Thank you for signing in early

The webinar will begin promptly at
12:00 pm ET, 9:00 am PT

SERDP
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SERDP and ESTCP Webinar Series

The webinar will begin promptly at 12:00 pm ET, 9:00 am PT

- You have two options for accessing the webinar
  1. Listen to the broadcast audio if your computer is equipped with speakers
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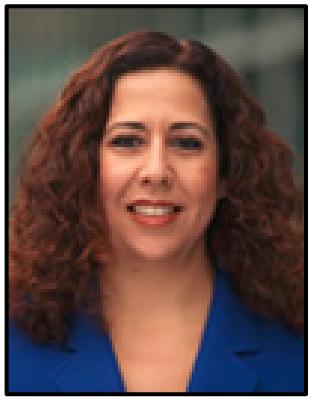
     Required conference ID: 6102000
- For any question or issues, please email serdp-estcp@noblis.org or call 571-372-6565

1,4-Dioxane Impacts and Environmental Cleanup Technologies at DoD Contaminated Sites

April 6, 2017

SERDP DOD • EPA • DOE | ESTCP

Welcome and Introductions

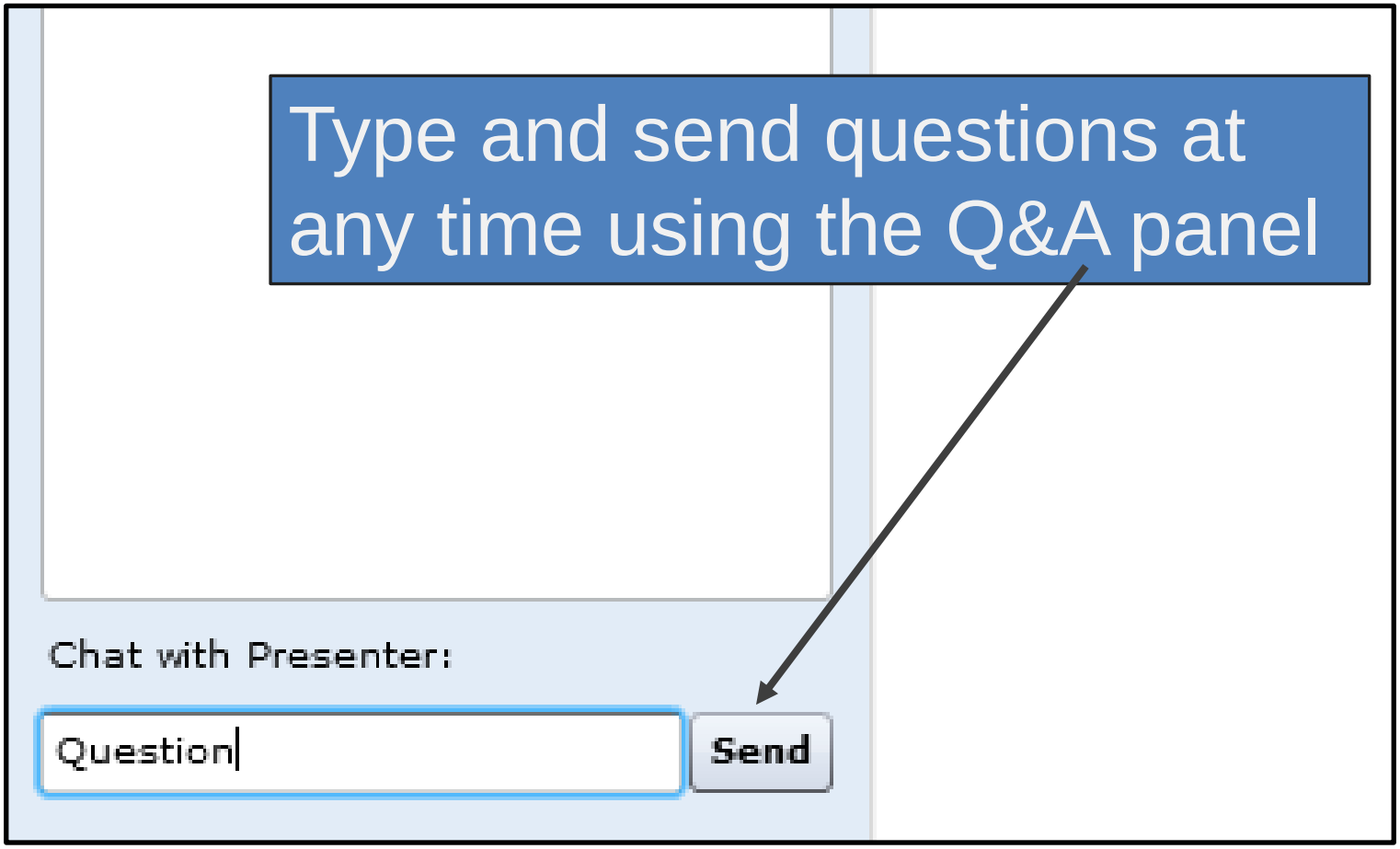


Rula A. Deeb, Ph.D.
Webinar Facilitator

Webinar Agenda

- **Webinar Logistics** (5 minutes)
  Dr. Rula A. Deeb, Geosyntec Consultants
- **Overview of SERDP and ESTCP** (5 minutes)
  Dr. Andrea Leeson, SERDP and ESTCP
- **An Overview of the U.S. Air Force's Programmatic Approach to Address the 1,4-Dioxane Problem** (10 minutes + Q&A)
  Dr. Hunter Anderson, U.S. Air Force Civil Engineer Center
- **Biodegradation of 1,4-Dioxane: Co-Contaminant Effects and Monitoring Tools** (20 minutes + Q&A)
  Dr. Shaily Mahendra, University of California, Los Angeles
- **1,4-Dioxane Vadose Remediation by Thermal Soil Vapor Extraction** (20 minutes + Q&A)
  Dr. Robert Hinchee, Integrated Science and Technology
- **Final Q&A Session**

How to Ask Questions



In Case of Technical Difficulties

- Delays in the broadcast audio
  - Click the mute/connect button
  - Wait 3-5 seconds
  - Click the mute/connect button again
  - If delays continue, call into the conference line
    - Call into the conference line: 303-248-0285
    - Required conference ID: 6102000
- Submit a question using the chat box

SERDP and ESTCP Overview

Andrea Leeson, Ph.D.
SERDP and ESTCP

SERDP

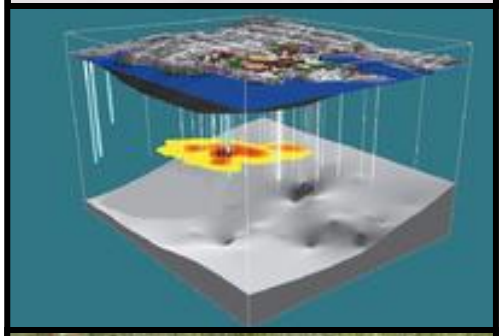
- Strategic Environmental Research and Development Program
- Established by Congress in FY 1991
  - DoD, DOE and EPA partnership
- SERDP is a requirements driven program which identifies high-priority environmental science and technology investment opportunities that address DoD requirements
  - Advanced 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

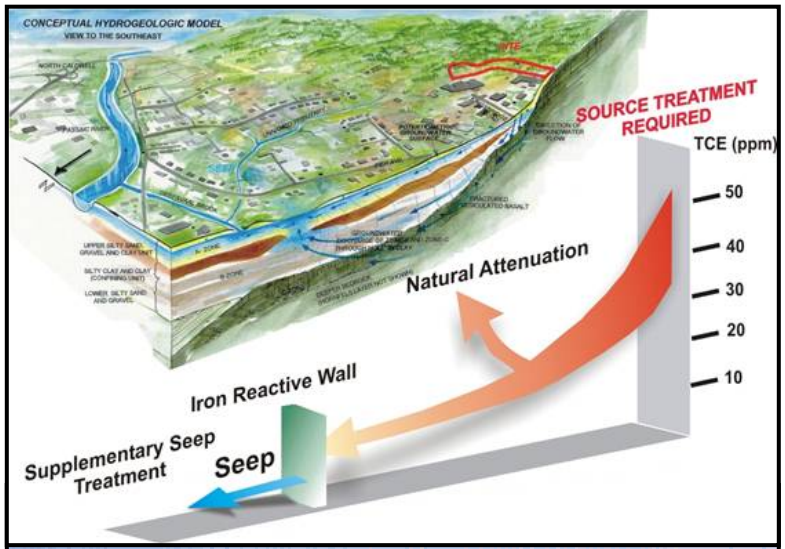
Program Areas

1. Energy and Water
2. Environmental Restoration
3. Munitions Response
4. Resource Conservation and Resiliency
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	Topic
April 20, 2017	Solutions for Installations' Participation in Energy Markets
May 4, 2017	Novel Coatings Systems for Use as High Performance Chemical Resistant Power Topcoats
May 18, 2017	High-Resolution Site Characterization at Chlorinated Solvents Sites
June 1, 2017	Tools for Risk-Based Remediation of Unexploded Ordnance
July 20, 2017	Management of Energetic and Propellant Material Releases on Testing and Training Ranges

For upcoming webinars, please visit

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

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SERDP • ESTCP SYMPOSIUM

2017 | Enhancing DoD's Mission Effectiveness

A three-day symposium showcasing the latest technologies that enhance DoD's mission through improved environmental and energy performance

- November 28 - November 30, 2017
- Washington Hilton Hotel
  1919 Connecticut Avenue, NW
  Washington, DC 20009
- ***Registration is open***

An Overview of the U.S. Air Force's Programmatic Approach to Address the 1,4-Dioxane Problem

Dr. Hunter Anderson
Air Force Civil Engineer Center

SERDP DOD • EPA • DOE | ESTCP

Agenda

- Regulatory overview
- Occurrence
- Sources
- AFCEC's data
- AFCEC's programmatic approach

Regulatory Overview

- Health effects
  - Probable human carcinogen (IARC, 1999; USEPA, 2010)
  - Non-cancer effects on liver/kidney (ATSDR, 2012; USEPA, 2010)
- Regulation
  - No federal MCL
  - Tier I tox values – USEPA/IRIS
  - Twelve states with promulgated water standards
  - Many other states with “guidance” values

