Emerging Contaminants: DoD Overview and State of Knowledge on Fluorochemicals and 1,4-Dioxane

December 3, 2015

SERDP DOD • EPA • DOE | ESTCP

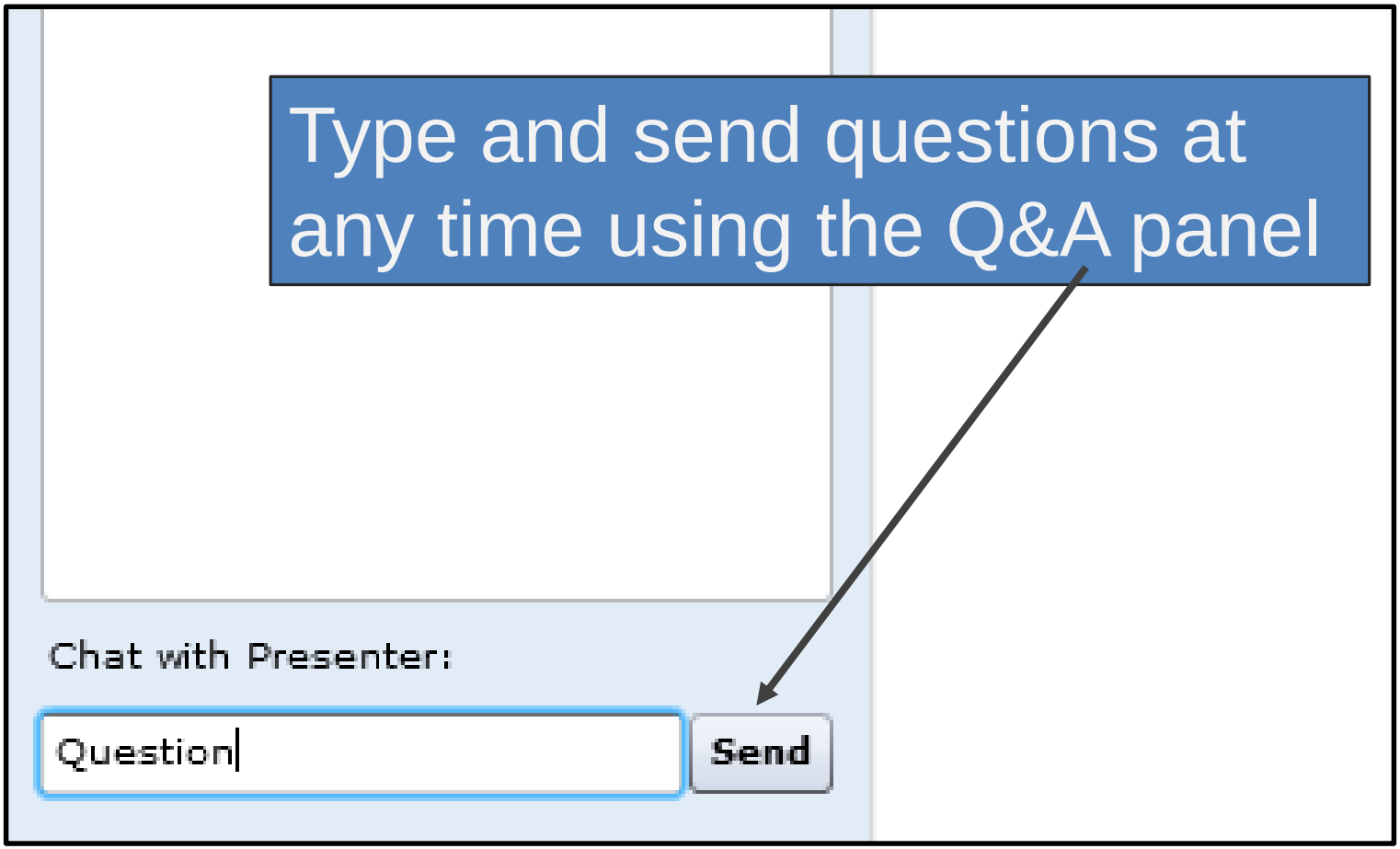
Welcome and Introductions

Jennifer Nyman, Ph.D.
Geosyntec Consultants

Agenda

- **Webinar Logistics**
  Dr. Jennifer Nyman, Geosyntec Consultants (5 minutes)
- **Overview of SERDP and ESTCP**
  Dr. Andrea Leeson, SERDP and ESTCP (5 minutes)
- **DoD Chemical and Material Risk Management Program: Emerging Risks**
  Mr. Paul Yaroschak, Office of the Assistant Secretary of Defense (12 minutes)
- **State of Knowledge on Per- and Polyfluoroalkyl Substances (PFASs) at Military Sites**
  Dr. Jennifer Field, Oregon State University (22 minutes + Q&A)
- **Treatment of 1,4-Dioxane and Chlorinated Solvents Using Sustained Slow Release Chemical Oxidant Cylinders**
  Dr. Pat Evans, CDM Smith (22 minutes + Q&A)
- **Final Q&A session**

How to Ask Questions



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  - Click the mute/connect button
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    - U.S./Canada: 1-877-776-3503
    - International: 330-871-6014
    - Required conference ID: 14228382
- Submit a question using the chat box

SERDP and ESTCP Overview

Andrea Leeson, Ph.D.
Environmental Restoration Program Manager

SERDP

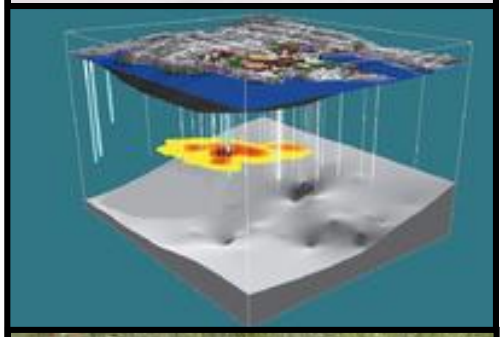
- Strategic Environmental Research and Development Program
- Established by Congress in FY 1991
  - DoD, DOE and EPA partnership
- SERDP is a requirements driven program which identifies high-priority environmental science and technology investment opportunities that address DoD requirements
  - Advanced technology development to address near term needs
  - Fundamental research to impact real world environmental management

ESTCP

- Environmental Security Technology Certification Program
- Demonstrate innovative cost-effective environmental and energy technologies
  - Capitalize on past investments
  - Transition technology out of the lab
- Promote implementation
  - Facilitate regulatory acceptance

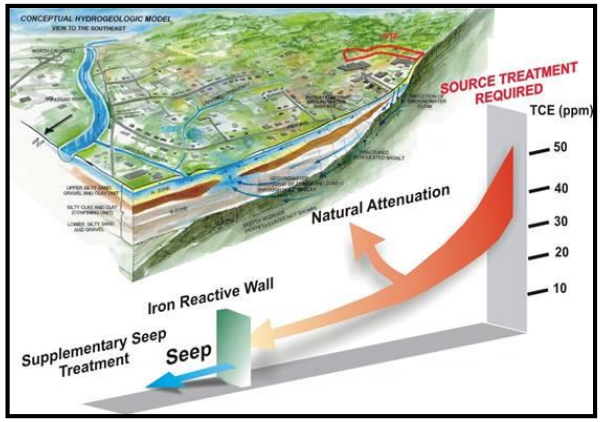
Program Areas

1. Energy and Water
2. Environmental Restoration
3. Munitions Response
4. Resource Conservation and Climate Change
5. Weapons Systems and Platforms



Environmental Restoration

- Major focus areas
  - Contaminated groundwater
  - Contaminants on ranges
  - Contaminated sediments
  - Wastewater treatment
  - Risk assessment



SERDP and ESTCP Webinar Series

DATE	Topics
December 17, 2015	Watershed Assessment and Stormwater Management Optimization Tools
January 14, 2016	Vapor Intrusion: Regulatory Update and Demonstration/Validation of Passive Samplers
January 28, 2016	Water Conservation
February 11, 2016	Chromate/Hazardous Material Free Coating Systems for Military Aircraft and Ground Support Equipment
February 25, 2016	Munitions Response
March 10, 2016	Fate, Transport and Effects of Insensitive Munitions
March 24, 2016	Cadmium and Chromate Elimination Efforts: Implementation Plans and Strategic Roadmaps for Three DoD Depots
April 7, 2016	Resource Conservation and Climate Change
April 21, 2016	Long Term Monitoring Issues at Chlorinated Solvent Sites

http://serdp-estcp.org/Tools-and-Training/Webinar-Series

SERDP
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ESTCP

DoD Emerging Contaminants Program Overview

Paul Yaroschak, P.E.
Office of the Assistant Secretary of Defense
(Energy, Installations and Environment)

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The Defense Context

- Equipment, weapon systems, and platforms provided to the war-fighter are made from, and depend on, chemicals and materials

- Vital chemicals and materials needed for production, performance and sustainment of systems are increasingly at risk from becoming non-available

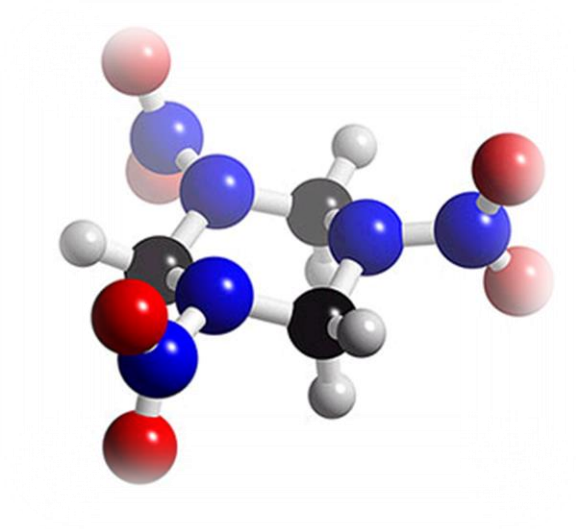
Global Trends

- Use of precautionary principle
  - Must understand health and environmental effects before using chemicals
- Biomonitoring – What's showing up in humans?
  - Centers for Disease Control's national bio-monitoring and California voluntary program
- Strict chemical management and green chemistry
  - Cradle to grave
- Evolving risk assessment science and process
  - EPA IRIS[1] program
- International, federal, and state toxic substances laws
  - EPA Chemical Action Plans
  - California Green Chemistry Law
  - European Union's REACH[2] regulation
  - Pending Toxic Substance Control Act reform

[1] Integrated Risk Information System
[2] Registration, Evaluation, Authorization and Restriction of Chemicals

What is an Emerging Contaminant?

