SERDP & ESTCP Research Efforts on Emerging Contaminants

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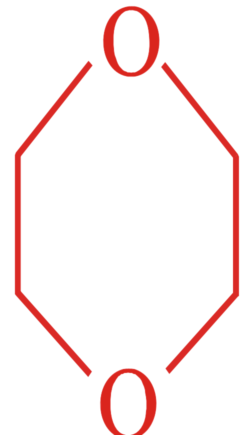
Current Research on Emerging Contaminants

- 1,4-Dioxane
- PFCs
- NDMA

The 1,4-Dioxane Problem

- Used extensively as a stabilizer in chlorinated solvents
  - ♦ Primarily used with 1,1,1-TCA
  - ♦ 1,1,1-TCA found at 809 NPL sites (www.atsdr.gov; 2004)

1,4-Dioxane



1,1,1-Trichloroethane

- 1,4-Dioxane has recently emerged as a contaminant of concern
  - Low action levels in several states: California (3 ppb); Florida (5ppb); Maine (70 ppb); Massachusetts (50 ppb); Michigan (1 ppb); North Carolina (7ppb)
  - Risk of closed sites being re-opened
- In a recent data review from 49 Air Force installations, Anderson et al. (2012) found 1,4-dioxane in groundwater at about 20% of all chlorinated solvent sites and found a strong correlation with both TCE and TCA. At Navy sites, over 200 sites have detected 1,4-dioxane above 3 μg/L.

Current Treatment Options for 1,4-Dioxane

- In situ oxidation
  - Reported to work in some cases
- Advanced oxidation
  - Some full-scale systems in place
- Biological treatment
  - Co-metabolic process (propane/THF)
  - Biological treatment has proven to be challenging
- No universal solution yet available
- SERDP initiated efforts in 2005 examining biodegradation of dioxane.

Previous Efforts

FY05 SON: Remediation of Emergent Contaminants

ER-1417
Oxygenase-Catalyzed Biodegradation of Emerging Water Contaminants: 1,4-Dioxane & NDMA

- Isolated culture capable of 1,4-dioxane mineralization.
- 1,1,1-trichloroethane and 1,1-dichloroethene inhibited dioxane degradation.

ER-1422
Biodegradation of 1,4-Dioxane

- Pure cultures were shown to degrade 1,4-dioxane via cometabolism during growth on propane or THF
- 1,4-dioxane not degraded in microcosms created with samples from 2 different aquifers regardless of redox conditions.

FY13 SERDP SON: In Situ Remediation of 1,4-Dioxane Contaminated Groundwater

- Objective: To develop cost effective in situ remedial alternatives for 1,4-dioxane-contaminated groundwater. Specific objectives include:
  - Develop cost effective, in situ remedial alternative to current approaches;
  - Elucidate the impact of co-contaminants on the remedial process; and
  - Evaluate whether remedial processes for 1,4-dioxane contamination can operate in parallel or in series with traditional treatment processes for co-contaminants.

Selected Projects: In Situ Remediation of 1,4-Dioxane-Contaminated Groundwater

	ER-2300 University of California, Los Angeles	ER-2301** Rice University	ER-2302 Pacific Northwest National Laboratory	ER-2303 North Carolina State University
Technology	Bioremediation	Monitoring	Chemical oxidation	Bioremediation
Objective	Quantify the effects of co-contaminants on the rates and mechanisms of 1,4-dioxane biodegradation.	Develop catabolic gene probe(s) to quantify the presence and expression of dioxane biodegradation capacity to aid in selection or rejection of MNA	Develop advanced-oxidation ISCO as a viable technology for treating 1,4-dioxane.	Evaluate the two simplest branched hydrocarbons as stimulants for the cometabolic degradation of 1,4-dioxane and its co-contaminants.

** Limited Scope Projects

In Situ Remediation of 1,4-Dioxane-Contaminated Groundwater

	ER-2304** University of Florida	ER-2305** Georgia Institute of Technology	ER-2306** Shaw Environmental	ER-2307 GSI Environmental Inc.
Technology	Monitoring	Chemical oxidation	Bioremediation	Catalyst-based oxidation & reduction, bioremediation & chemical oxidation
Objective	Develop a method for simultaneous in situ measurements of both 1,4-dioxane and water flux.	Demonstrate proof-of-concept that 1,4-dioxane and co-contaminants PCE and TCE are degraded simultaneously via application of a novel microbially-driven Fenton reaction	Measure and assess the extent to which 1,4-dioxane can be biodegraded by methane oxidizing bacteria under conditions typical of a down gradient ,co-mingled chlorinated solvent plume.	Develop integrated, site specific management approaches by identifying ways in which innovative and conventional technologies can be combined to treat 1,4-dioxane and CVOCs