1,4-Dioxane Regulatory Status

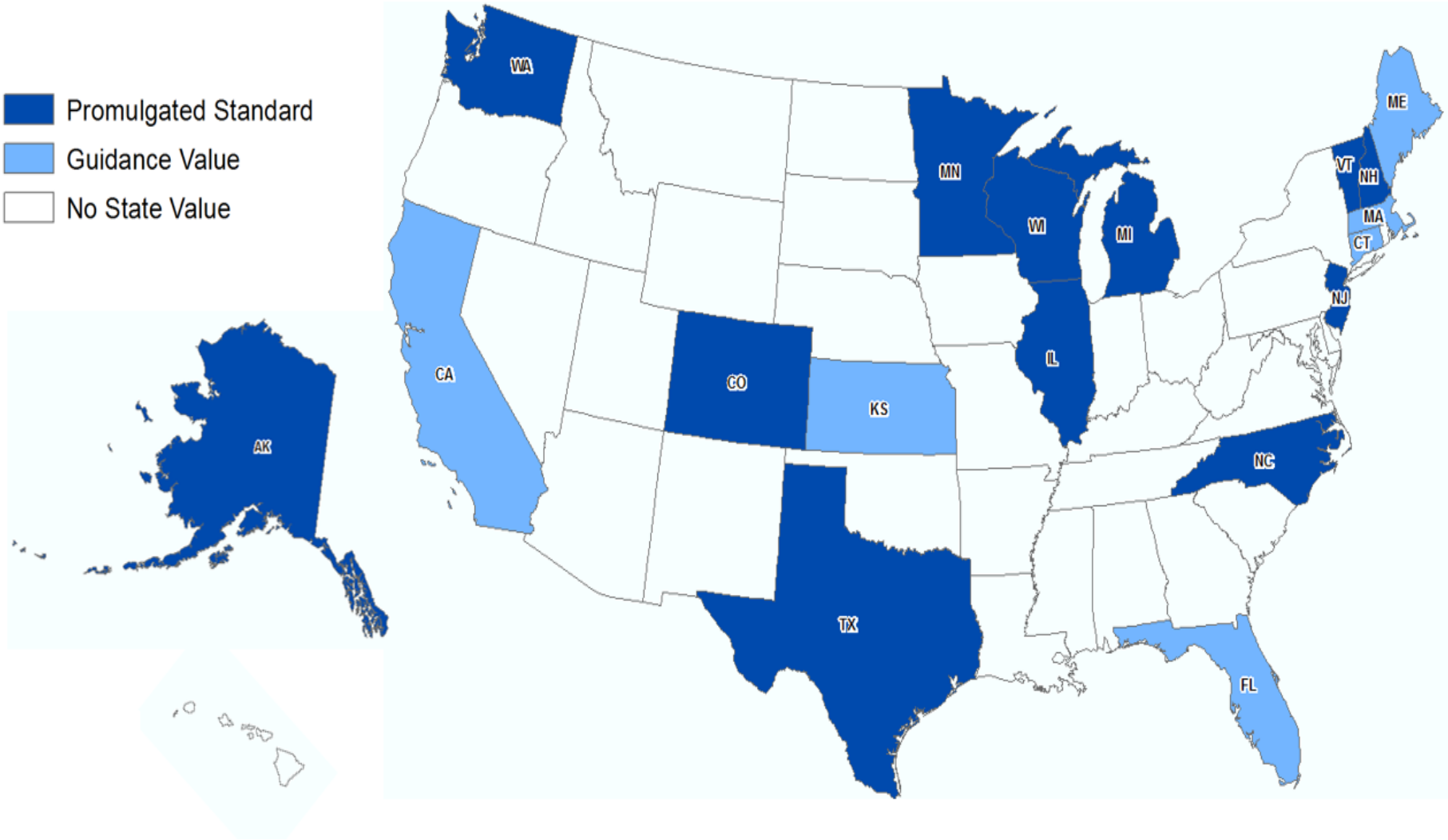
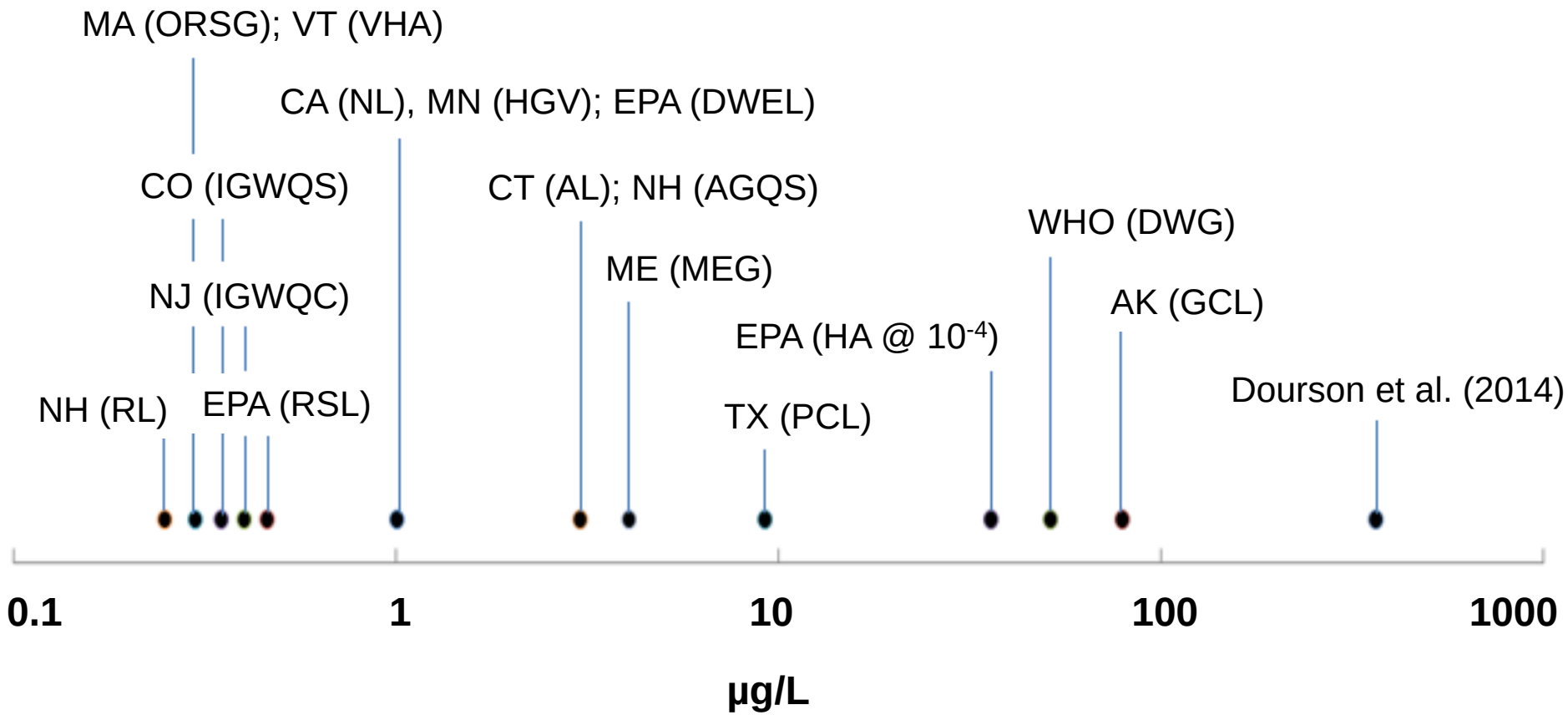
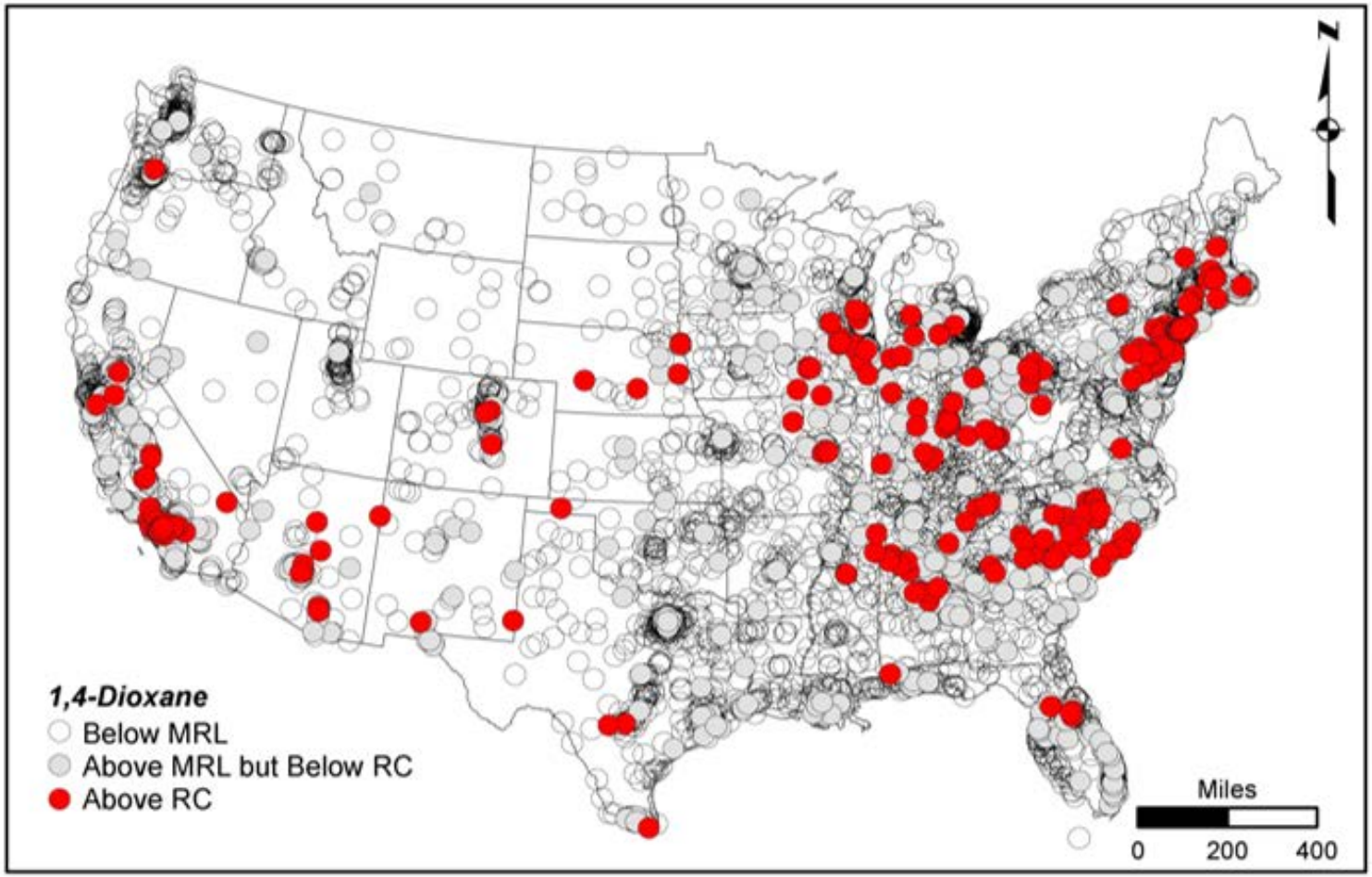


Figure courtesy of Integral Consulting

Sample of Risk-Based Values



Occurrence: UCMR3 Results

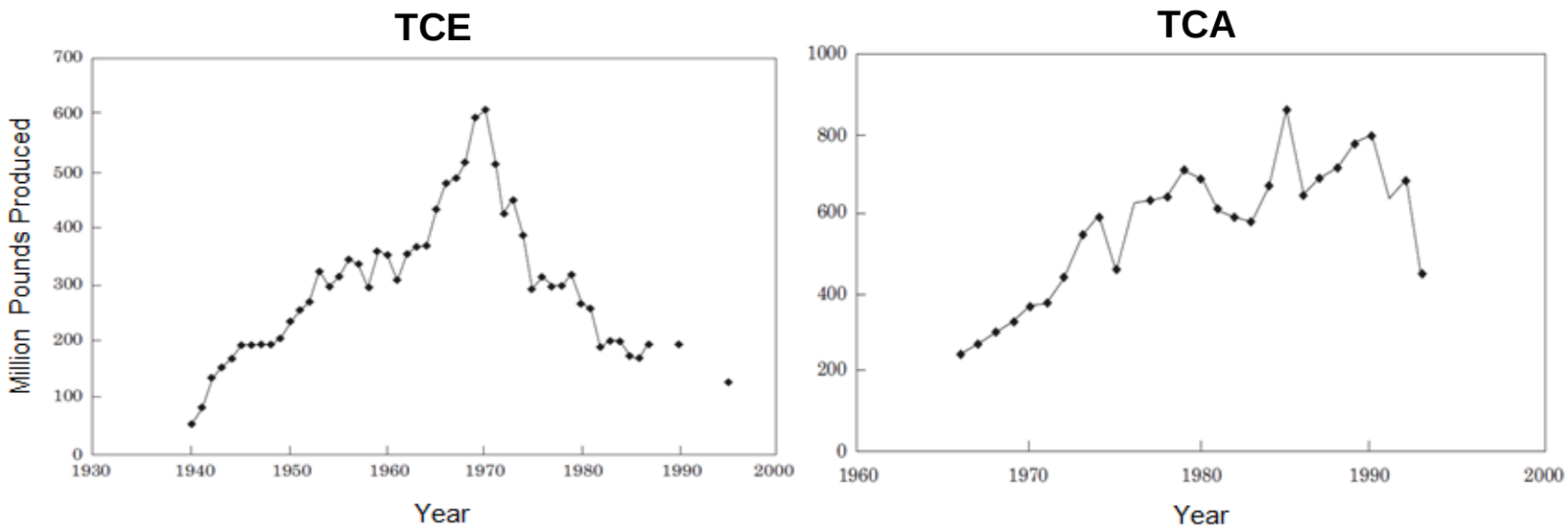


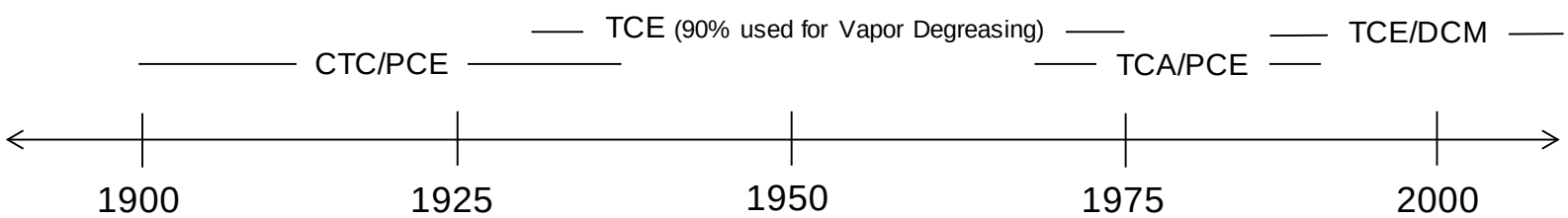
6.9% of PWSs > 0.35 µg/L; Adamson et al., STOTEN, in press

Sources

- Reagent grade solvent for specialized analytics
- Byproduct of surfactant production (ethoxylation)
  - Chemical food additives
  - Paints, detergents, coolants, de-icers
  - Black and Havery (2001)
    - Up to 279 mg/kg in cosmetic finished products
    - >85 mg/kg in children's shampoo
- Chlorinated solvent stabilizer
  - Majority of use throughout 20th century