- Chemicals and materials that have pathways to enter the environment and present real or potential unacceptable human health or environmental risks…



and either

- Do not have peer-reviewed human health standards

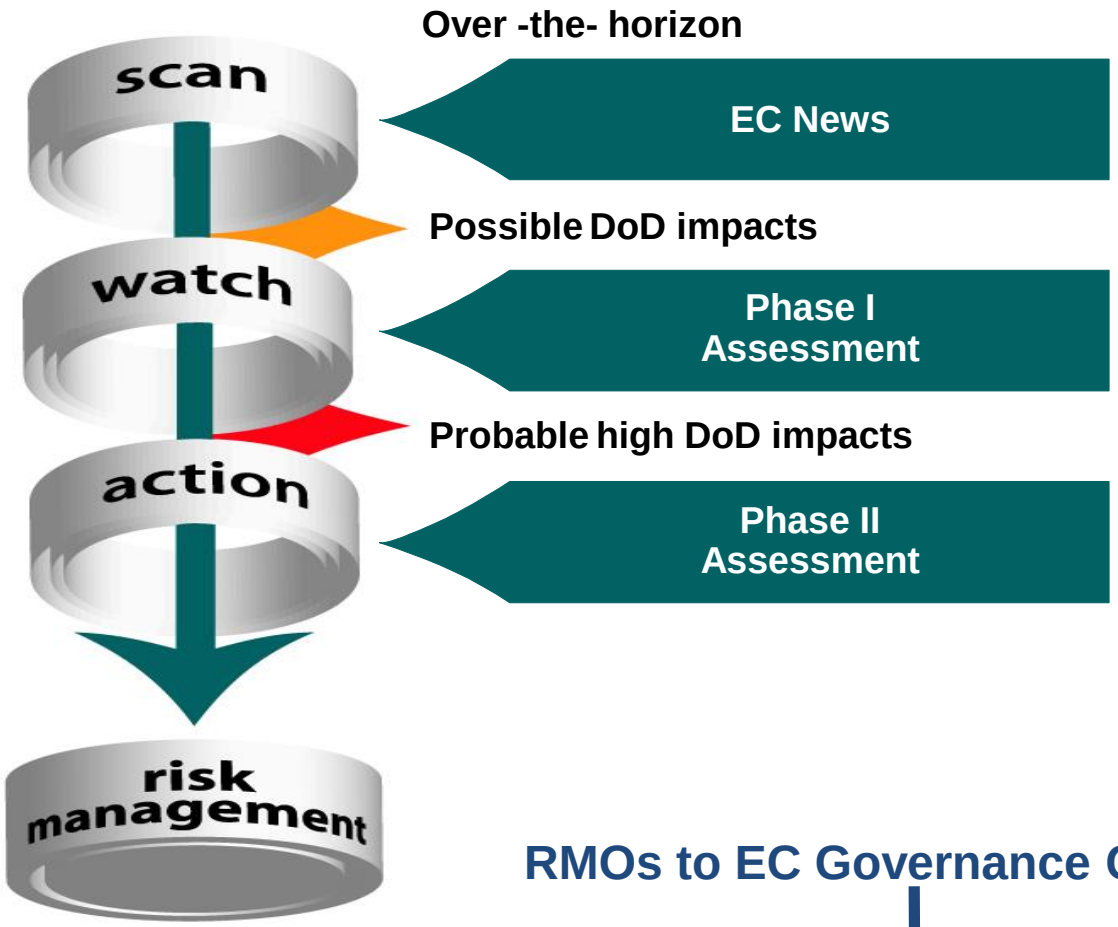
or

- Standards/regulations are evolving due to new science, detection capabilities or pathways

How Can ECs Affect DoD?

- Present risks to operating forces, DoD employees and/or public
  - Human health protection paramount
- Reduce training/readiness
  - Restrictions on use of ranges
- Restrict availability and/or cost of materials or chemicals
  - Adverse impact on mission-critical applications and industrial base community
- Increase O&M and/or cleanup costs
  - Diverts resources from core mission

EC "Scan-Watch-Action" Process



- Review literature, periodicals, regulatory communications, etc.
- Monitor events; Conduct Phase I qualitative impact assessment
- Conduct Phase II quantitative impact assessment; develop and rank Risk Management Options (RMOs)

RMOs to EC Governance Council

↓

Approved RMOs become Risk Management Actions

Functional Areas Assessed

Acquisitions / Research, Development, Testing and Evaluation

Environment, Safety and Health

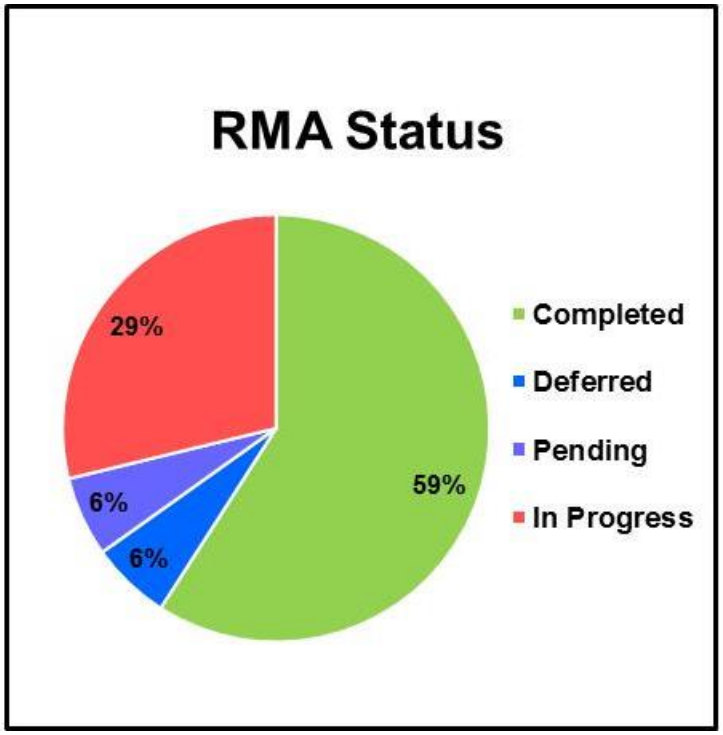
Production, Operation, Maintenance and Disposal of Assets

Cleanup/Remediation

Training and Readiness

EC Program Scorecard – Cumulative

- Potential ECs screened
  - >580
- Phase I Impact Assessments completed
  - 39
- Phase II Impact Assessments completed
  - 11
  - All current/former action list chemicals completed
- Risk Management Actions (RMAs)
  - 66



Examples of ECs that Can Impact Drinking Water

- Perchlorate
- RDX
  - Cyclotrimethylenetrinitramine, an explosive compound
- 1,4-dioxane
- Strontium
- PFOA and PFOA
- Lead

PFOA/PFOS History

1949	3M begins producing PFOS compounds
1956	3M begins marketing “Scotchgard”
1999	EPA begins investigating PFCs based on toxicity studies and prevalence in environment
Through 2001	PFOS used in making AFFF
2006	EPA and 8 companies announce PFC Stewardship program for production phase-outs by end of 2015
June 2007	DoD EC Program completes a Phase I Impact Assessment for PFOA and PFOS (Assessment notes risk related to PFOS releases at AFFF sites)
March 2008	State of MN issues Health Based Value for PFCs
January 2009	EPA issues Preliminary Health Advisories for PFOA and PFOS
November 2009	EPA Region 4 sets soil screening levels
July 2011	DoD EC Program issues Risk Alert for AFFF

Key Triggers and Response Actions for EC Releases

1. **Trigger**: Release or suspected release of EC by DoD
   Action: Confirmation sampling and initial characterization to determine if exposure exists

2. **Trigger**: Confirmed pathway and receptor for EC exposure
   Action: Eliminate “unacceptable” exposure via risk management actions

3. **Trigger**: Peer reviewed toxicity standard (e.g., RfD) is published; don’t need MCL
   Action: Site is integrated into DERP1 for site-specific risk assessment and possible remedial action

For additional information, please visit http://www.denix.osd.mil/cmrmd/ECMR/ECProgramBasics.cfm

Speaker Contact Information

Paul.J.Yaroschak.civ@mail.mil; 571-372-6810

State of Knowledge on Per- and Polyfluoroalkyl Substances (PFASs) at Military Sites

Jennifer Field, Ph.D.
Oregon State University

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Agenda

- Project team
- Unique chemistry
- Technical objectives and approach
- Results and significance
- Conclusions and benefits to DoD

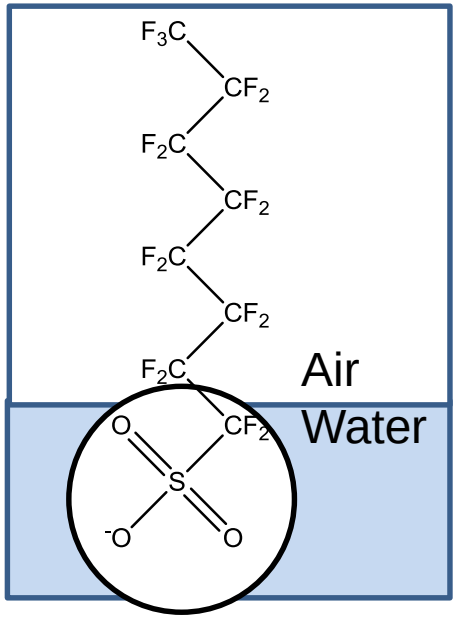
Project Team

- Dr. Jennifer A. Field, Oregon State University
  - Environmental analytical chemist
- Dr. David L. Sedlak, UC Berkeley
  - Advanced oxidation and contaminant fate expert
- Dr. Lisa Alvarez-Cohen UC Berkeley
  - Environmental microbiologist/engineer
- Dr. Markus Kleber, Oregon State University
  - Soil scientist

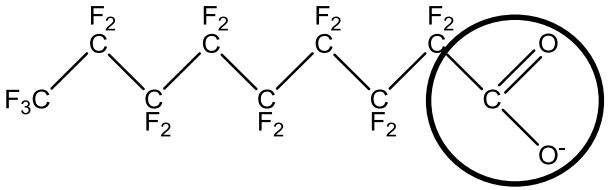
Unique Chemistry of PFASs

- C-F bond is the shortest and strongest bond in nature
- Less tendency to associate with oil and water compared to hydrocarbons (hydrophobic and oleophobic)
  - Few engineered or environmental degradation processes
  - Stable in acids, bases, oxidants, heat
  - Too much energy to break bonds
  - Microorganisms cannot gain energy from breaking the bond

PFOS (**per**fluorooctane sulfonate)

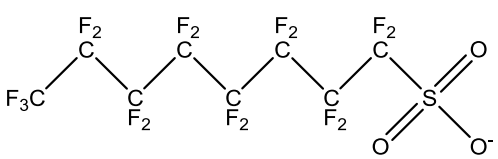


PFOA perfluorooctanoate)



Nomenclature

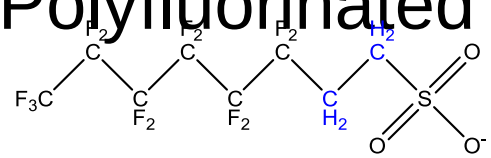
- Need to unify the nomenclature and acronyms
  - Internationally-accepted nomenclature
  - Communicate accurately inside and outside DoD
- P in PFC means perfluorinated chemical
  - Per = all carbons in aliphatic chain bonded only to F
  - Few chemicals fit this category (e.g., PFOS and PFOA)



PFOS (perfluorooctane sulfonate)

- Branched/linear isomers and odd/even chain lengths
- Persistent

- Polyfluorinated



6:2 FTSA (*poly*fluorotelomer sulfonate)

- -CH2- linkages = 'weakness' in molecule, susceptible to biodegradation and abiotic degradation (oxidation)

Technical Objectives

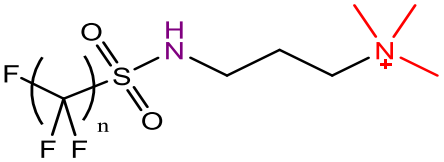
- Characterize per- and polyfluoroalkyl substances (PFAS) composition of aqueous film-forming foam (AFFF) formulations
- Characterize PFAS and precursor composition of AFFF-contaminated groundwater, sediment and soil
- Characterize PFAS biodegradation under aerobic and anaerobic conditions
- Characterize the sorption of the newly-identified anionic, cationic and zwitterionic PFASs

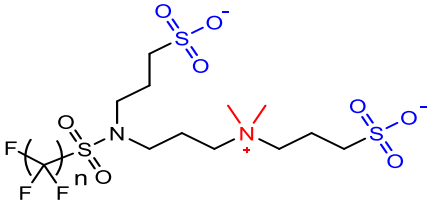
Approach

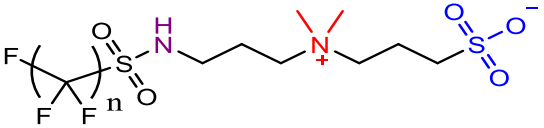
- Analytical characterization
  - Mass spectrometry and oxidation-based assays
  - PIGE (particle-induced gamma ray emission) spectroscopy for total fluorine
- Microcosm biodegradation experiments
  - Aerobic and anaerobic conditions
- Batch sorption experiments

