,900,000	± 25%	1,425,000 – 2,375,000
Other Petro-Chem	2,000,000	± 35%	1,300,000 – 2,700,000
Misc. Applications	150,000	± 35%	97,500 – 202,500
Total	**9,927,016**		**7,812,640 – 12,155,619**

[1]Robert Darwin, Hughes & Assoc., Aug 2004

DoD Fire/Crash/ Training Sites[2]

Service	Total Sites
Air Force	353
Army	94
Navy	132
DLA	3
FUDS	12
Total	***594***

[2]DoD Knowledge Based Corporate Reporting System, 2008

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Background/Overview – Chemical Properties

Chemical Properties	PCB (Arochlor 1260)	PFOA	PFOS	TCE	Benzene
Molecular Weight	357.7	414.07	538	131.5	78.11
Solubility	0.0027 mg/L @24°C	3400 – 9500 mg/L @25°C	519 mg/L @20°C	1100 mg/L @ 20°C	1780 mg/L@20° C
Vapor Pressure (@25°C)	4.05×10^{-5} mmHg	0.5-10 mmHg	2.48×10^{-6} mmHg	77.5 mmHg	97mmHg
Henry's Constant	4.6×10^{-3} atm-m^3/mol	0.0908 atm-m^3/mol	3.05×10^{-6} atm-m^3/mol	0.0103 atm-m^3/mol	0.0056 atm-m^3/mol

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Regulatory Status – Increasing Concerns

- Concerns originated in 1999 - 3M submitted information to US EPA regarding potential risks, 3M phased out PFOS production in 2002
- 2002 market shift in focus to C4-C6 chain length sulfonates and fluoro-telemer sulfonates (Fts)
- Several EPA, OECD, and UK Environmental Hazard/Risk Assessments between 2002 and 2006
- 2005 Stockholm Convention on Persistent Organic Pollutants listing
- EPA included several PFCs on Contaminant Candidate List-3 in 2009
- EPA included 6 PFCs in Unregulated Contaminant Monitoring Rule-3
- 2014 – US EPA OSWER crafting PFC screening levels, established Health Advisory Levels
- At present, no ‘regulatory driver’ or minimum risk level (MRL) in US

Stockholm Convention on persistent organic pollutants (POPs)

Background/Overview - Other PFCs

Analyte	Acronym	Chemical Abstract Services Registry Number (CASRN)
N-ethyl perfluorooctanesulfonamidoacetic acid	NEtFOSAA	–
N-methyl perfluorooctanesulfonamidoacetic acid	NMeFOSAA	–
Perfluorobutanesulfonic acid	**PFBS**	**375-73-5**
Perfluorodecanoic acid	PFDA	335-76-2
Perfluorododecanoic acid	PFDoA	307-55-1
Perfluoroheptanoic acid	**PFHpA**	**375-85-9**
Perfluorohexanesulfonic acid	**PFHxS**	**355-46-4**
Perfluorohexanoic acid	PFHxA	307-24-4
Perfluorononanoic acid	**PFNA**	**375-95-1**
Perfluorooctanesulfonic acid	PFOS	1763-23-1
Perfluorooctanoic acid	PFOA	335-67-1
Perfluorotetradecanoic acid	PFTA	376-06-7
Perfluorotridecanoic acid	PFTrDA	72629-94-8
	PFUnA	2058-94-8

Bold = on UCMR3 monitoring list plus PFOS/PFOA

Site Characterization - Recommended Sampling Procedures

- Sampling & QAPPs must address potential for cross contamination and/or false positives, sources include:
  - Water proof field notebooks
  - Teflon® Liner in bottles
  - Teflon® bailers or wells
  - Decon 90 decon solution, possibly others
  - Fast food wrappers
  - Tyvek® suits

- Preference for a 250 mL HDPE bottle, no preservatives
- 7-14 day holding time, Preserve on ice
- No commercially demonstrated screening kit/tools, several under development
  - Ziltek Remscan Infrared scanner (AUS)
  - CRC Care (AUS)
  - Methylene Blue Active Substance – Colorimetric test for Anionic Surfactants

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Site Characterization - Laboratory Analysis

- Liquid Chromatography – Mass Spectrometry – EPA Method 537
  - LC / MS /MS
- International Standard ISO 25101
  - PFOS and PFOA in water
- Extraction / Holding Time
  - Water 7 days / 40 days
  - Soils 14 days / 40 days
- Method Detection Limits
  - Water
    - PFOS – 0.015 to 0.001 ug/L
    - PFOA – 0.010 to 0.004 ug/L
  - Soil
    - PFOS – 0.4 to 0.01 ug/kg
    - PFOA – 1.0 to 0.5 ug/kg
- Limited Certified Laboratories
  - USA Laboratories
    - Test America – Denver, CO
    - MPI Research Inc. – State College, PA
    - Pace Analytical
    - UL Laboratories – South Bend, IN
  - German Laboratories
    - Fresenius
    - Analytis
  - Canada Laboratories
    - Axys Analytical Services
    - Maxxam
  - Intertek – United Kingdom
- Data comparability between laboratories is difficult
- Costs
  - $250 to $500 per sample (US $)

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Risk Assessment – What we know/don't know

- Important to note that there are 2 distinct focuses on PFC risks
  - General exposures via non-environmental media (e.g. Teflon cooking products and food packaging materials)
  - Site-specific exposures by way of contaminated environmental media
- What we do know
  - Toxicity to animals
  - Bioaccumulates
  - Environmentally persistent
  - Widespread in human population around globe

- What we don't know
  - Widespread Exposure at unacceptable concentrations?
  - Toxicity to humans?
  - Issue of potential for prostate cancer is contentious
  - Potential link to Autism is contentious
  - 2012 C8 Panel conclusions (Kidney Cancer) – 1st carcinogenic evidence?