Chlorinated Solvent Usage

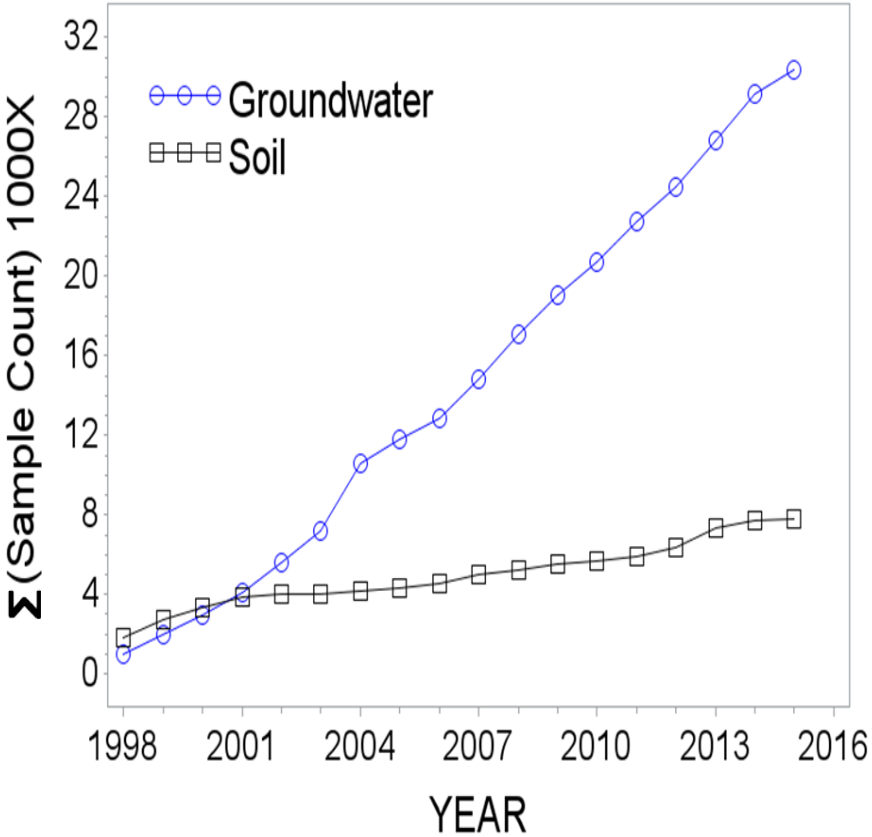




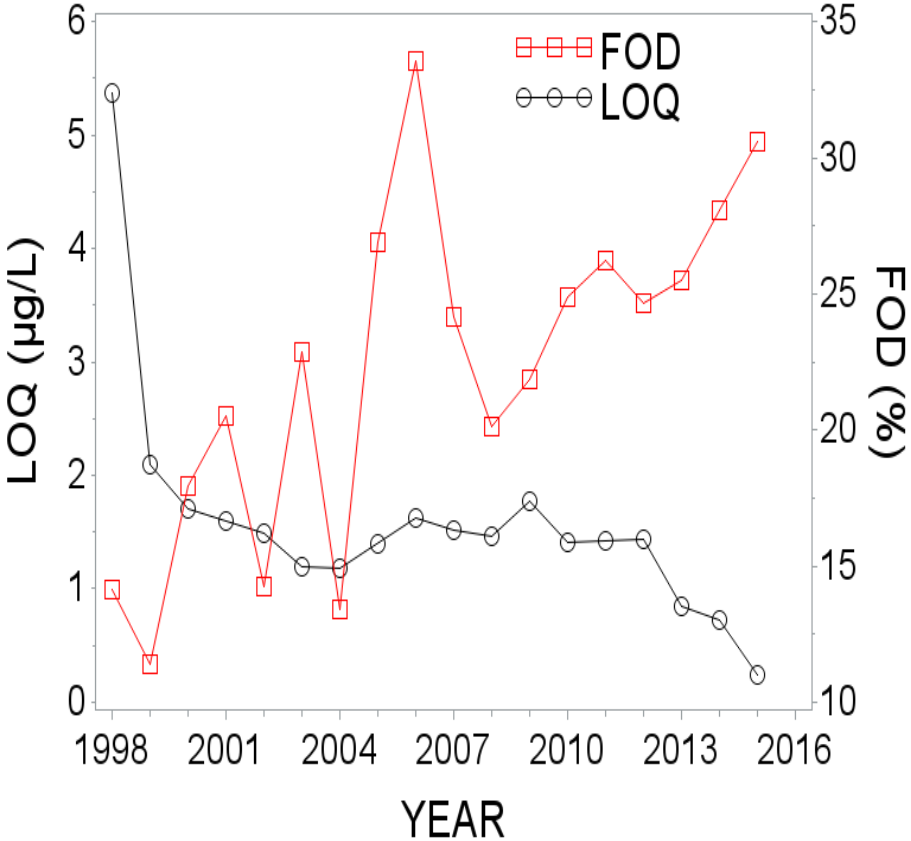
Doherty, R.E. (2000), J Environ Forensics; Morrison et al. (2005), Chapter 12, Chlorinated Solvents, in Environmental Forensics

USAF 1,4-Dioxane Data

All USAF Dioxane Records to Date



GW Frequency of Detection (FOD)

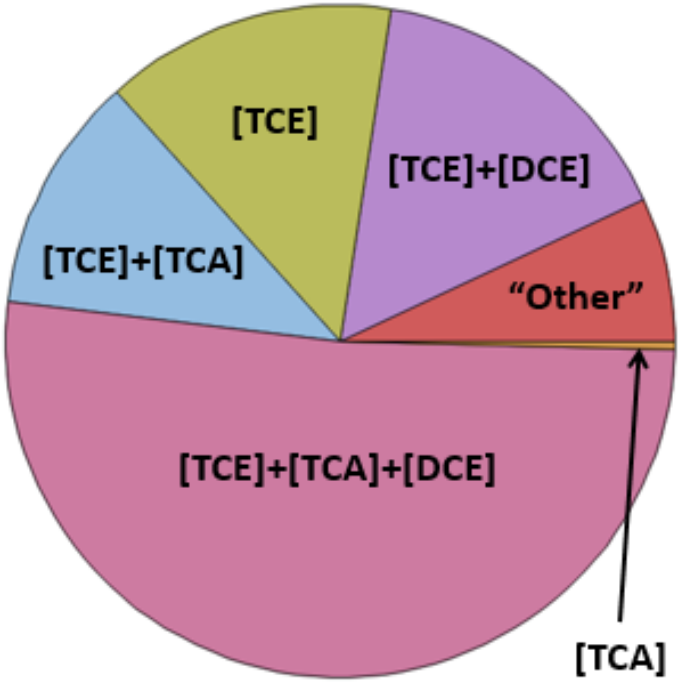


USAF Dioxane Data

Co-Occurrence

Includes "J" Flags

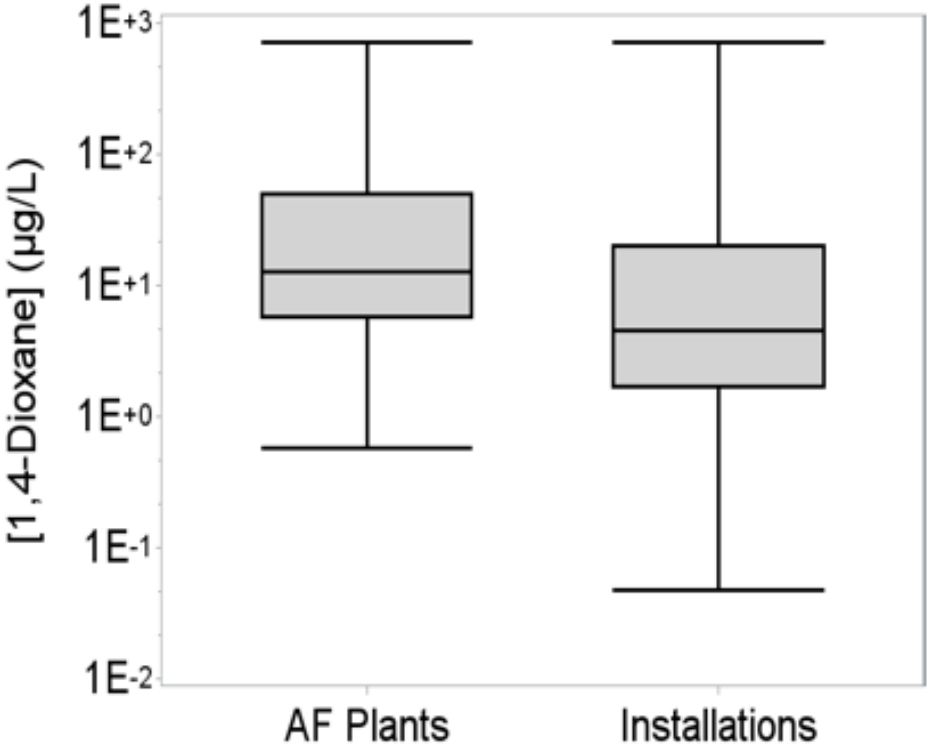
1,758 Wells



Historic Max Concentrations

Excludes "J" Flags

1,045 Wells

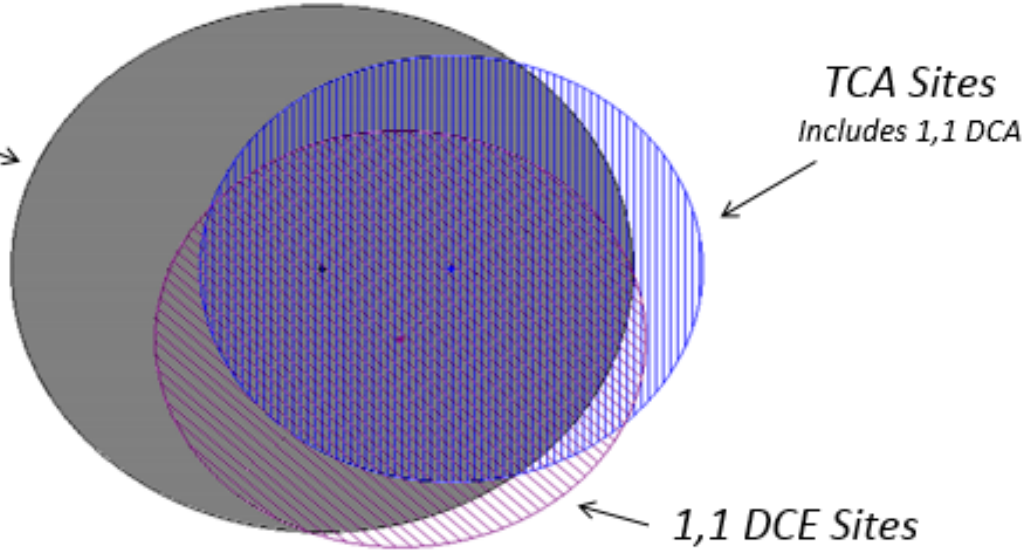


[TCE] - TCE and/or 1,2 DCE and/or VC
[TCA] - 1,1,1 TCA and/or 1,1 DCA
[DCE] - 1,1 DCE

USAF Programmatic Approach

Groundwater Sites (pre-RC) with TCA and/or TCE Past/Present Sources

(Emphasis on Waste Solvent Disposal Sites)



DEPARTMENT OF THE AIR FORCE
HEADQUARTERS UNITED STATES AIR FORCE
WASHINGTON, DC

MEMORANDUM FOR SEE DISTRIBUTION LIST

FROM: HQ USAF/A7C
1260 Air Force Pentagon
Washington, DC 20330-1260

SUBJECT: Guidance on 1,4 Dioxane, Environmental Restoration Program

This memorandum serves as Air Staff guidance for responding in a standardized way to 1,4 Dioxane, a solvent stabilizer. Some regulatory agencies have expressed concerns regarding 1,4 Dioxane during the cleanup process. Due to evolving science and regulatory standards, 1,4 Dioxane presents a potentially unacceptable human health or environmental risk. As a result, the Air Force will respond to 1,4 Dioxane subject to DoDI 4715.18, *Emerging Contaminants*. The following actions apply:

a. AFCEC and the NGB should implement the DoDI and the attached guidance at active installations, BRAC installations, transferring properties, GOCO properties, NGB properties, other than operational ranges and active ranges (for the non-munitions constituents) accordingly by providing technical guidance to the MAJCOMs and installations as necessary.

b. AFCEC and the NGB should program and budget for appropriate response actions when warranted.

MAJCOMs and installations should refer requests for sampling and other response actions to Mr. William Ryan, AFCEC/CER, DSN 969-8783, william.ryan.1@us.af.mil. NGB installations should contact Mr. Hans Dyer, NGB/A7OR, DSN 612-0149, russell.dyer@ang.af.mil, and BRAC installations should contact Dr. Steve Tornatsik, AFCEC/CIB, DSN 969-9438, stephen.tornatsik@us.af.mil. Any further questions on Emerging Contaminants should be addressed to Ms. Elaine Ross, A7CEV, DSN 612-4200, elaine.ross@pentagon.af.mil.