AFFF Characterization

- 3M AFFF
  - PFOS was a major component of 3M AFFF
  - PFHxS (C6) > PFOS in 3M AFFF
  - PFOA minor component in AFFF
  - Ultra-short sulfonates as well as cationic and zwitterionic structures
  - Many PFOS-like structures due to 'messy' chemistry
- Telomer-based AFFF
  - PFOS not present in telomer-based AFFF
  - Fluorotelomer sulfonates (FTSAs) minor component
  - Anionic, cationic and zwitterionic structures







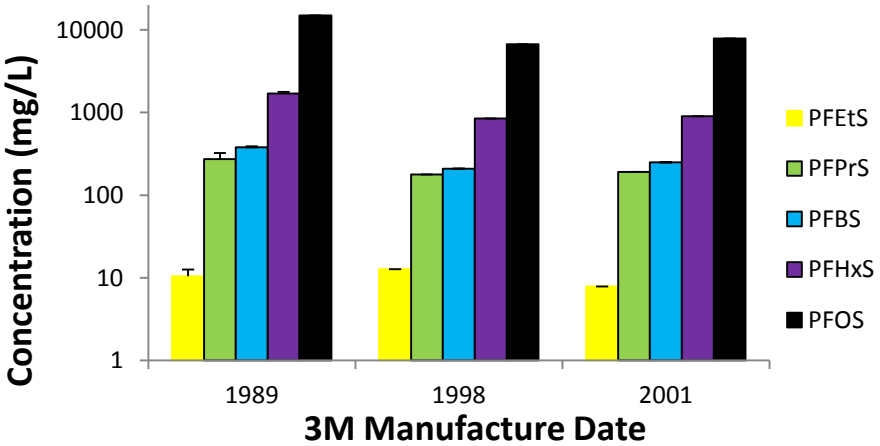
Site Characterization

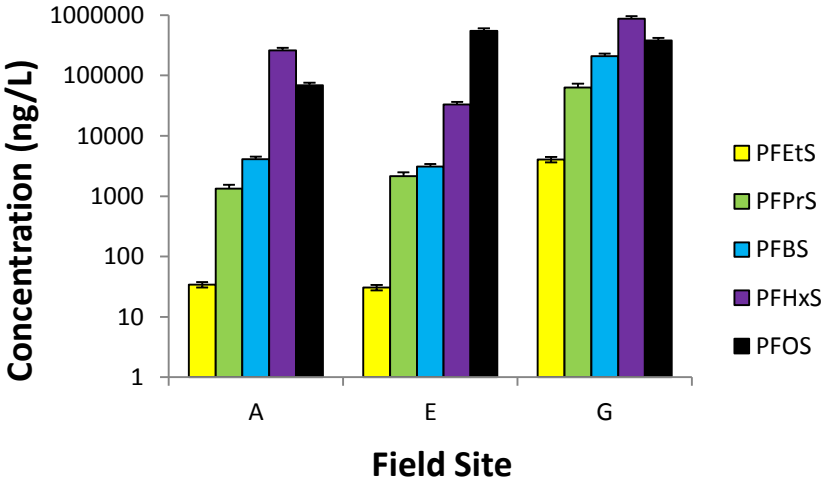
	PFAS	Site 1 (µg/L)	Site 2 (µg/L)
FTSA	6:2 FtTAoS	18	6.9
	6:2 FTSA	230	220
C4-C8 PFSAs	PFBS	65	43
	PFPeS	49	NA
	PFHxS	380	240
	PFHpS	5.9	11
	PFOS	1,000	78
C4-C8 PFCAs	PFBA	28	24
	PFPeA	66	69
	PFHxA	140	130
	PFHpA	26	15
	PFOA	94	51

- Only 5 on UCMR3 (in red) and EPA Method 537, and 6 not in listed in EPA Method 537 (in **purple**)
- PFOS and PFOA >> EPA provisional health advisory levels (0.2 and 0.4 µg/L)
- PFBS and PFBA >> State of MN chronic noncancer health risk limits (7 µg/L)
- World records
  - PFOS = 1 mg/L
  - PFOA = 6.6 mg/L
  - 6:2 FTSA = 14.6 mg/L

Site Characterization

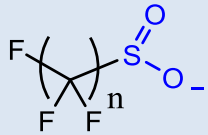
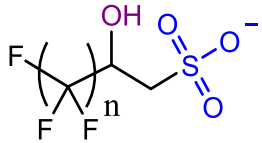
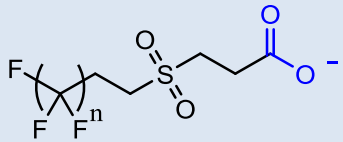
- Ultra-short sulfonates
  - C2 (PFEtS) and C3 (PFPrS) in groundwater and 3M AFFF (source)
  - Concentrations > MN health risk limit (7 µg/L) for PFBS
  - Highly mobile - likely at leading edge of plumes
  - Challenging to remove by GAC





Site Characterization

- Identify indicators of in situ (bio)transformation
- Identify remedial targets
- Prioritize PFASs that pose higher risk

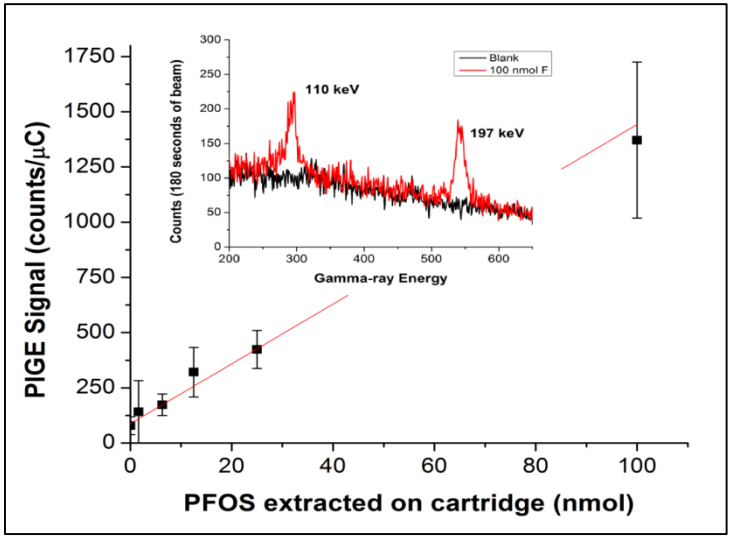
Structure	Frequency of Detection (13 sites)	Charged State Source
	9 sites	**Anion** 3M
	6 sites	**Zwitterion** Ansul
	3 sites	**Anion** Ansul

Significance: Structure Determines Properties, Fate and Transport

- Properties
  - High aqueous solubility and low vapor pressure
  - Low Henry's Law (not removed by air sparging)
- Transport potential
  - Anionic > zwitterionic > cationic
  - Cation exchange may create immobile source zones
- Biodegradation
  - Few data for anions
  - No data for zwitterions and cations
- Toxicity
  - Data for PFOS/PFOA/PFBS
  - No data on zwitterions/cations

Site Characterization

- Total oxidizable precursor (TOP) assay
  - Quantifies precursor (total PFASs) in groundwater, sediment, soil
  - Closes mass balance in microcosm studies
- Total fluorine by PIGE
  - PFAS in groundwater sorbed onto media to create 'target'
  - 10 nA of 3.4 MeV protons for 180 s
  - Quantitative, high-throughput
  - Inexpensive screening tool

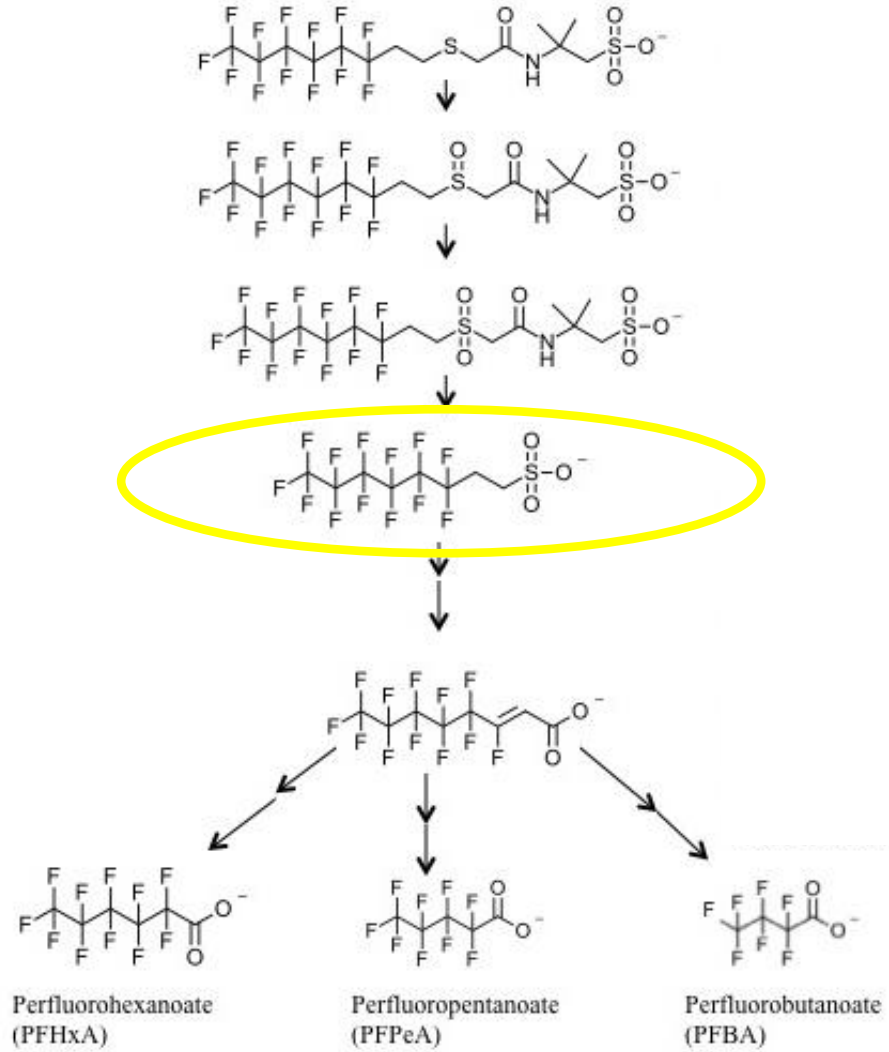


Significance for Site Characterization

- Close the mass balance
- Differentiate AFFF sources from landfill leachate, wastewater effluent, atmospheric deposition
- Develop conceptual site models
- Understand potential human and wildlife exposure
- Design remedial treatment strategies
- Close data gaps on transport, biodegradation and toxicity

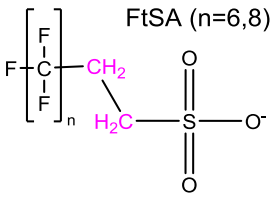
Biotransformation

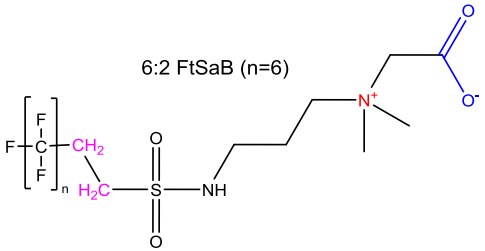
- Telomer sulfonates are biodegradation products
- Telomer sulfonates >> precursors in site groundwater
- Stable under anoxic conditions
- Aerobically degraded to short-chain carboxylates

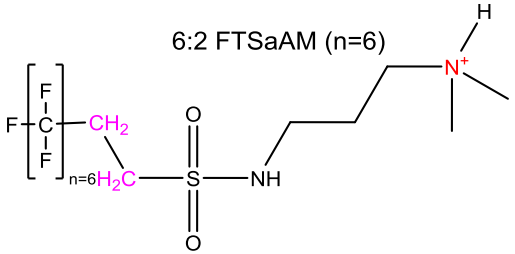


Sorption to Sediment

- Longer chain lengths = greater affinity for sediment
- Sorption of 6:2 FTSA (same C number) < PFOS (more mobile)
- Zwitterionic FTSAB (+/-) sorb less than anions (same chain length)
- Cationic (FtSaAm) sorbs strongly to sediment, mobility low, may form source zones
- pH will impact mobility in subsurface