** Limited Scope Projects

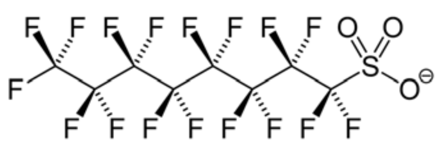
ESTCP Projects Addressing 1,4-Dioxane

- ER-201324: Sustained In Situ Chemical Oxidation (ISCO) of 1,4-Dioxane Using Slow Release Chemical Oxidant Candles
  - Pat Evans, Ph.D. (CDM)
  - Specific technical objectives:
    - Demonstrate use of permanganate & unactivated persulfate in the slow-release candles to couple oxidant release rate, dioxane transport rate, & dioxane destruction rate.
    - Demonstrate that slow-release candle delivery vehicle can minimize potential secondary effects such as metals mobilization & permeability reduction.
- ER-201326: 1,4-Dioxane Remediation by Extreme Soil Vapor Extraction (XSVE)
  - Rob Hinchee, Ph.D. (IST)
  - XSVE is a combination of increased air flow, sweeping with drier air, increased temperature, decreased infiltration, and more focused vapor extraction.

What Are Perfluorochemicals (PFCs)?

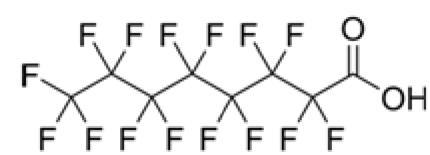
- General formula: $F(CF_2)_n$–R
  - Hydrophobic alkyl chain of varying length (typically C_4 to C_{16})
  - Hydrophilic end group
- Man-made compounds with unique chemical properties
  - Very stable and persistent in the environment
  - Ionic form of PFCs – highly soluble, non-volatile, and poorly sorb to soil
- Primary PFCs of interest
  - Perfluorooctane sulfonate (PFOS)

    $C_8HF_{17}O_3S$

  - Perfluorooctanoic acid (PFOA)

    $C_8HF_{15}O_2$

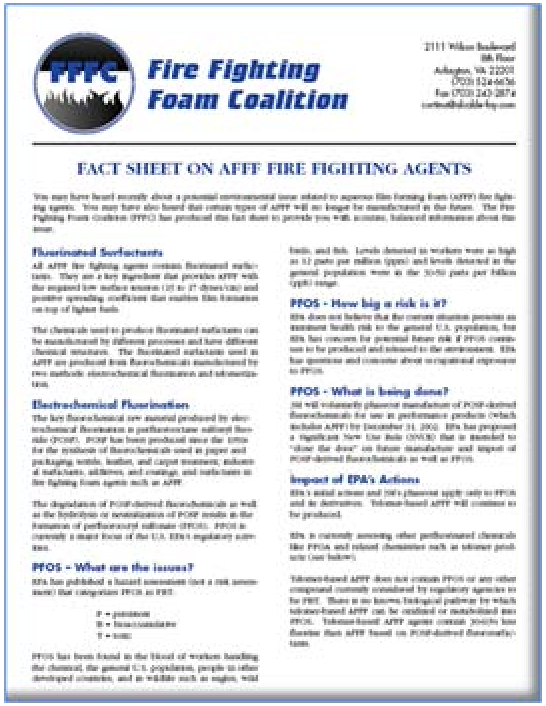
    

Aqueous Film Forming Foam

- AFFF
  - Developed in 1960s by 3M and U.S. Navy for use on Class B fires (flammable liquids)
  - Contains fluorosurfactants (and other compounds as required) per MILSPEC MIL-F-24385F(SH)
  - Low surface tension and positive spreading coefficient enable film formation on top of lighter fuels

AFFF and PFCs

- PFCs in AFFF
  - Historically, AFFF contained PFOS and small percentage of PFO (disassociated form of PFOA)
  - 3M, sole producer of PFOS in the U.S., discontinued production of PFOS in 2001
  - Continued use of stockpiled PFOS-based AFFF not currently restricted under U.S. regulations
  - AFFF now produced using smaller chain PFCs ($<C_6$)


FFFC
Fire Fighting Foam Coalition

FACT SHEET ON AFFF FIRE FIGHTING AGENTS

Fluorinated Surfactants

Electrochemical Fluorination

PFOS - What are the issues?

PFOS - How big a risk is it?

PFOS - What is being done?

Impact of EPA's Actions

http://www.fffc.org/

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Scope of the PFC Issue

- Environmental release of PFCs from:
  - Historical testing or emergency activation of fire suppression systems in hangars
  - Leaks from storage tanks and pipelines
  - Historical fire fighter training exercises
- Scope of potential impact difficult to define
- Site investigations have not typically included analysis for PFCs, given their emerging status

- Scope of potential problem can be estimated using the number of “Fire Training” sites (~600) as a surrogate for actual site data
  - May underestimate problem by not including spills, pipeline leaks, or testing/emergency activation of aircraft hangar fire suppression systems

Cleanup Challenges

- Many conventional treatment approaches are not effective for PFCs in water (e.g., direct oxidation, air stripping, vapor extraction)
- Technologies currently available to treat PFCs in water include
  - ♦ Granular activated carbon (GAC) is most effective method
    - Drinking water treatment (municipal and private wells)
    - Landfill water treatment
  - ♦ Reverse osmosis is effective for higher concentration industrial waste streams
- Bench-scale research to develop alterative treatment approaches continues