MARK A. CORRELL, SES, P.E.
The Deputy Civil Engineer
DCS/Logistics, Installations & Mission Support

Phased Execution Approach:

1. Confirmation Sampling → ~ 50% Complete
2. Full-Scale Delineation
3. Remedy Evaluation

For additional information, please visit

http://www.afcec.af.mil/Home/Environment/Technical-Support-Division/Environmental-Restoration-Technical-Support-Branch/BAA/

Speaker Contact Information

Richard.Anderson.55@us.af.mil; 210-395-0625

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Q&A Session 1

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Biodegradation of 1,4-Dioxane: Co-Contaminant Effects and Monitoring Tools

Dr. Shaily Mahendra
University of California, Los Angeles

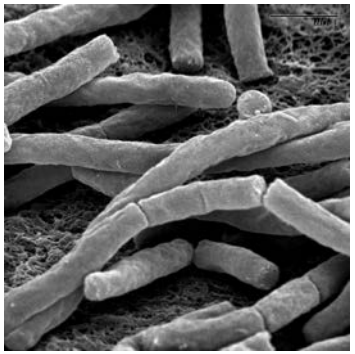
SERDP DOD • EPA • DOE | ESTCP

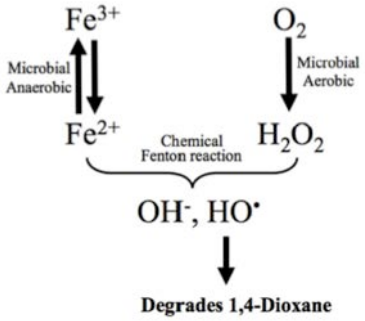
Agenda

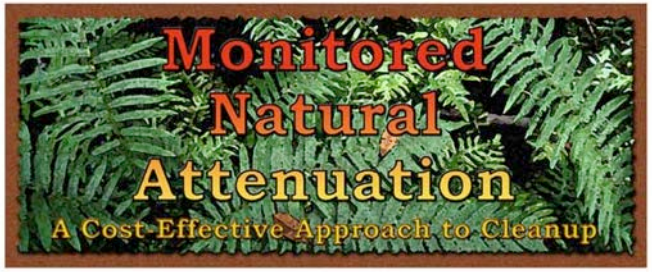
- 1,4-Dioxane biodegradation
  - Metabolism and cometabolism
  - Biodegradation pathway
- Effects of co-contaminants
  - Chlorinated solvents
  - Trace metals
- Monitoring tools
  - Identification of biomarker genes
  - Application in groundwater

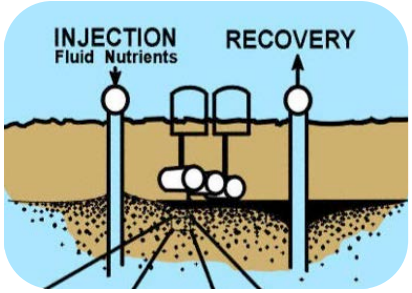
1,4-Dioxane is Biodegradable!

- Pure cultures of aerobic bacteria and fungi
- Cometabolism induced by methane, propane, toluene, tetrahydrofuran, branched aliphatics
- Mixed communities in industrial sludge
- Abiotic-biotic treatment trains
- Anaerobic-aerobic microbial Fenton reaction
- Field efforts (biostimulation and bioaugmentation)
- Limited, but growing evidence of monitored natural attenuation (MNA) in groundwater



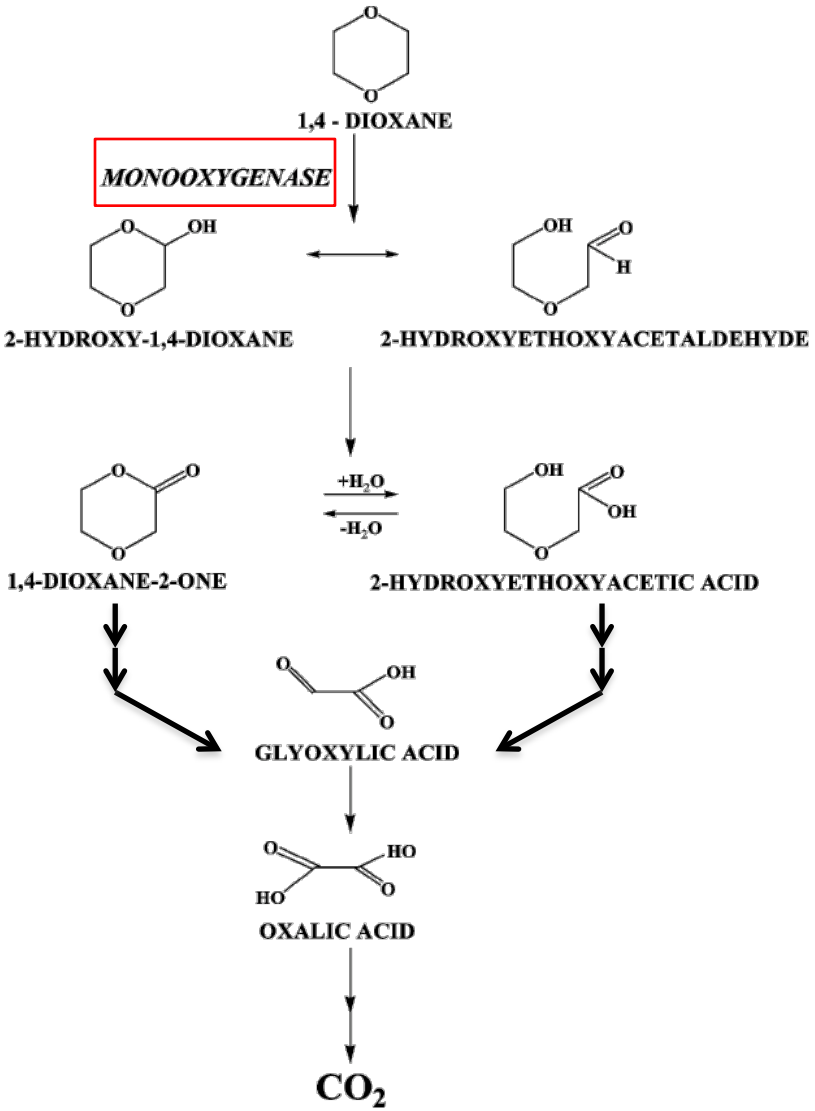






Biodegradation Pathways

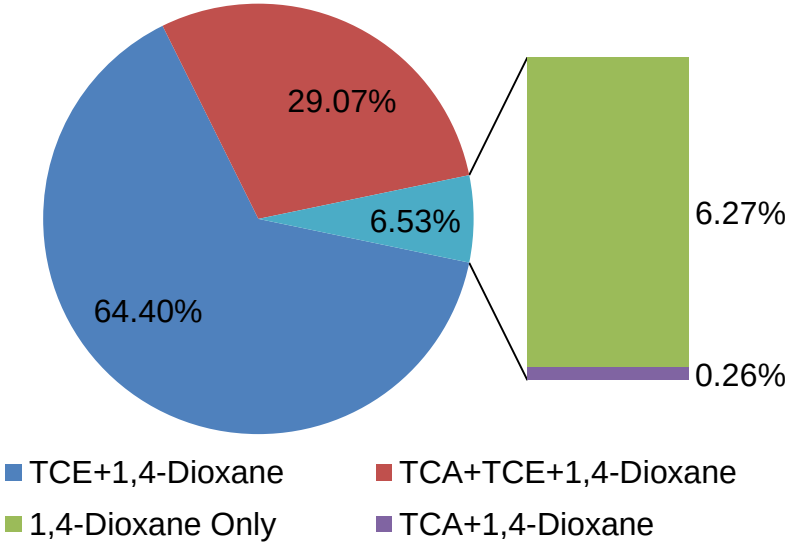
- Monooxygenase involved in initial hydroxylation of ether bond
- No accumulation of toxic byproducts
- Complete conversion to CO_2
- Similar pathway for metabolic and cometabolic processes
- Glyoxalic acid is key metabolic intermediate

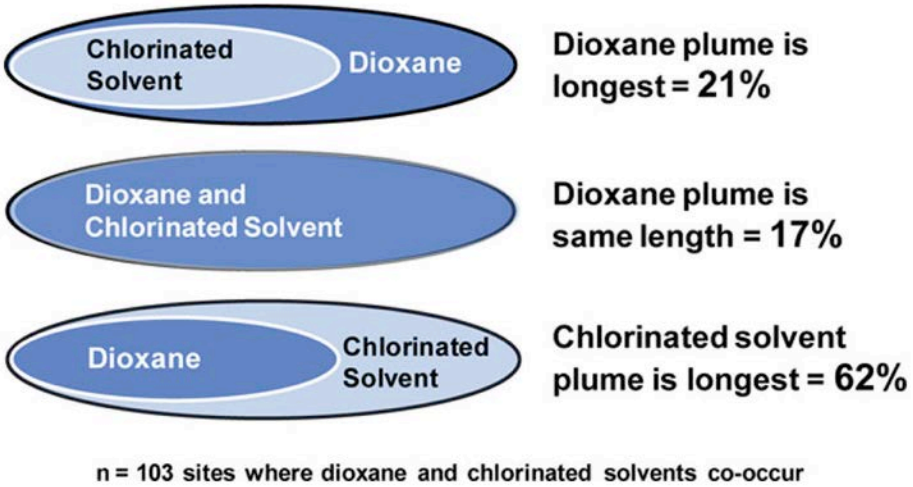


Mahendra et al., ES&T, 2007; Grostern et al., AEM, 2012

Chlorinated Solvents as Co-Contaminants

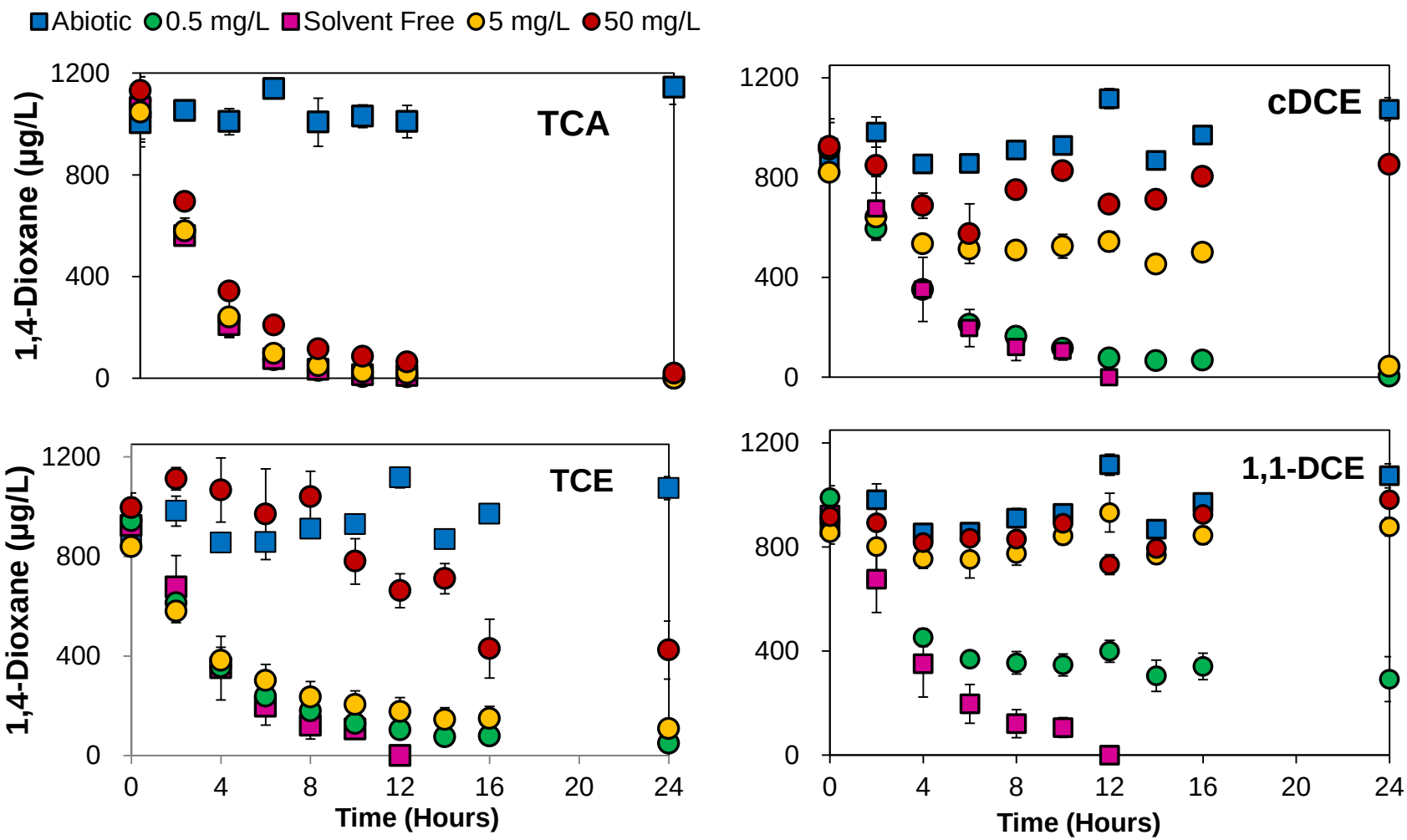
- 1,4-Dioxane was used as a stabilizer of some chlorinated solvents
- Monooxygenase-expressing bacteria biodegrade 1,4-dioxane and chlorinated compounds