Next Steps

- ESTCP Project ER-201574-T2 "Catalyzing Rapid Information Transfer Among Key Stakeholders on Per- and Polyfluoroalkyl Substances (PFASs) at Contaminated Military Sites" OSU lead (J. Field)
- SERDP Project ER-2627 "Advancing the Understanding of the Ecological Risk of Per- and Polyfluoroalkyl Substances" Townson University (C. Salice)
- ESTCP Project ER-201633 "Characterization of the Nature and Extent of Per- and Polyfluoroalkyl Substance (PFASs) in Environmental Media at DoD Sites for Informed Decision-Making" Navy lead (J. Kornuc)

Conclusions

- PFOS and PFOA are important but not the only major PFASs at AFFF-contaminated sites
- Telomer-based substances biodegrade to metastable intermediates but not PFOS
- Mobility in groundwater anions > zwitterions > cations
- Anion mobility depends on chain length
- Mobility of many substances influenced by sediment, soil and water geochemistry

Benefits to DoD

- Hundreds of fire/crash testing (mixed waste) sites
- Full characterization of PFAS contamination
  - More accurate conceptual site models
  - Identify remedial approaches that decrease time and cost
  - Optimized monitoring
  - Fingerprinting to differentiate AFFF from other sources
  - Source zone identification
  - Accurate predictions of transport
  - Indicators of in situ biotransformation
- Groundwater contaminated by PFAS used as drinking water source is a potential exposure pathway for humans and wildlife
  - Attention to short-chain PFAS highly mobile, difficult to remove from water

For additional information, please visit
https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Emerging-Issues/ER-2128

Speaker Contact Information

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Q&A Session 1

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1,4-Dioxane: Remediation Solutions

Pat Evans, Ph.D.
CDM Smith

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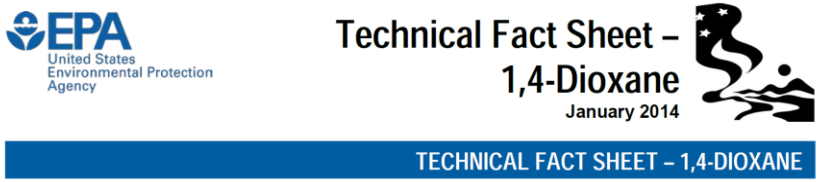
Dioxane Agenda

- What is it?
- Where is it?
- Why do we care?
- Technical challenges
- Research snapshots
- Slow release chemical o
- Is the sky falling?

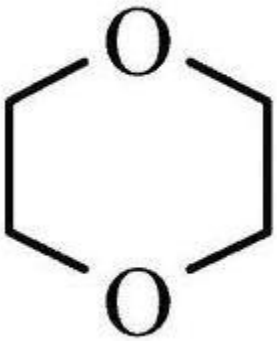
Chicken Little courtesy of H. Penny, Ph.D. and www.know-bull.com

What Is It?

- Solvent and solvent stabilizer
- Boiling point
  - 101.1°C
- Vapor pressure
  - 38.1 mm Hg @ 25°C
- Log KOW
  - - 0.27
- Water solubility
  - Miscible
- Henry's Constant
  - 4.8×10^{-6} atm m^3 mol^{-1}

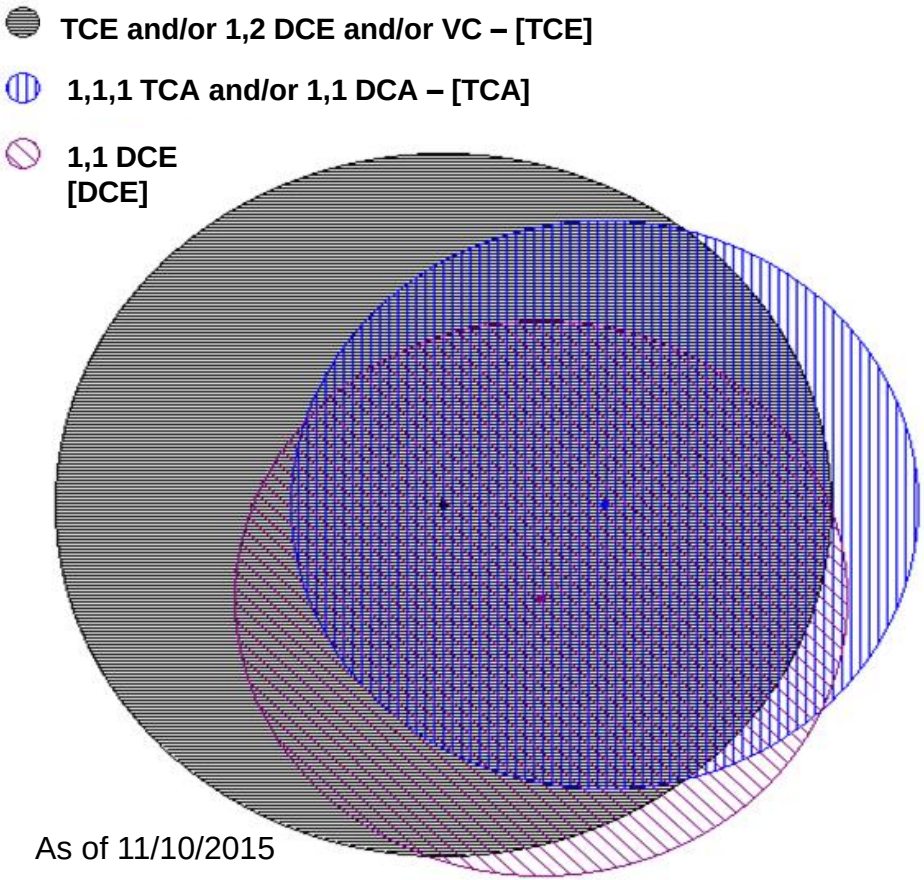


USEPA. 2014. Technical Fact Sheet – 1,4-Dioxane. EPA 505-F-14-011



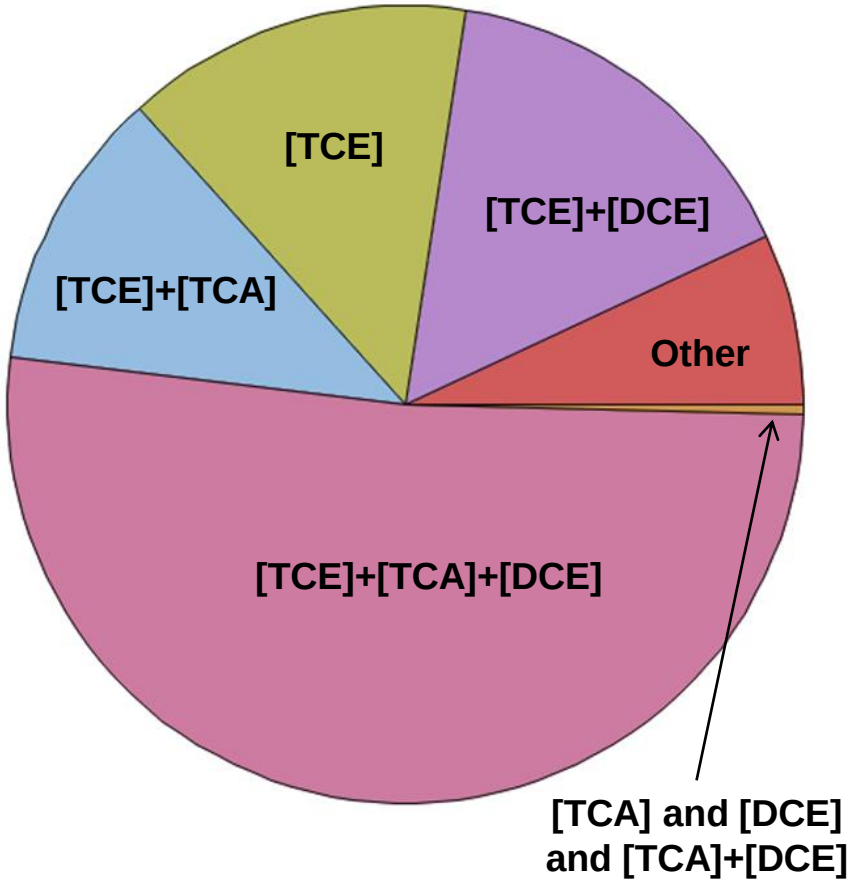
Dioxane and Solvents Co-Occur

cVOC co-Occurrence at USAF Sites



As of 11/10/2015

Dioxane Detections at USAF Sites (n = 1,663 wells)



Slide courtesy of Hunter Anderson

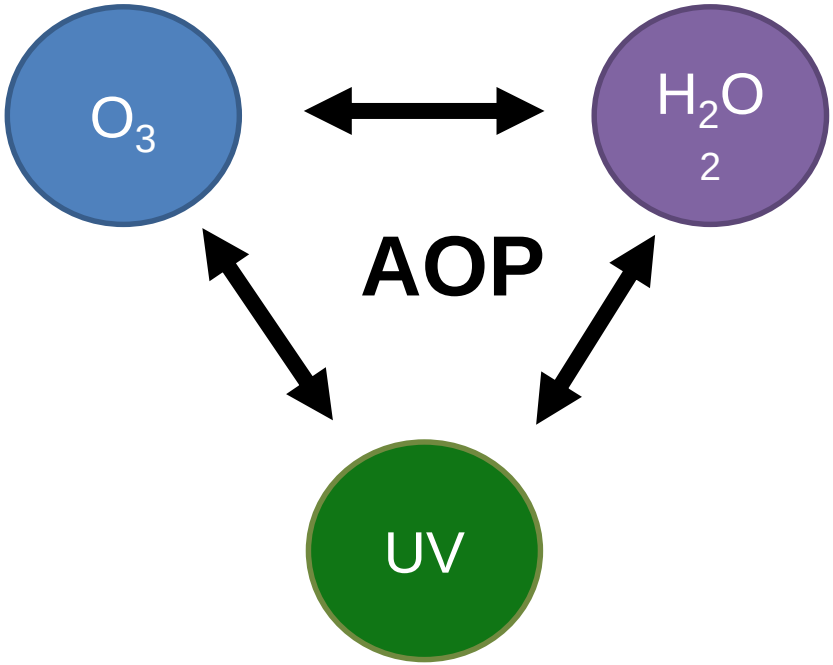
Why Do We Care?

- EPA probable carcinogen (Group B2)
- Carcinogen slope factor = 0.1 mg/kg/d
- 10^{-6} cancer risk → 0.35 ppb
- No EPA MCL but on UCMR3
- Guidelines in states vary

USEPA. 2014. Technical Fact Sheet – 1,4-Dioxane. EPA 505-F-14-011

Technical Challenges

- You can't air strip it
- You can't adsorb it very well
- Advanced oxidation is expensive
  - UV/H_2O_2
  - O_3/H_2O_2
  - $HOCl/H_2O_2$
  - UV/TiO_2
- What can I do?