FY11 SON: In Situ Remediation of Perfluoroalkyl Contaminated Groundwater

- Objectives:
  - ♦ Improve understanding of mechanisms involved in F&T processes in groundwater under varying natural & engineered conditions.
  - ♦ Determine impact of co-contaminants on F&T processes.
  - ♦ Improve understanding of behavior of perfluoroalkyl contaminants under typical remedial technologies for co-contaminants.
  - ♦ Develop remedial strategies for perfluororalkyl contaminants, including consideration of the necessity for treatment train approaches to facilitate treatment of co-contaminants.

FY11 Selected Projects: In Situ Remediation of Perfluoroalkyl Contaminated Groundwater

	ER-2126 Colorado School of Mines	ER-2127** University of Georgia	ER-2128 Oregon State University
SON	Objective 2 & 3	Objective 4	Objective 1 & 3
Objective	To evaluate the relative importance of key physicochemical and biological parameters in determining the fate and transport of PFCs in groundwater in the presence of co-contaminants and during remediation of co-contaminants.	To investigate the feasibility of a novel scheme for the remediation of PFCs contaminated groundwater.	To delineate the fluorochemicals that persist in aqueous film forming foam (AFFF) –contaminated groundwater, sediment, and soil and evaluate their impact on priority pollutant transport and bioremediation.

FY14 SON: In Situ Remediation of Perfluoroalkyl Contaminated Groundwater

Objective:

Applied research to develop cost effective in situ remedial alternatives for perfluoroalkyl contaminated groundwater. Specific objectives:

- Develop cost effective, in situ remedial approaches for treating perfluoroalkyl contaminated groundwater.
- Assess the impact of common co-contaminants on the remedial process given that these compounds were commonly utilized at sites contaminated with petroleum hydrocarbons and possibly chlorinated solvents (e.g., historical fire training sites).
- Determine the necessity for treatment train approaches to facilitate treatment of co-contaminants.

FY14 Selected Projects: In Situ Remediation of Perfluoroalkyl Contaminated Groundwater

	ER-2423 Clarkson University	ER-2424 Shaw Environmental	ER-2425 University of Minnesota	ER-2426 Purdue University
Technology	GAC sorption combined with destruction using activated persulfate oxidation	Electrocatalytic and catalytic approaches	Chemical coagulants	Coupled reductive & oxidative processes
Objective	Evaluate feasibility, effectiveness, & sustainability of treatment train approach where activated carbon is used to sorb & concentrate contaminants, followed by contaminant destruction & carbon regeneration in situ using activated persulfate	Develop & assess use of electrocatalytic & catalytic approaches for in situ treatment of PFASs in groundwater	Develop cost-effective, in situ method using coagulants to sequester six PFAS in groundwater systems	Test effectiveness of reductive technologies & couple most successful to oxidative technologies to obtain highly effective destruction in a cost effective in situ treatment train

NDMA

- Toxicology
  - NDMA is a potent mutagen, teratogen, & carcinogen.
  - EPA 10^{-6} Lifetime Cancer Risk = 0.7 ng/L.
  - California DHS; 10 ng/L Action Level;
    California OEEHA 3 ng/L PHG (12/2006)
- Sources
  - 1,1-Dimethylhydrazine Rocket Fuel[$(CH_3)_2NNH_2$]
  - Aerozine 50 (Mixture of Hydrazine and 1,1DMH)
  - Disinfection Byproduct (Chloramine)
  - Industrial, Agricultural and Food Sources.
- Treatment
  - Pump-and-Treat with UV Irradiation
  - 1000 mj/cm^2 for 10-fold reduction
  - (10X for *Cryptosporidium*)

Potential Remedial Applications

NDMA Summary of Efforts

- SERDP efforts initiated in 2005
- Technologies matured to demonstrations under ESTCP

- **Field Demonstration of Propane Biosparging for In Situ Remediation of N-Nitrosodimethylamine in Groundwater** (ER-200828)
- Principal Investigator: **Paul Hatzinger** (Shaw Environmental, Inc.
- In situ bioremediation treatment of groundwater with propane gas and oxygen distributed in the subsurface to stimulate propanotrophs.

- **Treatment of N-Nitrosodimethylamine (NDMA) in Groundwater Using a Fluidized Bed Bioreactor** (ER-200829)
- Principal Investigator: **Paul Hatzinger** (Shaw Environmental, Inc.)
- Ex situ treatment of groundwater using biological fluidized bed reactor (FBR).

NDMA Summary

- Treatable by UV Oxidation
- *In Situ* and *Ex Situ* Biotreatment Possible
    - May require propane biostimulation to reach low levels
- *Ex Situ* Metal Catalyst Treatment Showing Promise (*Data not shown*)

Home Pages

http://www.serdp.org

http://www.estcp.org