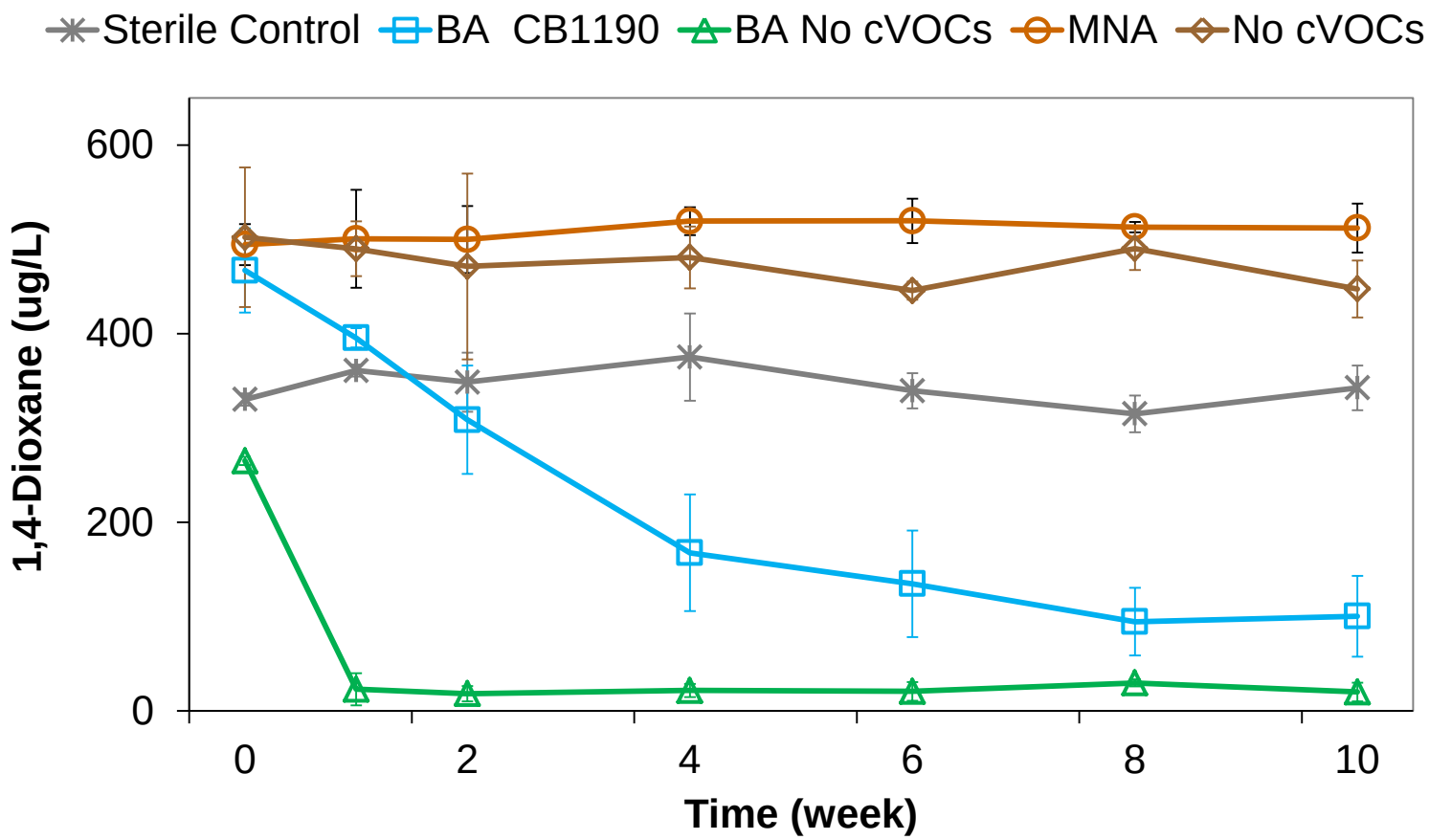
Anderson et al., Integr. Enviro. Assess. Manage., 2012; Mahendra et al., Chemosphere, 2013; Adamson et al., ES&TL, 2014

Chlorinated Solvents Inhibit 1,4-Dioxane Degradation



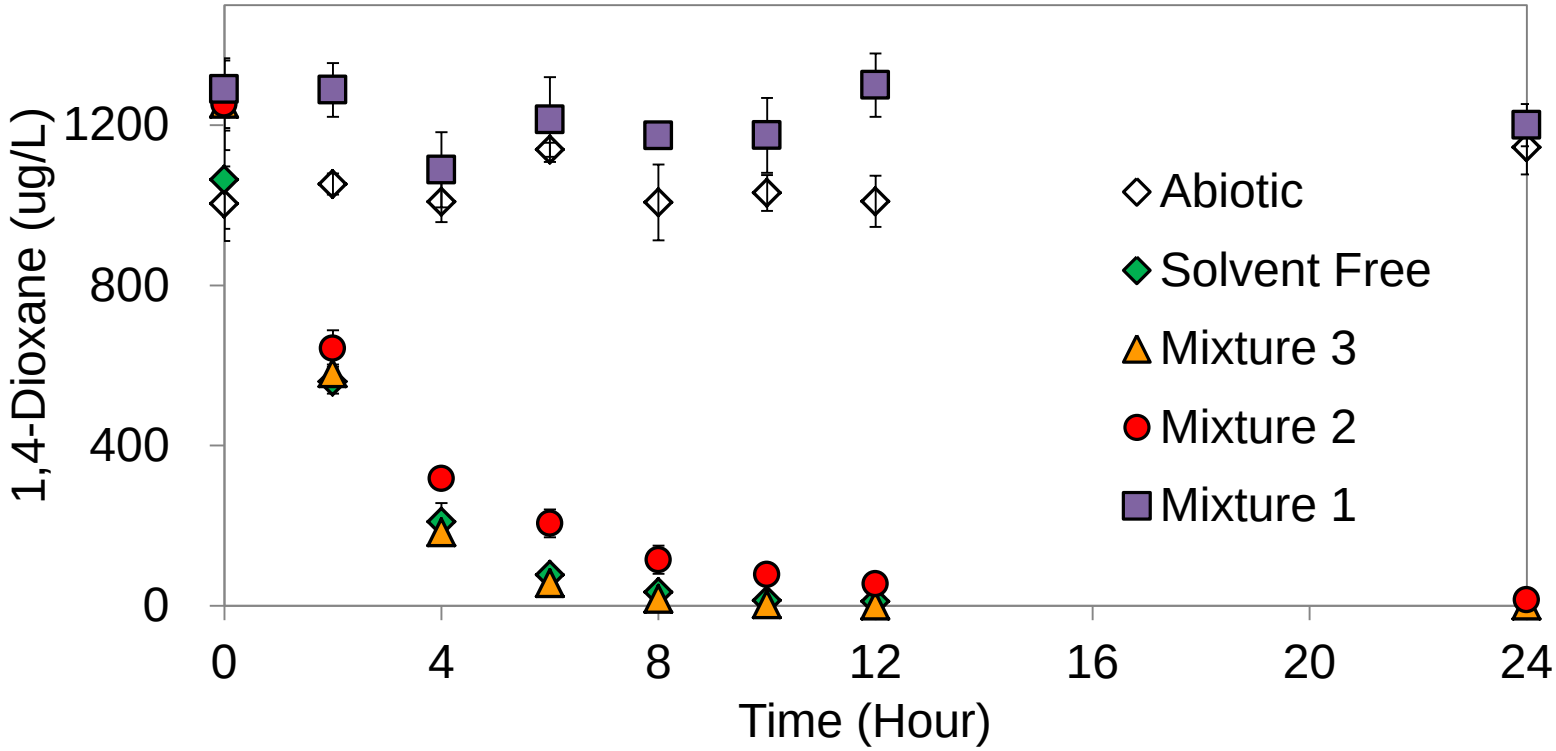
Zhang et al., ES&T, 2016

Removal of Chlorinated Solvents Increased 1,4-Dioxane Biodegradation in Microcosms



Zhang et al., ES&T, 2016

1,1-DCE is Key Inhibitor Even in Chlorinated Solvent Mixtures



Mixture 1: 700 µg/L TCE + 120 µg/L TCA + 450 µg/L cis-1,2-DCE + 5000 µg/L 1,1-DCE

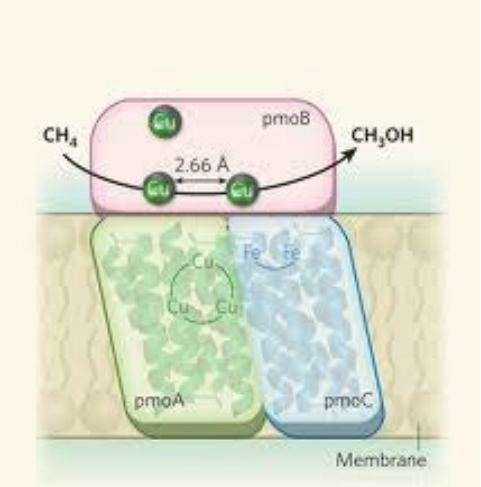
Mixture 2: 700 µg/L TCE + 120 µg/L TCA + 450 µg/L cis-1,2-DCE

Mixture 3: 700 µg/L TCE + 120 mµ/L TCA

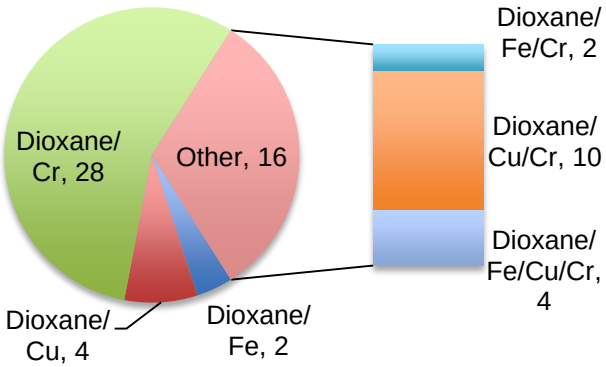
Zhang et al., ES&T, 2016

Importance of Metals for Dioxane Biodegradation

- Effects on enzymatic activity
  - Transition metals are cofactors at catalytic sites
  - Metals were shown to inhibit oxidation of organic compounds by soluble methane monooxygenase (sMMO)
- Co-contaminants at sites impacted by 1,4-dioxane and chlorinated solvents
  - Iron and copper at high concentrations on DoD sites with small arms ranges
  - Cu(II) and Cr(VI) range from 1-48,000 ppb at 1,4-dioxane-contaminated Superfund sites

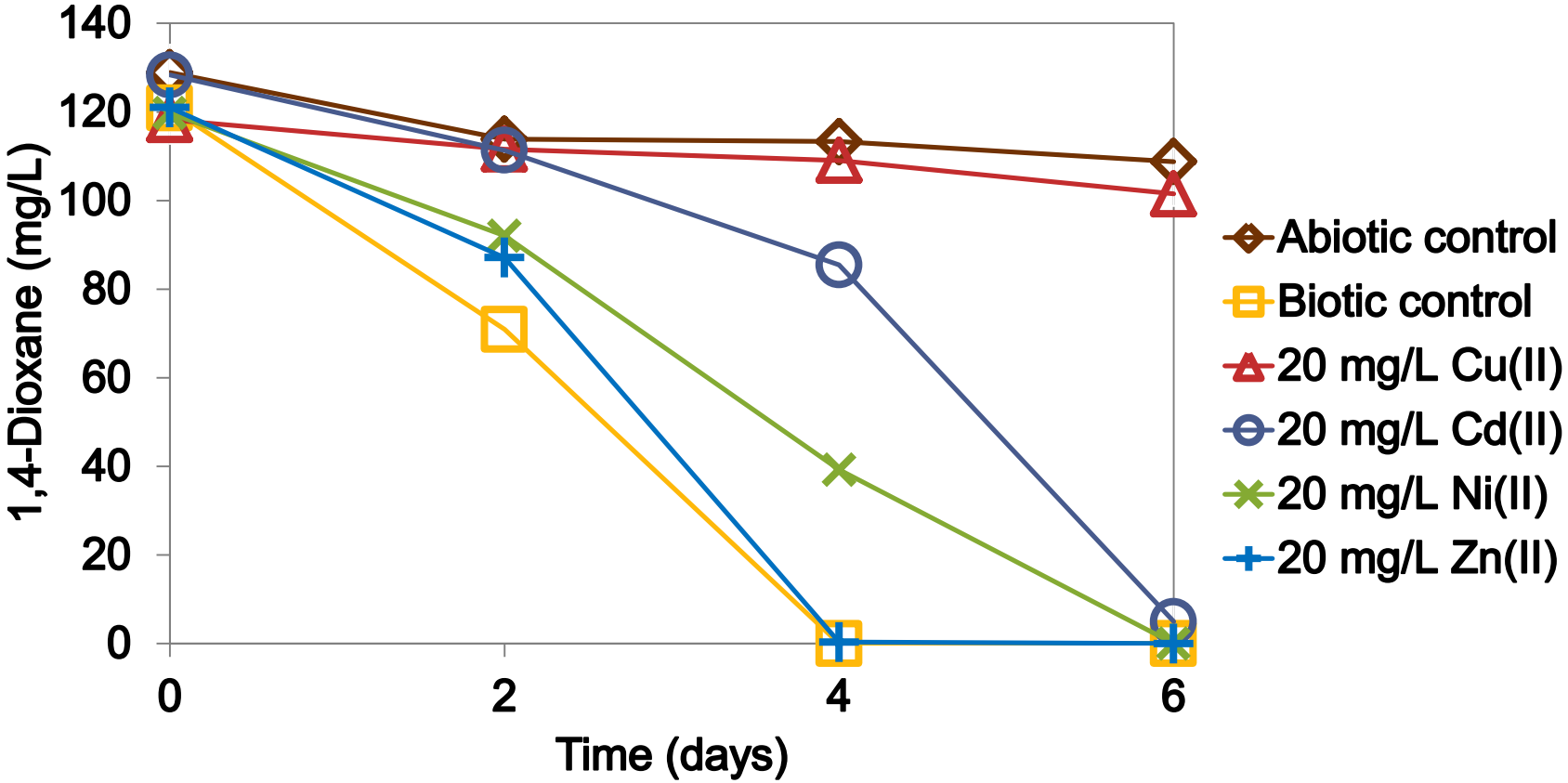


Bollinger *et al., 2010*



Source: ERPIMS & CERCLIS, (*n* = 50)