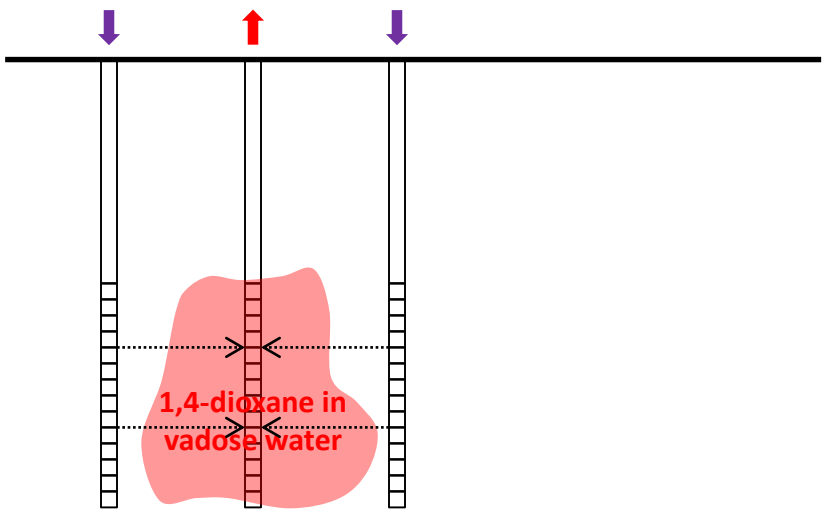
Extreme SVE (XSVE) for Soil Treatment

ESTCP Project ER-201326

- Objective
  - Demonstrate XSVE to dry soil and overcome Henry's Law limitations
- Results
  - Estimated dioxane mass removed from soil
- Impact
  - Vadose-zone sources of groundwater contamination can be mitigated

XSVE Focus

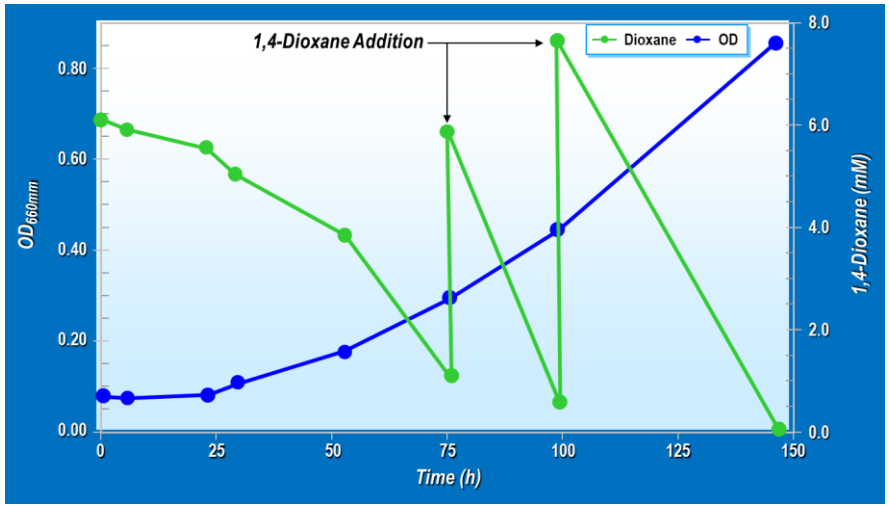
Removal of both vadose water and 1,4-dioxane

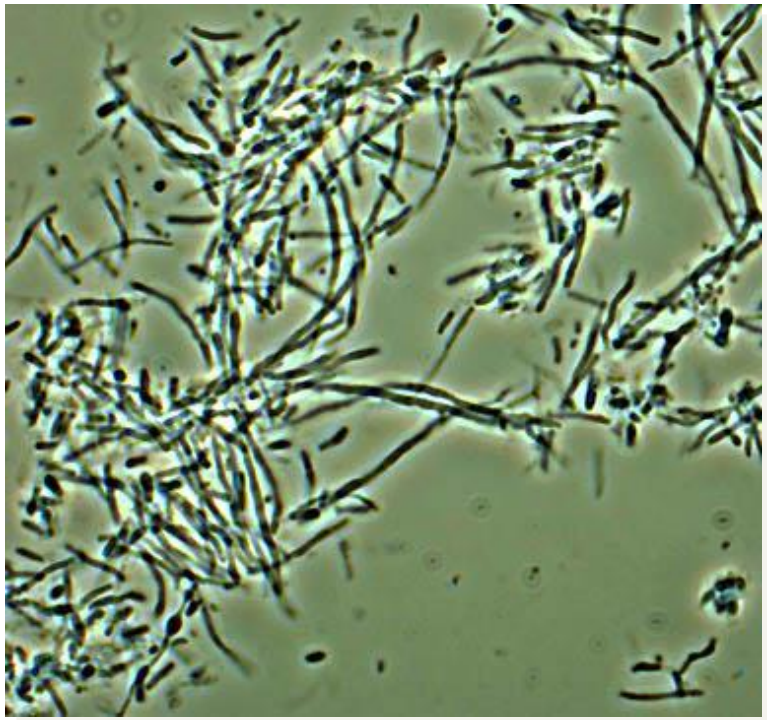


Slide courtesy of Rob Hinchee

Can Dioxane Be Biodegraded?

- *Pseudonocardia dioxanivorans* CB1190, the first bacterium capable of dioxane metabolism



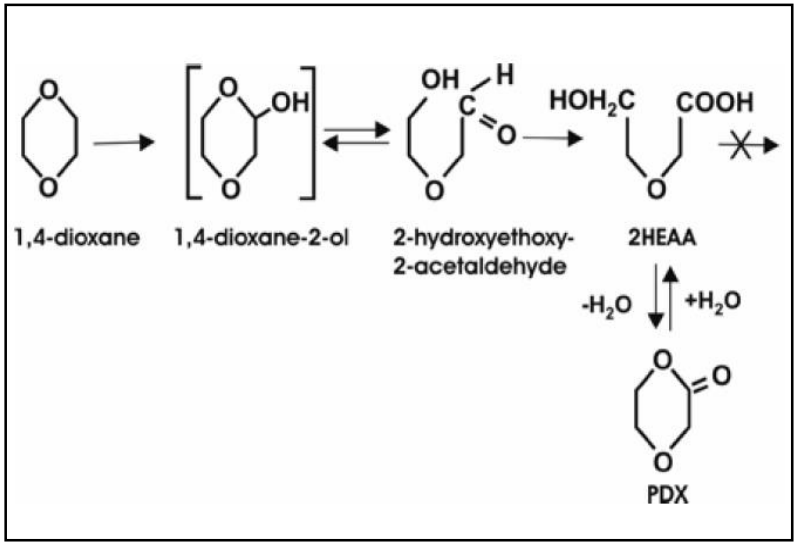


- Parales et al. 1994. Appl. Environ. Microbiol. 60:4527-4530
- J. Adamus et al., 1995. US Patent 5,474,934

Bacteria, Genes and Pathways Identified

SERDP Projects ER-1417 and ER-1422

- Objective
  - To identify organisms, enzymes and pathways for aerobic biodegradation of dioxane
- Results
  - Recalcitrant under many conditions. Activity was common among monooxygenase-bacteria
- Impact
  - Natural attenuation may be slow. Cometabolism possible. Genetic tools developed

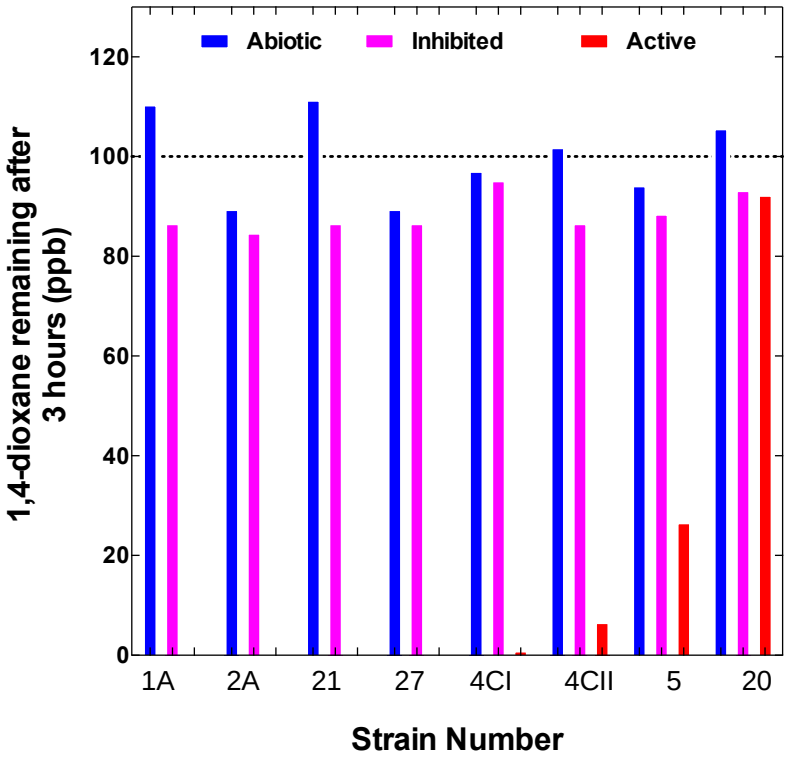


Proposed pathway of 1,4-dioxane degradation by strain ENV478 after growth on propane or tetrahydrofuran

Slide courtesy of Paul Hatzinger, Rob Steffan, Shaily Mahendra and Lisa Alvarez-Cohen

Branched Hydrocarbons for Cometabolism
SERDP Project ER-2303

- Objective
  - Evaluate isobutane- and isobutene-oxidizing bacteria for cometabolism
- Results
  - Both bacteria tested degrade dioxane; chlorinated co-contaminant degradation more variable
- Impact
  - Potentially new options for dioxane cometabolism

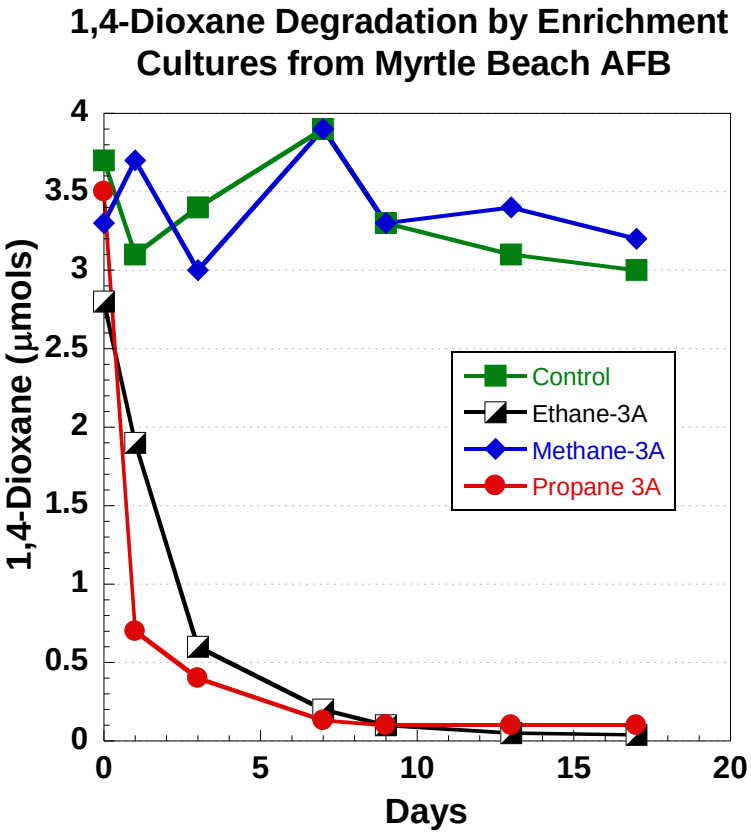


Slide courtesy of Michael Hyman

Dioxane Co-Metabolites Are Not Equal

SERDP Project ER-2306

- Objective
  - Evaluate potential for naturally occurring and enhanced 1,4-dioxane co-metabolism
- Results
  - Ethane and propane were effective co-metabolites at multiple sites. Methane was not effective at any site
- Impact
  - Potential for co-metabolism by daughter products (e.g., ethane) and/or enhancing process with propane or ethane

