SERDP & ESTCP Research Efforts on Emerging Contaminants

Andrea Leeson, Ph.D. Environmental Restoration Program Manager SERDP & ESTCP





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)

AST MAARASC COMPANY CCC WARRANCE WARRANCE COMPANY WARRANC



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 μ g/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 1,1dichloroethene 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 slowrelease 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(CF₂)_n-R
 - Hydrophobic alkyl chain of varying length (typically C₄ to C₁₆)
 - 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)

Perfluorooctanoic acid (PFOA)



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 (<C₆)



2111 Wilson Baskwood B6. Floor Adaptes, VA 22201 (703) 524-6636 Fee (703) 343-2874

as 12 pate per million (ppm) and levels detend in the general population were in the 30-50 parts per billion (ppR) integer.

82% does not helieve that the current situation persons an another bould this to the general U.S. propulation, hus

Alls, has concorn for powerski heave rok if PPUS comm-

use to be produced and admost to the appropriate. ED has questions and concerns about to capational expression to PPUS.

Relation APP) by Deconduct 31, 2002. HPs has proposed a togetificant New Use Bulk (NNO) that in Remained to

slow the door" on throw manufacture and segon or print derived flags a flagshouth as well as PRUS.

Ets v suital activate and SN's phaseout apply only to PPCA and in derivatives. Telescar-based APTY will continue to be produced.

the is raisonly assessing other performant changed like PPCA and related chemistics such as selence products (see bulker).

Through hand APPT does not created Print or any other

PPOS - How big a rick is it?

PFOS - What is being done? 34 vill volumely plassed pandatum of POP-derival devicements for use in performance produce (which

Impact of EPA's Actions

FACT SHEET ON AFFF FIRE FIGHTING AGENTS

Vin may have been increase about a protessial environmental increased and to aspersso like forming lease (APPP) the light-ing again. This may have also beend that retrace types of APPP will no leage be manufactured in the form-lighting from Contents (PPC) has produced the list factor to provide yes with sources, balanced interasement devi-

Phoneiranted Sourfacturets

All ATT The Eighting against orekant. Environment works-tame. They are a key segredness that provides ATT with the resparse live orders assument 12 to 21 dense/2001 and positive operading northiness that seations this formation memory of induced adult. on imp of lighter fault.

the changeds used to produce Receiptand nationany can to executionated by different processes and have different foreintal solutions. The foreintance surfactance used in APIT are produced from forein-formulat manufactaned by to methodic electrichemical theoremies and advances

Betrachemical Plasmation

The key floor of lossical new manuful produced by elec-trachemical flooringment is particulated address filling Har (PCM). PCMP has been produced more the Error for the synthesis of theorethematule oned in paper and packaging words, leather, and carpst treatment, indexto. d suffactures, allfalves, and country, and instactures to fee fighting from agence with an APPE

the degradation of POH-detred Bacardonacule as well as the hydrolysis or neutralization of POSP results in the humanon of perflorements suffering difficit. Photos arenally a major locus of the U.S. EDUX regulatory activ-

PFOS - What are the issues?

076 has published a hazard assessment (not a rok arrest mere) that categorians PPCB as P97.

1+100

print has been frand in the blood of workers handing e chemical, the general U.S. population, people to infer-redrighed scientifies, and an wildlife such as sugars, with

Telement-based APTY does not concern Proto or any other compound controlly concerned by the protocol of the PRE. Base is no known backgold pathway by which informer-based APTY cat, be confided or monibilitied mo-tricate-based APTY cat, by confided or monibilitied mo-PES. Tokenarbased APTY agoing contail (3016) have farster flats APP based on POSP-datived flaterourla;

http://www.fffc.org/



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 cocontaminants.
 - 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[(CH₃)₂NNH₂]
- 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/cm² 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