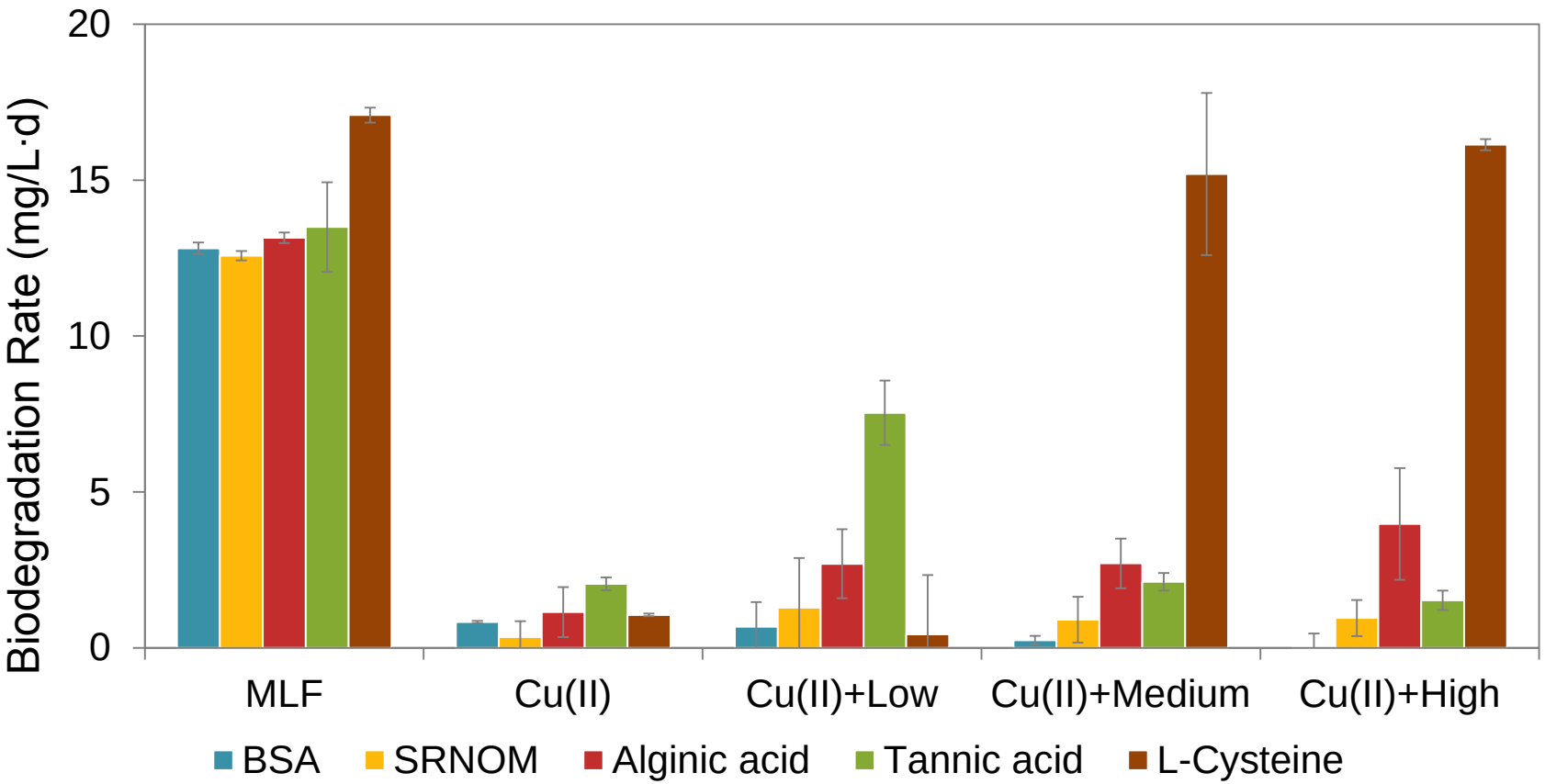
Trace Metals Inhibit 1,4-Dioxane Degradation



Inhibition: Cu(II) > Cd(II) > Ni(II) > Zn(II)

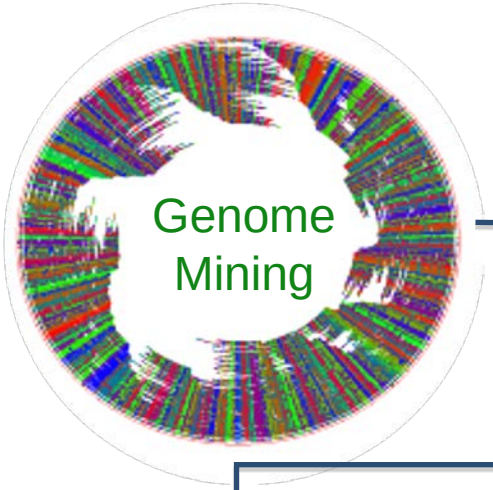
Pornwongthong et al., ABAB, 2014

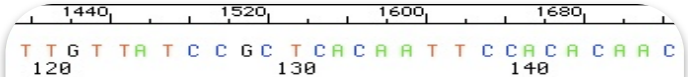
Cysteine and Tannin Mitigate Toxicity from Copper Ions



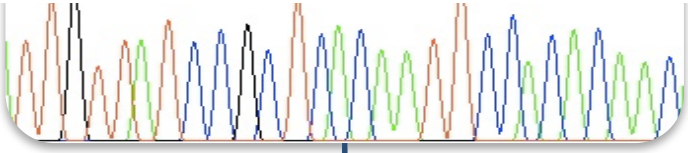
Pornwongthong et al., ABAB, 2014

Nucleic Acid-Based Biomarkers





Biomarker Selection and Primer Design



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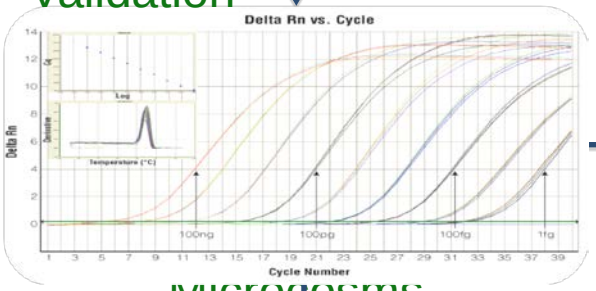
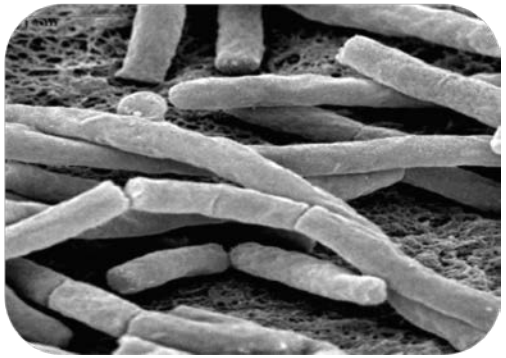
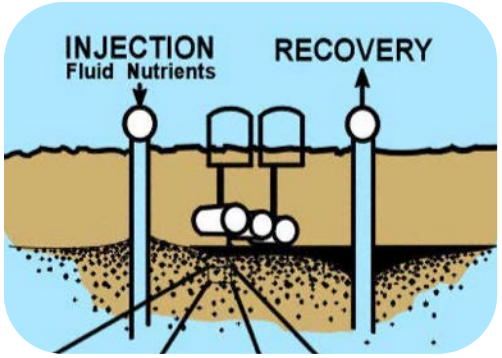