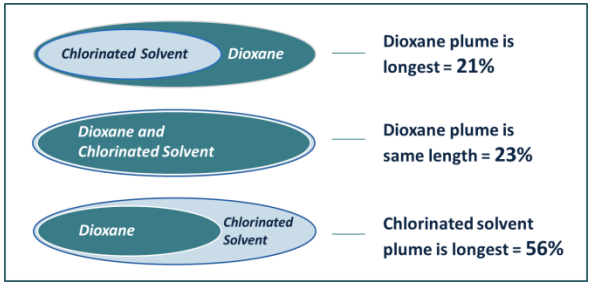


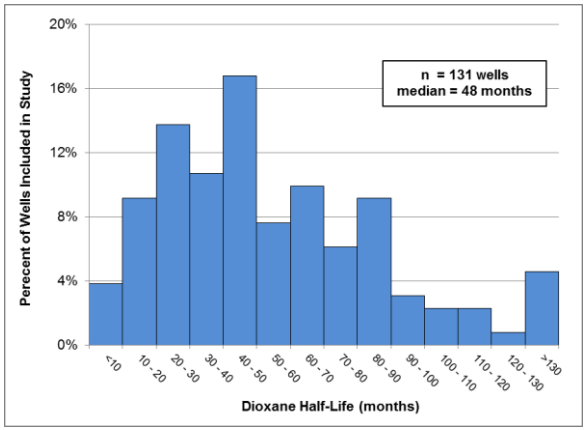
Slide courtesy of Charles Schaefer and Paul Hatzinger

Management Strategies for Dioxane

SERDP Project ER-2307

- Objective
  - Evaluate factors that control plume size and attenuation
- Results
  - MNA occurs with reasonable half-lives. Back diffusion can be important
- Impact
  - Dioxane sites may be more manageable than previously thought





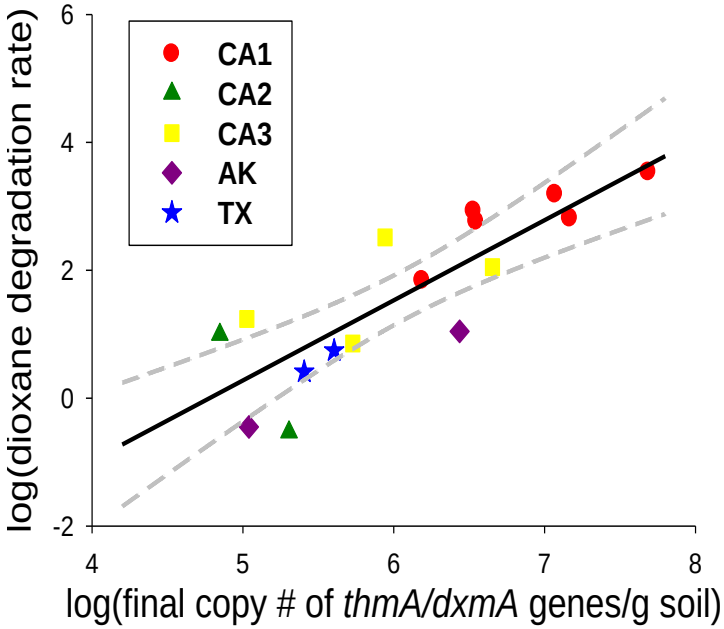
- Adamson et al., *ES&T Letters*, 2014
- Adamson et al., *ES&T*, 2015

Slide courtesy of Dave Adamson

Genetic Probes for Assessing MNA

SERDP Project ER-2301

- Objective
  - Develop functional gene probes to quantify degradation capacity
- Results
  - Biomarkers for monooxygenase genes correlated to degradation rates
- Impact
  - Genetic techniques available that can be used to predict MNA potential



- Li, M., J. Mathieu, et al. (2013). ES&T Letters 1(1): 122-127
- Li, M., J. Mathieu, et al. (2013). ES&T 47(17): 9950-9958

Slide courtesy of Pedro Alvarez

CSIA for MNA Evaluations at Low Concentration SERDP Project ER-2535

- Objective
  - Develop method for reliable characterization of low-ppb dioxane plumes
- Results
  - Pre-concentration onto resin is used to achieve detection limits
- Impact
  - Potentially valuable tool for investigating MNA and cometabolic biodegradation

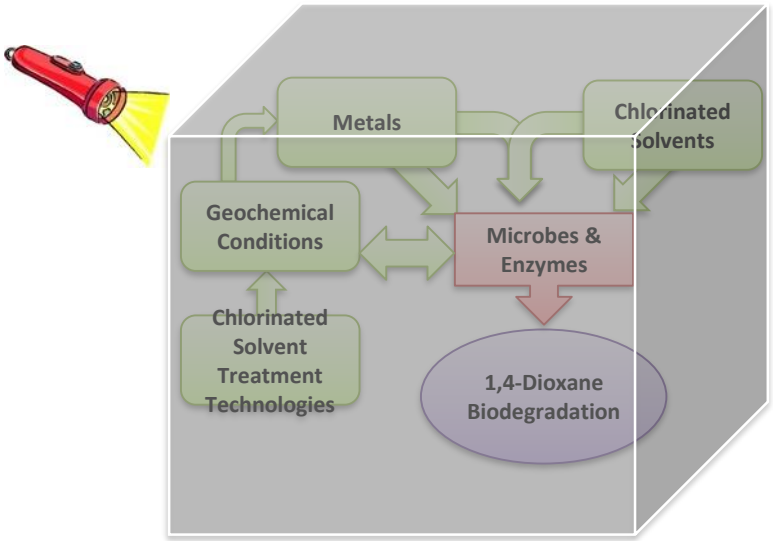
Hydrophobic resin used to concentrate dioxane

Slide courtesy of Peter Bennett

Effects of Metals and Chlorinated Solvents

SERDP Project ER-2300

- Objective
  - Quantify the effects of chlorinated ethenes and trace metals on dioxane biodegradation
- Results
  - Biodegradation inhibited by solvents and metals in a dose-response manner
- Impact
  - Better prediction of biodegradation and MNA potential



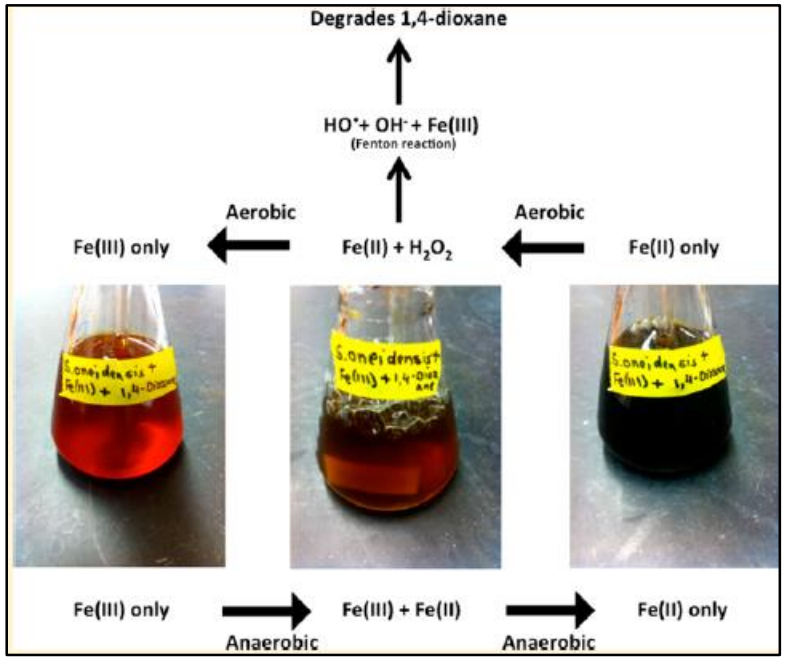
- Pornwongthong et al. (2014). Appl. Biochem. Biotechnol 173 (1): 291-306
- Zhang et al. (2015). RemTEC, Denver, CO

Slide courtesy of Shaily Mahendra

Microbially Driven Fenton Reaction

SERDP Project ER-2305

- Objective
  - Explore use of iron-reducing bacteria for generation of dioxane-degrading hydroxyl radicals
- Results
  - Cycling anaerobic and aerobic conditions with *Shewanella oneidensis* promoted dioxane destruction
- Impact
  - Potential MNA strategy for dioxane at aerobic/anerobic plume fringes



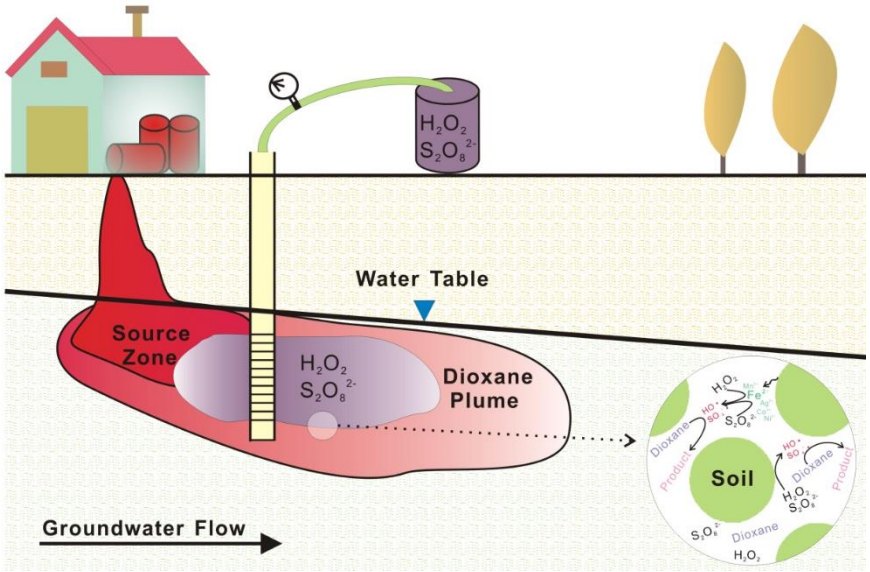
Sekar and DiChristina. 2014. Environ. Sci. Technol. 48:12858-12867

Slide courtesy of Tom DiChristina

Facilitated-Transport Enabled ISCO

SERDP Project ER-2302

- Objective
  - Enhance oxidant solubility, stability, and transport
- Results
  - Cyclodextrin+ozone, peroxone+persulfate, and persulfate+ZVI enhance ISCO performance
- Impact
  - Innovative reagent combinations offer new remediation opportunities



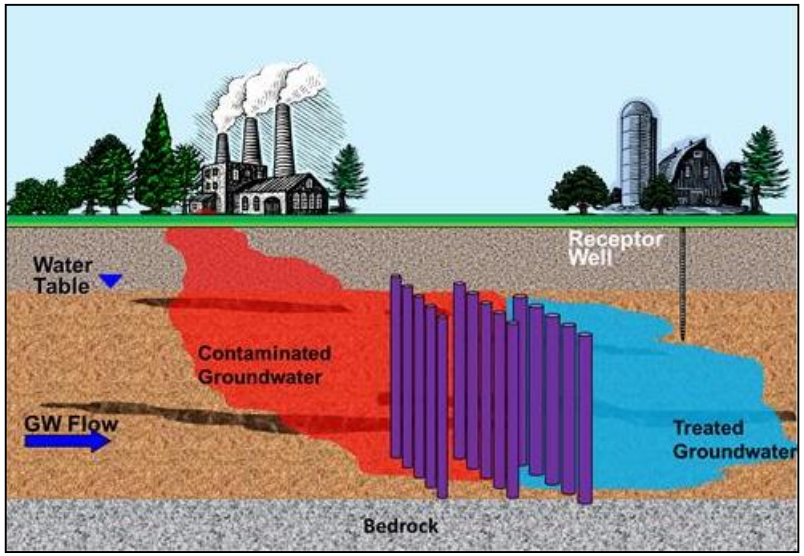
- H. Zhong et al. 2015 *Water Research.* 83: 104-111
- D. Eberle et al. 2015 *Chemosphere*. 144: 728–735
- A. Dettmer et al. *Chemosphere*. In Review