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Remedial Action Implications – Standards/SL's

Regulatory Agency	PFOS	PFOA
	Soil	
MPCA – Residential SRV	2100 µg/kg	2100 µg/kg
MPCA– Recreational SRV	2500 µg/kg	2600 µg/kg
MPCA – Industrial SRV	14000 µg/kg	13000 µg/kg
US EPA Region 4 – Residential	6000 µg/kg	16000 µg/kg
	Groundwater	
US EPA – drinking water HAL	0.2 µg/L	0.4 µg/L
MDH – groundwater	0.3 µg/L	0.3 µg/L
New Jersey – drinking water	---	0.04 µg/L
North Carolina – groundwater	----	2 µg/L
Canada DW Guidance Value	0.7 µg/L	0.7 µg/L
UK DEFRA – drinking water	0.3 µg/L	10 µg/L
Germany – drinking water	0.1 – 0.3 µg/L	0.1 – 0.3 µg/L

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Remedial Action Implications - Challenges

- Emerging concern with significant Site characterization challenges
  - large dilute plumes will likely form and a "source area" may not exist
  - co-mingled plumes (e.g. BTEX, TPH, Fuels)
  - Many sources, opportunites for cross contamination
- Limited remediation experience and almost no previous commercial focus on developing remediation technologies
- Chemical property challenges
  - resistant to most conventional treatment technologies
  - high solubility and low Henry's law constant

- Existing aerobic bio or ISCO treatment may partially oxidize other AFFF compounds (e.g. precursors) and produce additional PFOS/PFOA

Treatment of Solids

- Landfill
  - Commercially available vs. special construction
  - Leachate management & treatment considerations
- Isolate in place
  - Site specific considerations
  - Capping
  - Landfill reconstruction
- Incineration
  - Proven technology
  - Generally for lower Volume, higher Concentration materials

Treatment of Water

Mechanism	Technology	Scale
Separation	Filtration	Lab
	Adsorption	Full
Destruction	Reduction	Lab
	Oxidation	Lab
	Pyrolysis	Lab
	Photochemical	Lab
	Thermal Oxidation	Full

Optimal treatment technology would be highly dependent on the initial PFC concentration (i.e., high for manufacturing waste or low for environmental distributed) and the matrix in question.

Remedial Action Implications – Scenarios

- No current remediation with potential or confirmed presence of PFOA/PFOS
  - Potential - when to look and why?
  - Confirmed – Pump and treat likely best current option
- Existing pump and treat remedy with treatment via industrial WWTP
  - May or may not address PFOS/PFOA
  - Potential for PFC concentrations to increase
- Existing pump and treat remedy with independent GW treatment system
  - May or may not address PFOS/PFOA
- Existing in situ or approved Monitored Natural Attenuation remedy
  - Not likely to address PFOS/PFOA

Possible In-Situ Treatment Technologies

- FMC (now PeroxyChem) - testing activated persulfate and Fenton's reagent to treat PFOS/PFOA
- Washington State University – testing degradation of PFOA through catalyzed hydrogen peroxide propagation reaction
- ES&T - Reductive Defluorination: Vitamin B12 as electron transfer mediator for PFOS reduction, Ti(III)-citrate as the bulk electron source
- Removals of PFOA/PFOS in pilot-scale constructed wetland
- University of Arizona - Boron-Doped Diamond Film Electrodes for oxidation of PFOS and TCE

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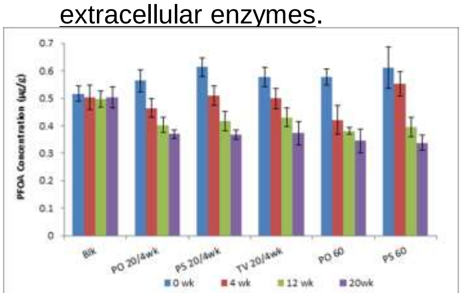
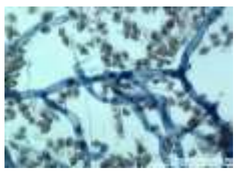
Enzyme Catalyzed Oxidative Coupling

- UGA/AECOM has been funded by AFCEC to evaluate "Enzyme Catalyzed Oxidative Coupling (ECOC) Reactions" to treat PFCs. This technology was originally developed for treatment of other persistent organics (PCBs, PAHs)
- ECOC is a process that is inspired by how natural organic matters are broken down naturally through enzyme catalyzed oxidation process
- In this process PFC is oxidized by organic radicals catalyzed by extracellular enzymes.





Phanerochaete chrysosporium
(Genus of White Rot Fungi)

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Summary

- Primary sources of potential PFOS/PFOA includes AFFF releases, plating facilities, and landfills.
- AFFFs represent the likely most significant source, were produced in at least 9 different formulations, and contain many different PFCs
- Significant potential for background contamination/other sources
- Compounds are very soluble, recalcitrant and persistent
- Large dilute plumes will form and can represent potential financial and receptor risks, especially for surface water/ecological receptors
- No current ‘regulatory driver’ or MRL in US but EPA crafting screening levels and requesting sampling/analysis

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Summary

- More cleanup standards will likely be established and trend downward
- Existing remediation systems are not likely addressing PFCs, could exacerbate problems (e.g. PFOS as metabolite of precursors)
- Landfill, isolation or incineration are likely best current soil treatment options
- P&T with GAC may be best current GW treatment option; Biological and Enzymatic treatment promising
- PFCs will likely increasingly become problematic for PRPs with a focus beyond PFOS/PFOA
- PFCs appear to be unlike anything we’ve dealt with before and represent a significant challenge.

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Questions and Discussion

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Key PFC Resources

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