Pure Cultures

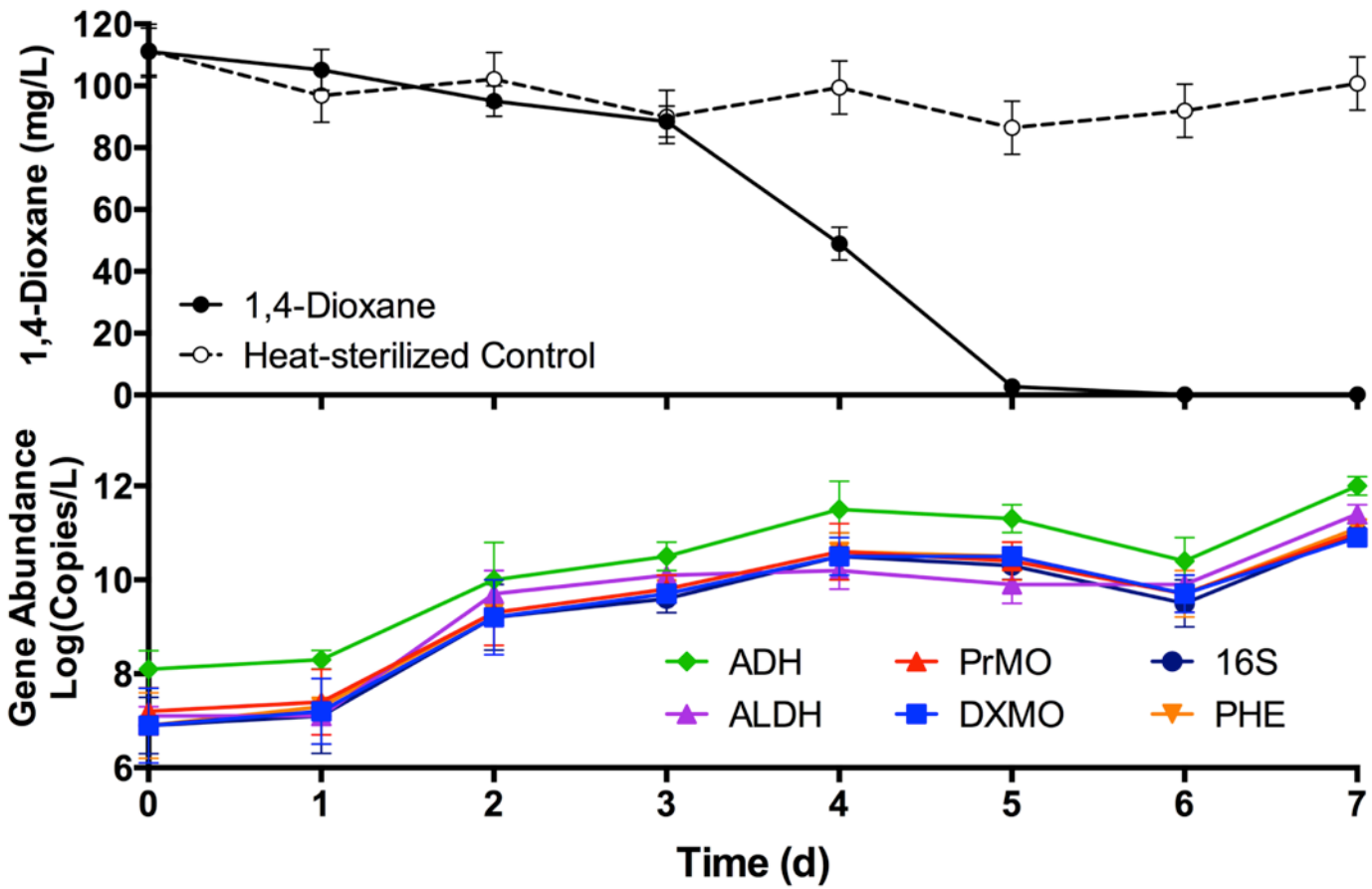


Microcosms

Field Experiments

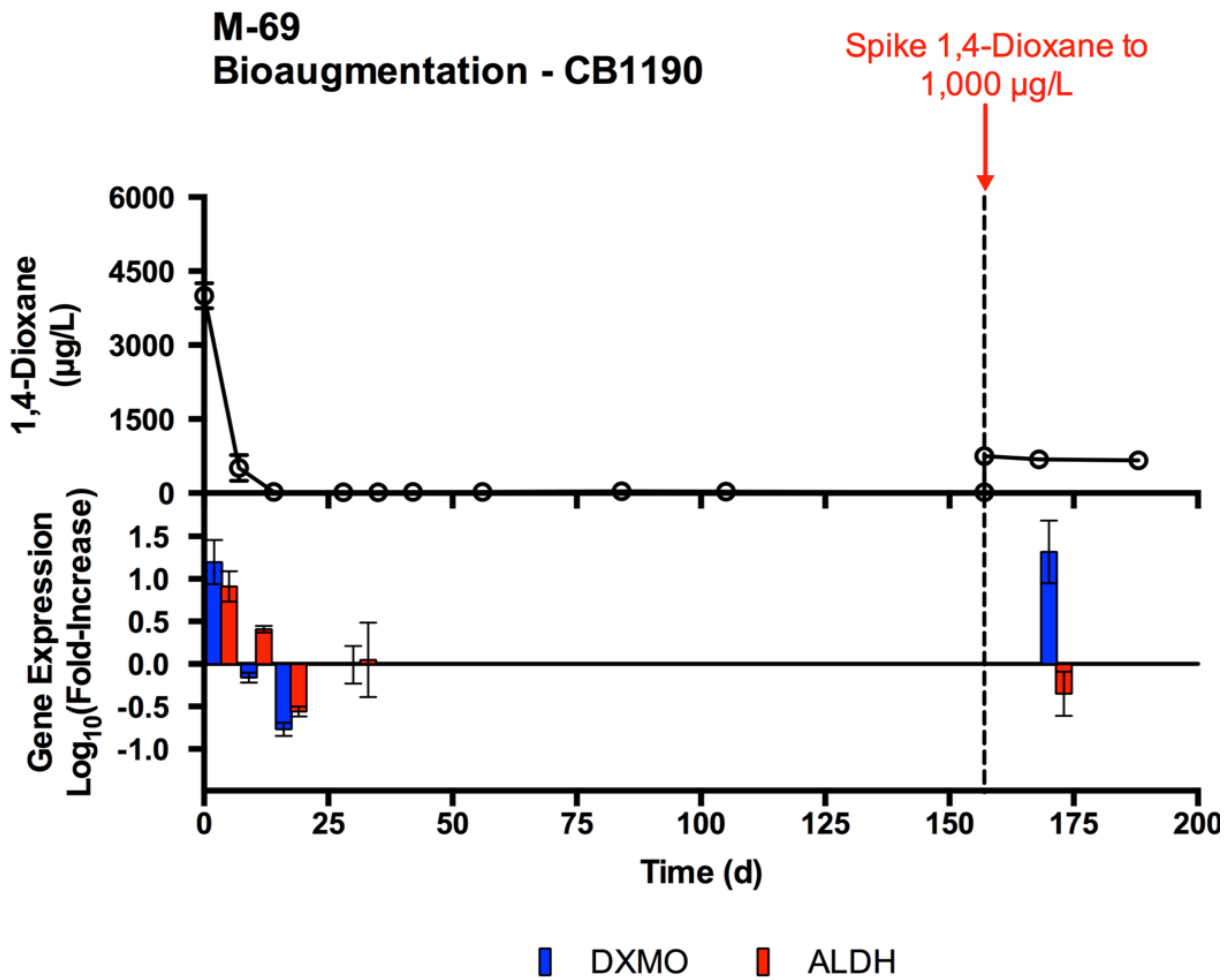


Gene Abundance in CB1190 Degrading 1,4-Dioxane



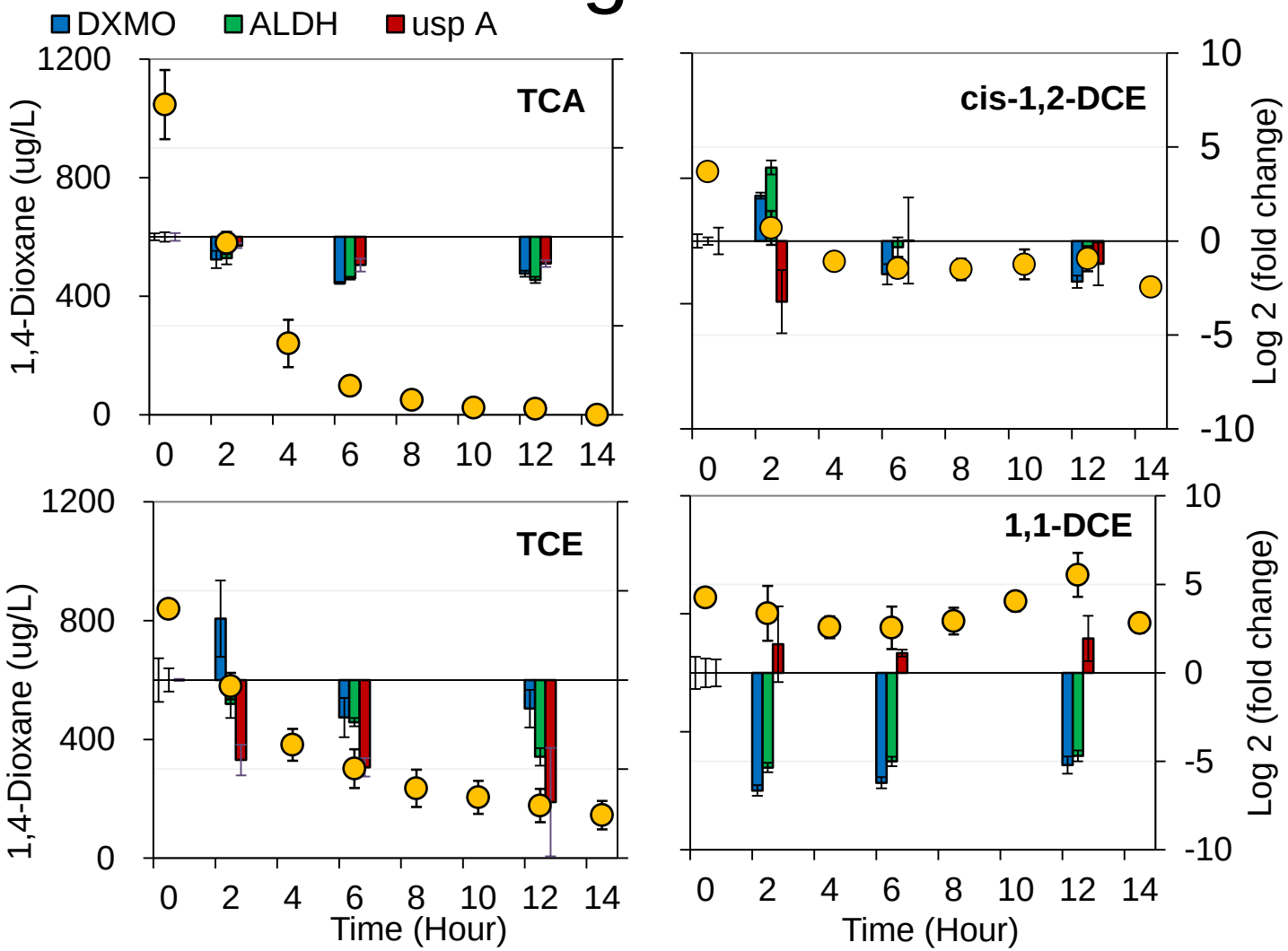
Gedalanga et al., AEM, 2014

DXMO Gene Responds to 1,4-Dioxane ALDH Responds to Degradation Products



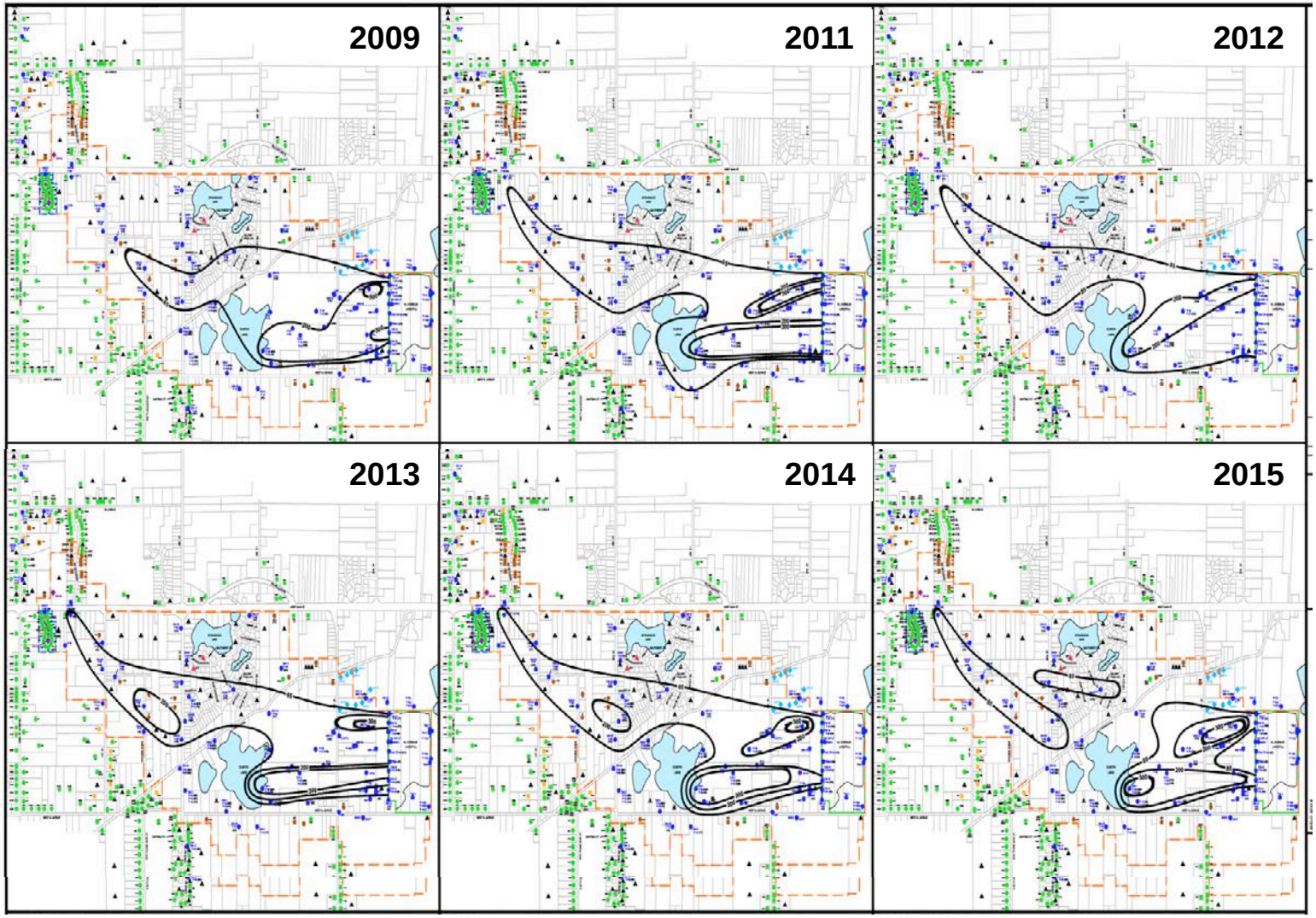
Gedalanga et al., in preparation, 2017

Genes for DXMO and ALDH Down-Regulated

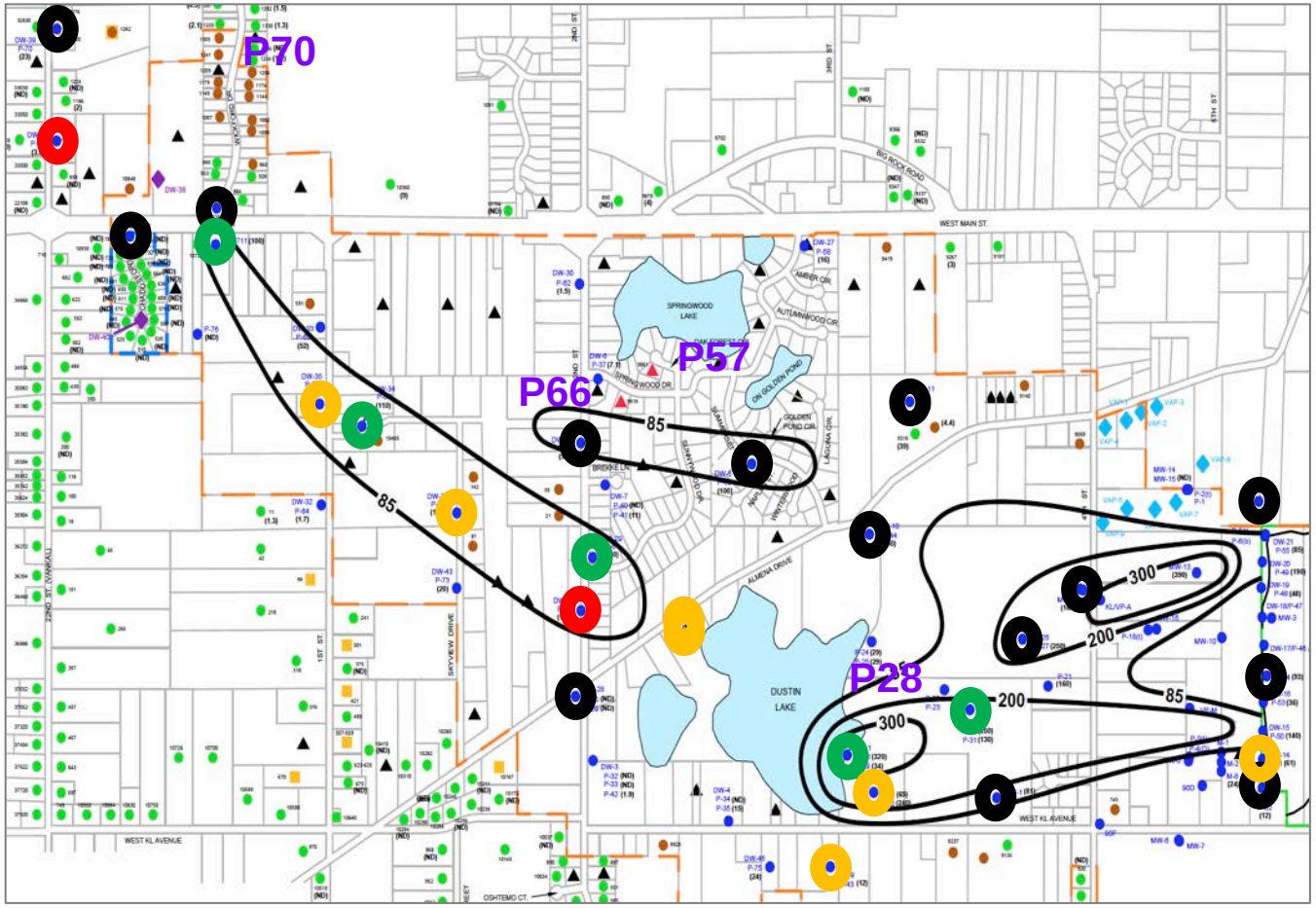


Zhang et al., ES&T 2016

1,4-Dioxane Groundwater Plume



Presence of DXMO and ALDH Genes Tracks with the Receding Plume



Biomarker Detections

- DXMO
- ALDH
- DXMO+ALDH
- Not Detected

Gedalanga et al., Remediation J., 2016

Conclusions

- Chlorinated ethenes inhibit 1,4-dioxane biodegradation
  - 1,1-DCE is the strongest inhibitor even in chlorinated solvent mixtures
- Trace metals, such as Cu(II), Cd(II), Ni(II), Zn(II), inhibit 1,4-dioxane biodegradation in a dose-dependent manner
  - Alginin, L-cysteine, and tannin may bind with divalent metal cations, alleviating toxicity
- A set of genes (dxmB/aldH) serve as specific biomarkers for 1,4-dioxane biodegradation
  - Useful in making decisions for MNA or enhanced bioremediation and post-remediation monitoring
- Cometabolism can only be indirectly verified using nucleic acid-based biomarkers