Slide courtesy of Kenneth C. Carroll

Slow-Release Chemical Oxidants

ESTCP Project ER-201324

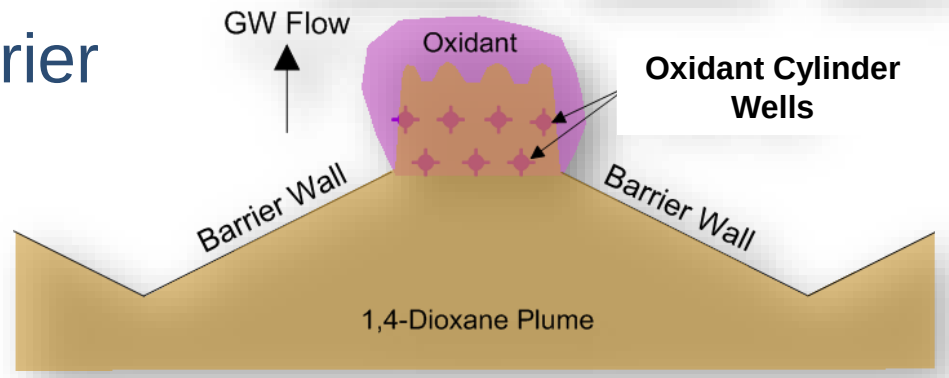
- Objective
  - Demonstrate slow-release oxidants for passive in situ treatment and develop design tool
- Results
  - Permanganate and unactivated persulfate oxidize dioxane and slow-release oxidants are sustainable
- Impact
  - Innovative delivery vehicle for sustained remediation of dioxane/chlorinated solvent plumes



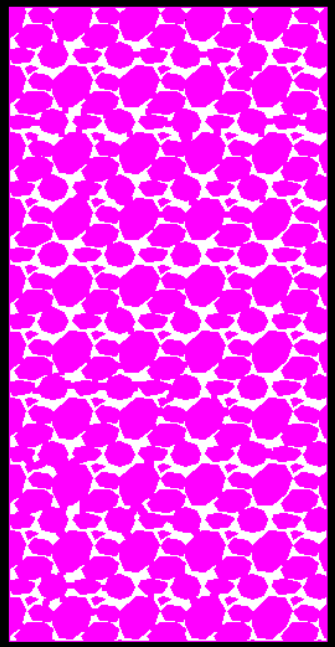
Slide courtesy of Pat Evans, Pamela Dugan and Michelle Crimi

Slow Release Chemical Oxidants

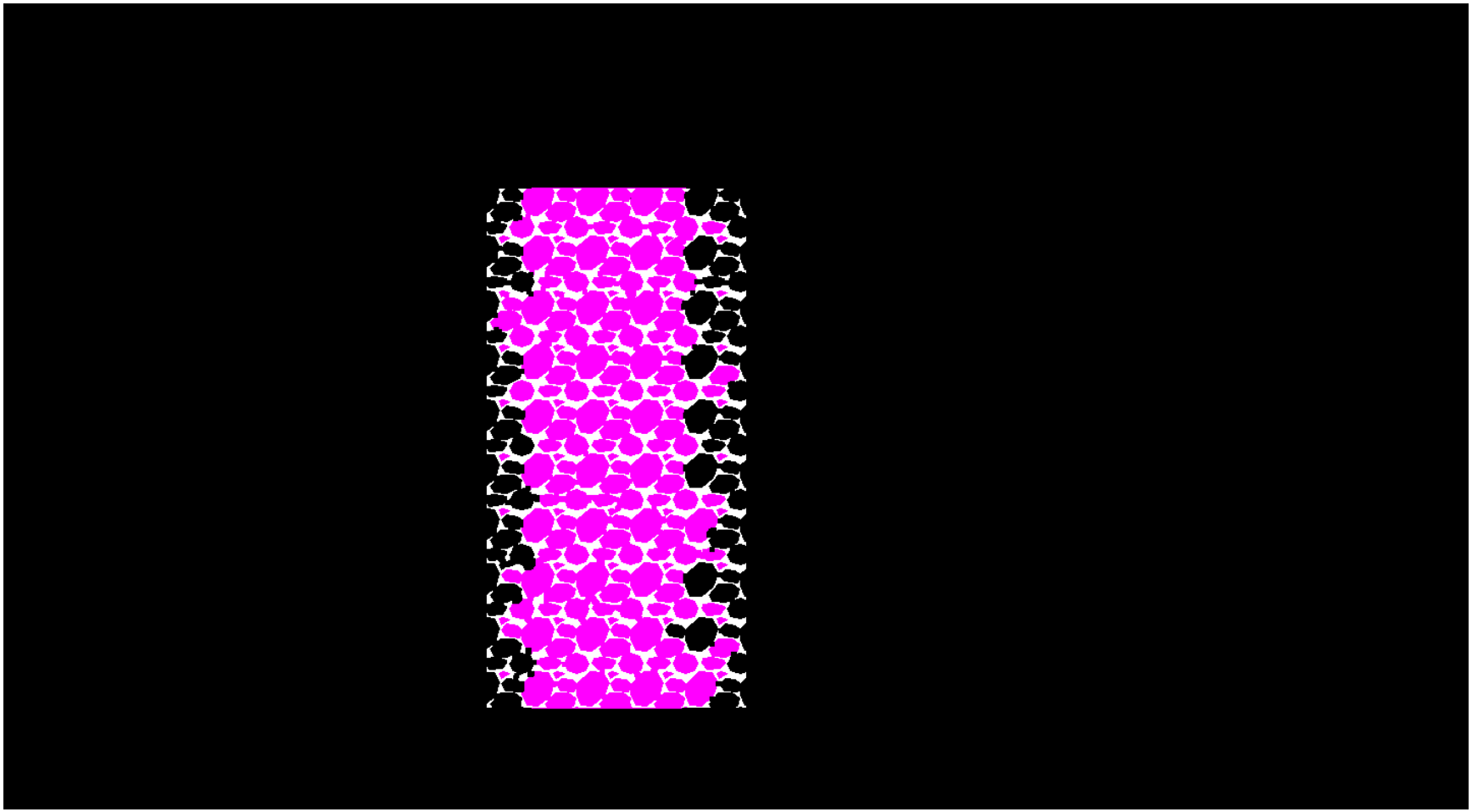
- Formed in a wax cylinder
  - 1.35 or 2.5” diameter
  - 18” length
- Oxidants
  - Permanganate
  - *Unactivated* persulfate
- Possible configurations
  - Permeable reactive barrier (PRB)
  - Funnel and gate (F&G)
  - Grid



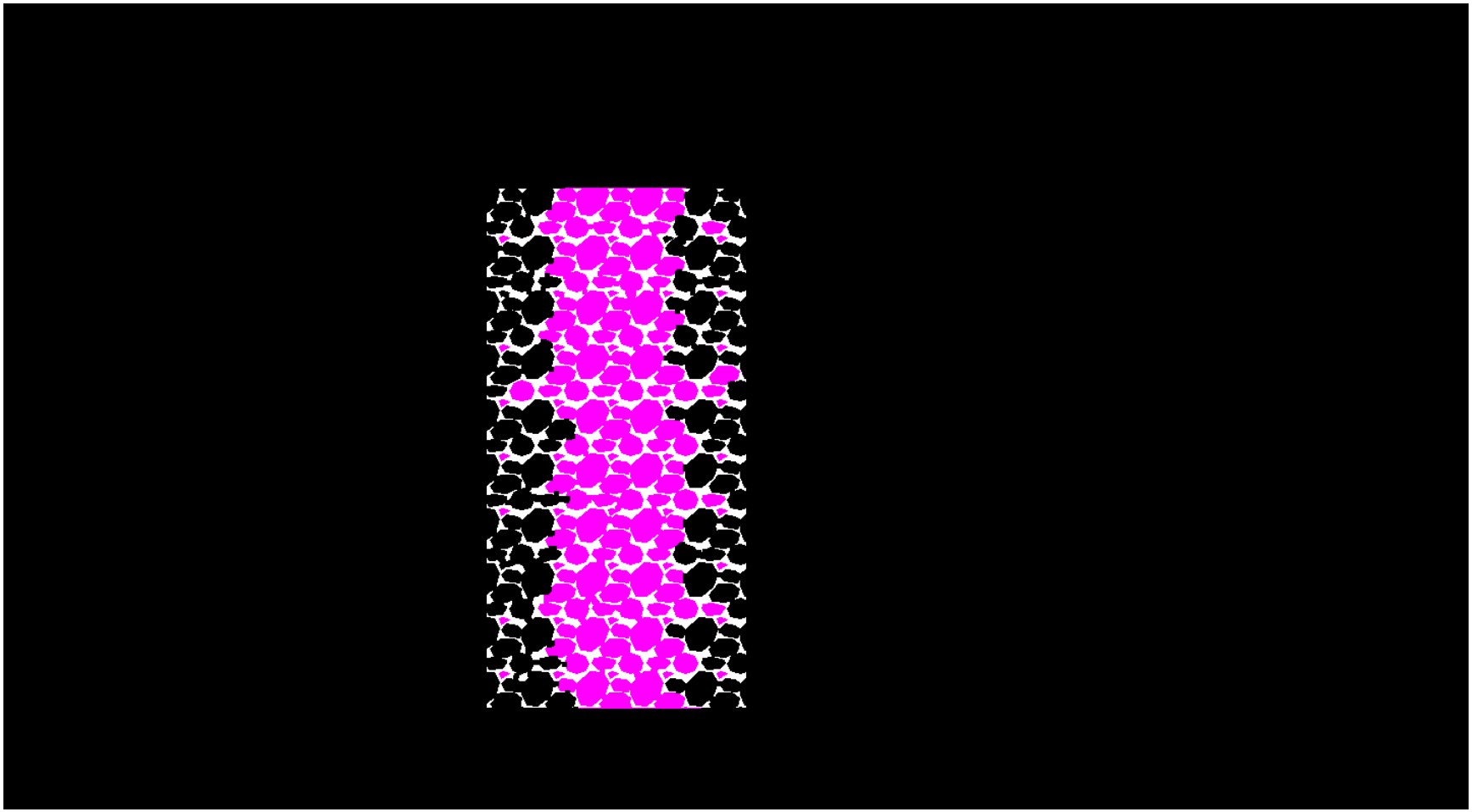
Permanganate Cylinder Release from Wax



Permanganate Cylinder Release from Wax



Permanganate Cylinder Release from Wax



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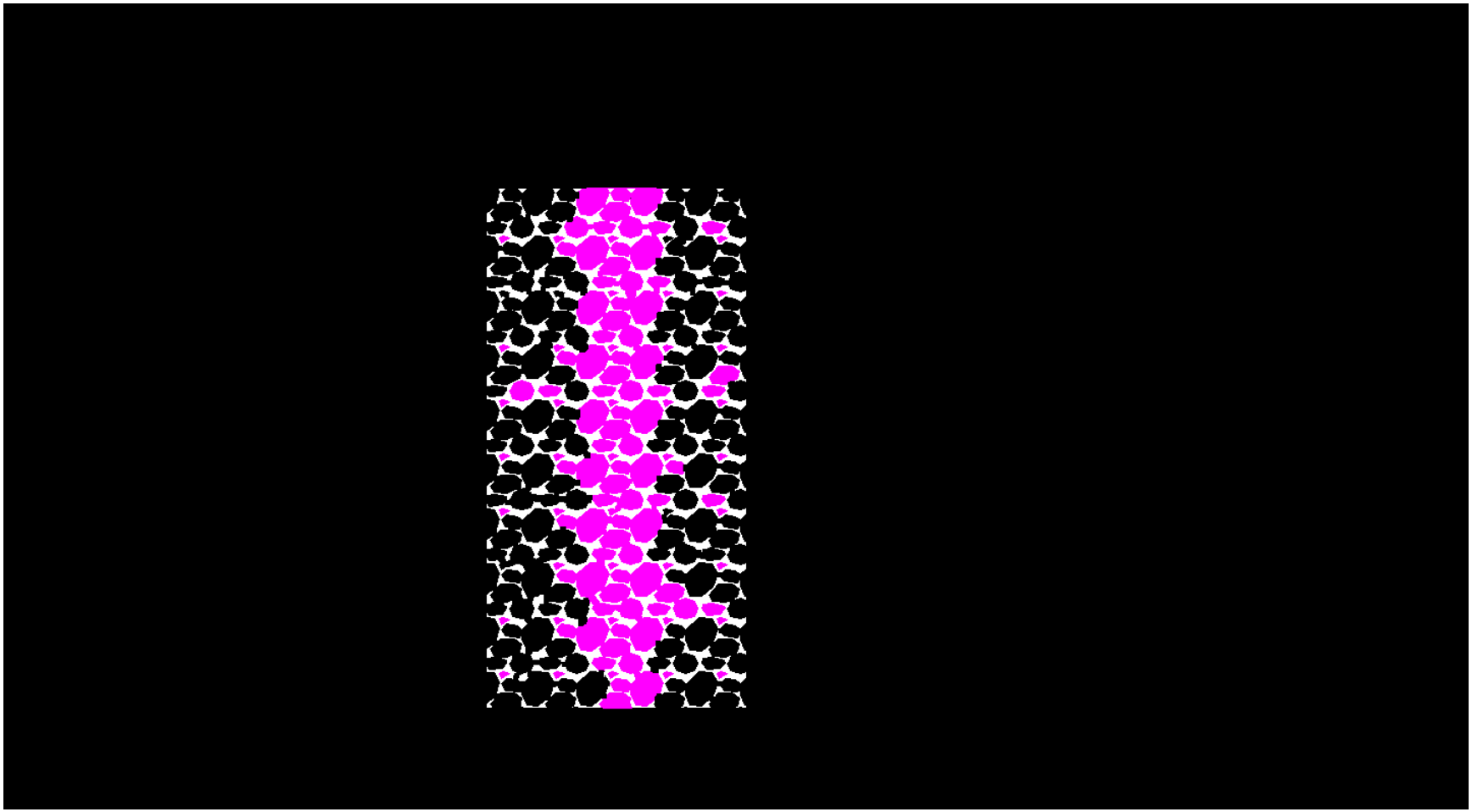

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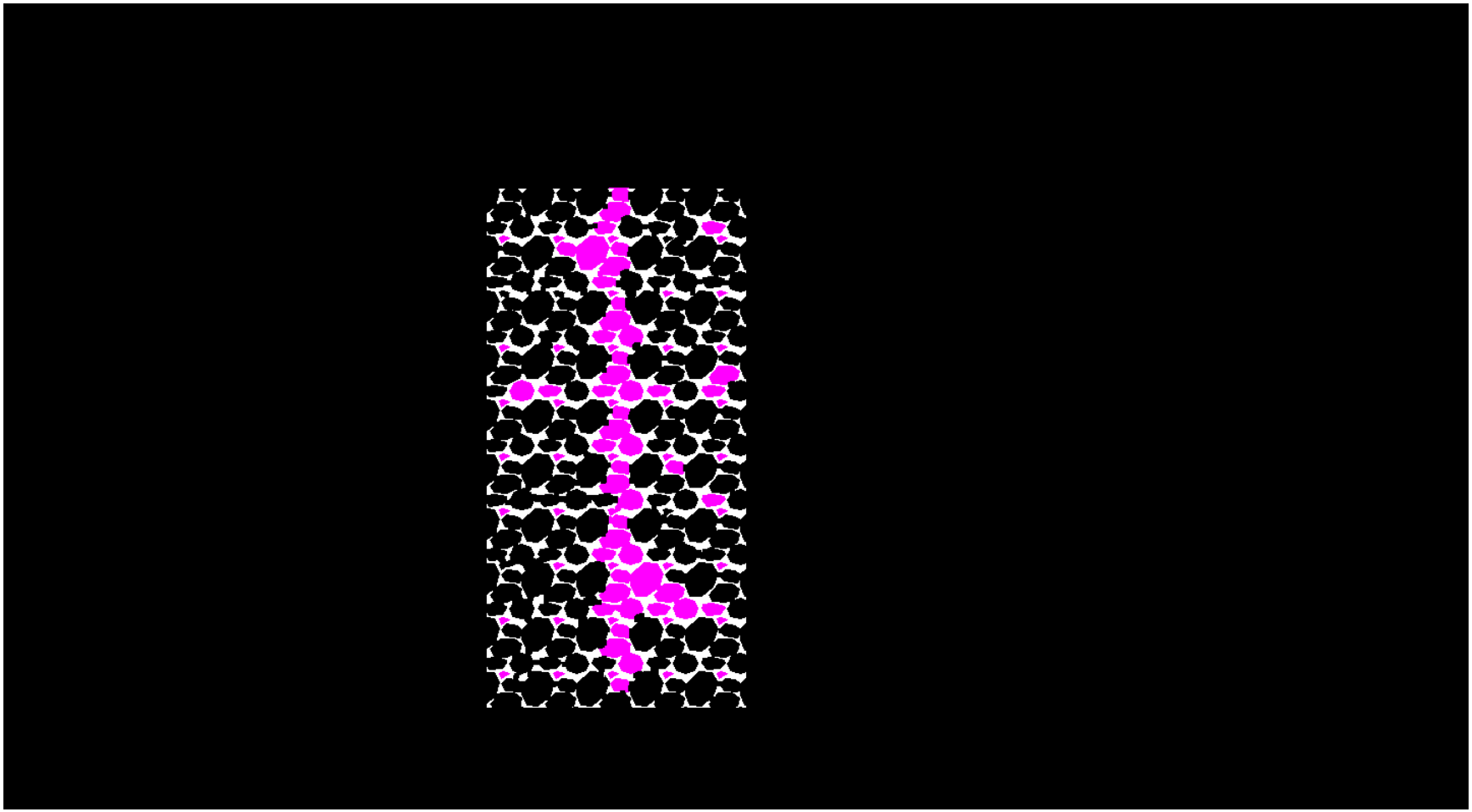
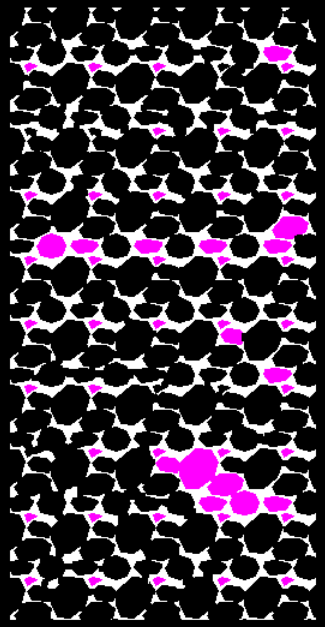
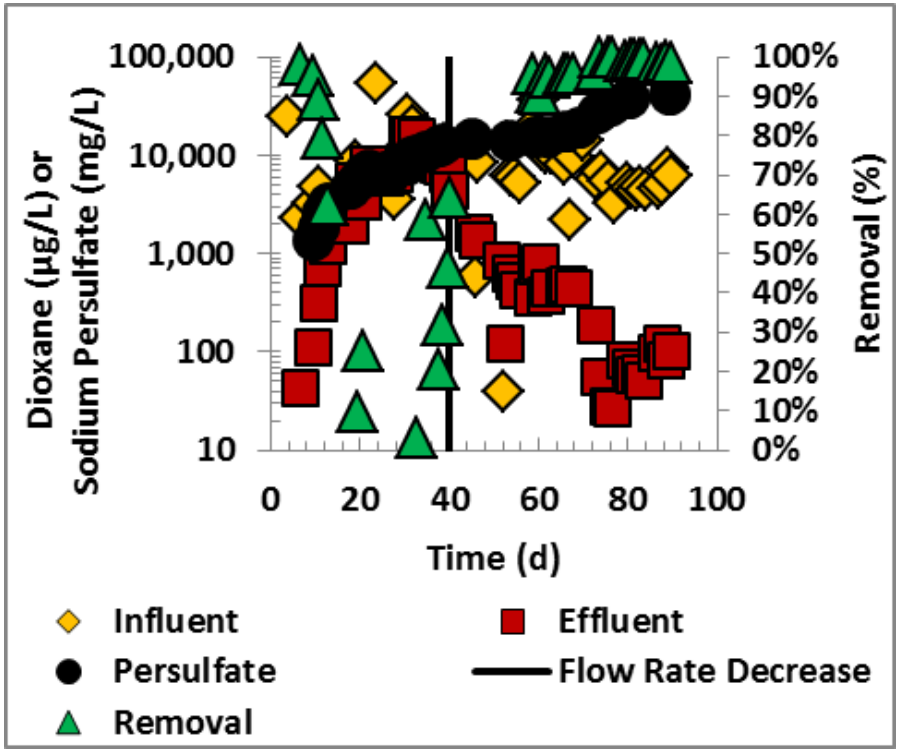
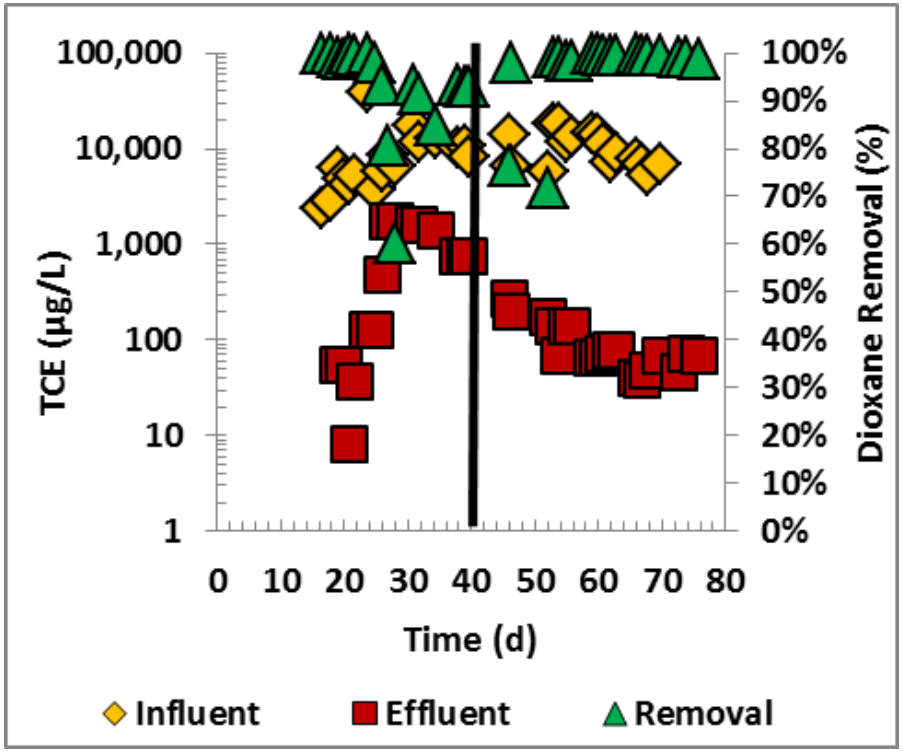


Permanganate Cylinder Release from Wax



Dioxane and TCE Removal Using Persulfate





The Sky Is Not Falling

- Dioxane is more widespread than thought
  - If you haven't analyzed for it, you should
- But, many tools are available or being developed
  - Site characterization tools
  - Remediation technologies
  - Remediation/MNA monitoring and optimization
- Alternatives to pump and treat exist
  - XSVE
  - Cometabolic biodegradation
  - ISCO including slow-release chemical oxidants
  - MNA

For additional information, please visit
www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Emerging-Issues/ER-201324

Speaker Contact Information

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Q&A Session 2

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The next webinar is on December 17, 2015

"Watershed Assessment and Stormwater Management Optimization Tools"

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Please take a moment to complete the survey that will pop up on your screen when the webinar ends

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