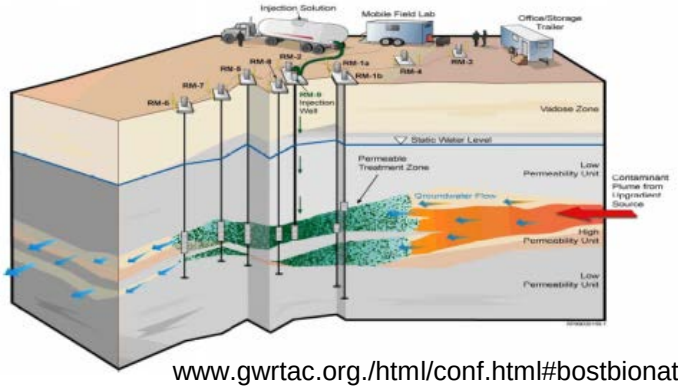
Applications and Technology Transfer

Outputs

- Selection of inducing substrates and bioaugmentation cultures/enzymes
- Co-contaminant tolerance, and optimum field conditions
- Quantitative data and models for design of reactors and in-situ bioremediation systems
- Biomarkers, isotope-based tools, monitoring of intermediates and end-products

DoD Benefits

- Changing the industrial and regulatory perception of 1,4-dioxane biodegradability
- Understanding treatment mechanisms especially in contaminant mixtures
- Improving tools to validate natural or enhanced remediation effectiveness



www.gwrtac.org./html/conf.html#bostbionatatten

For additional information, please visit
https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Emerging-Issues/ER-2300

Speaker Contact Information

mahendra@seas.ucla.edu; 310-794-9850

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Q&A Session 2

SERDP DOD • EPA • DOE | ESTCP

1,4-Dioxane Vadose Remediation by Thermal Soil Vapor Extraction (XSVE)

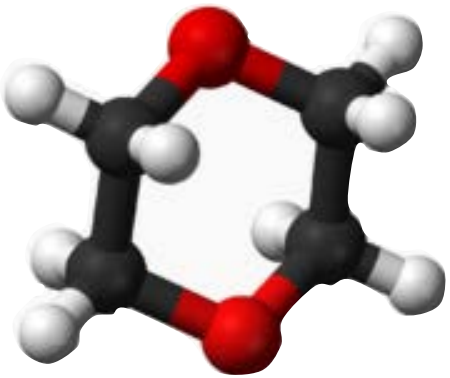
Dr. Rob Hinchee

Integrated Science & Technology

SERDP DOD • EPA • DOE | ESTCP

Agenda

- Need and objectives
- Approach
- Demonstration site
- XSVE performance
- HypeVent model for XSVE
  - Sensitivity Analysis
- Key take-home messages

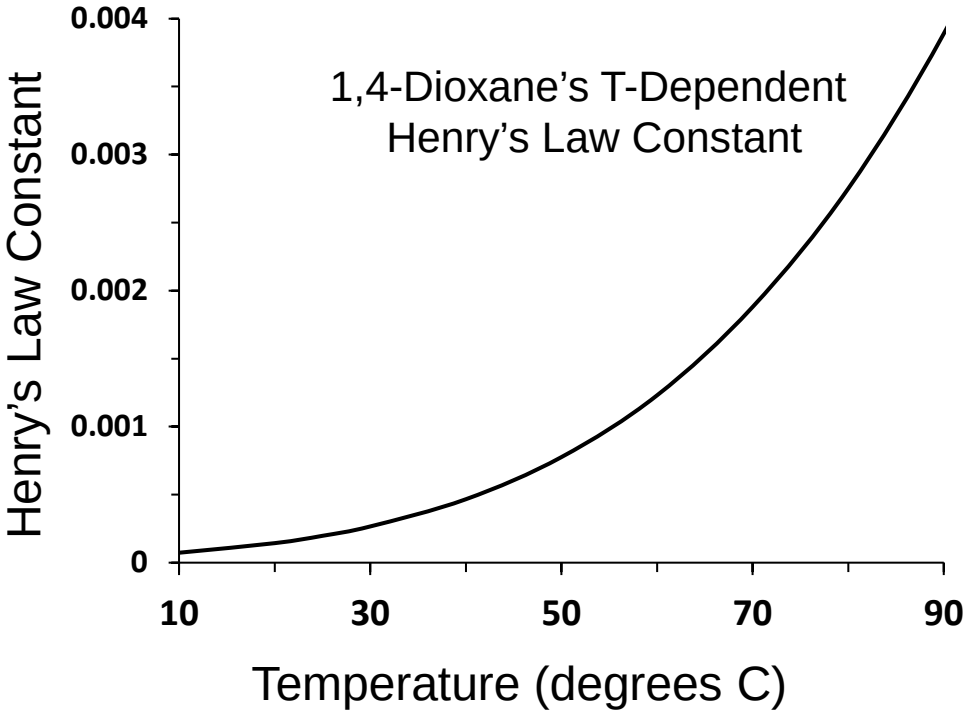


Project Need and Objective

- Project need
  - Vadose zone 1,4-dioxane sources persist and lead to groundwater contamination
  - These sources are not sufficiently removed by conventional soil vapor extraction (SVE)
- Project objective
  - Design, implement, and document successful remediation of 1,4-dioxane in the vadose zone by enhanced soil vapor extraction (XSVE)

Approach

- Use focused extraction and heated air injection to enhance SVE performance

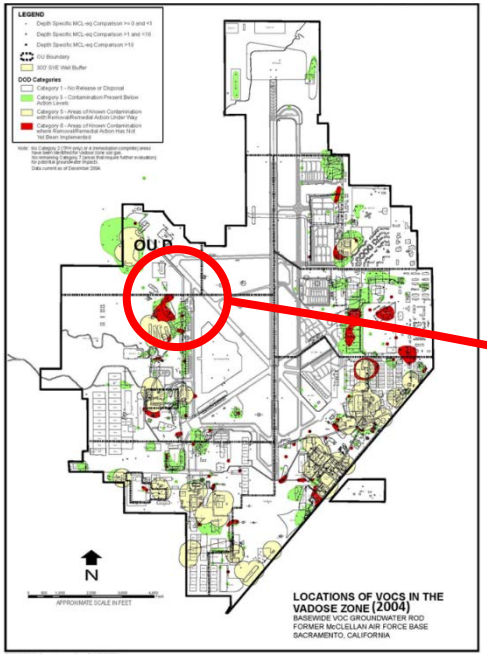


<u>Henry's for Other VOCs</u>
Benzene = 0.2
TCE = 0.4

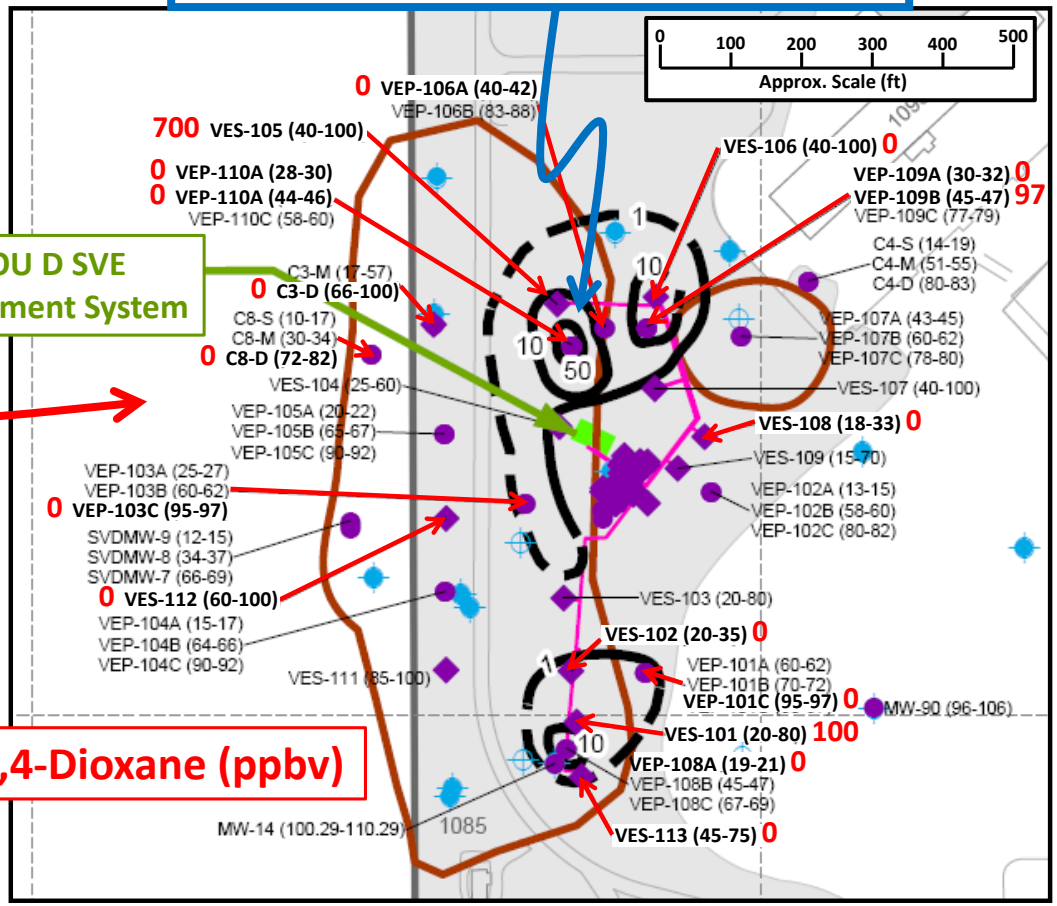
Demonstration Site

1,4-Dioxane Vadose Zone Source Area, Former McClellan AFB OU D

SVE Well **VES-105**
1,4-Dioxane: 1,000 ppb_v range



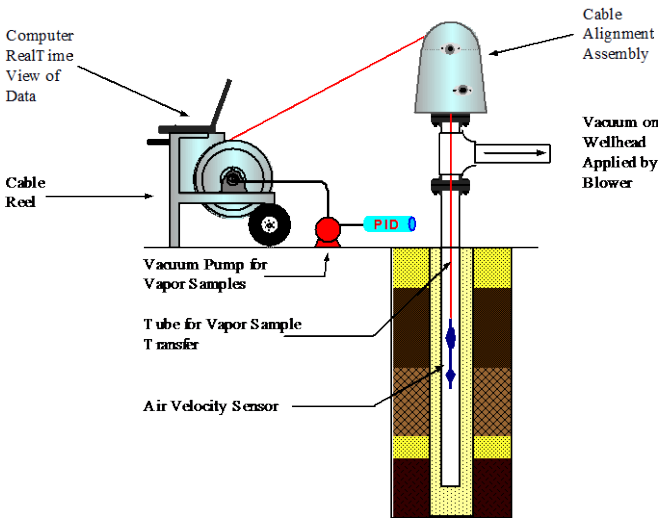
OU D SVE Treatment System

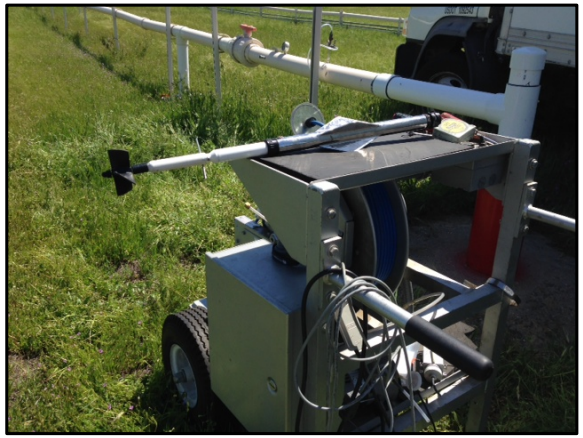


1,4-Dioxane (ppbv)

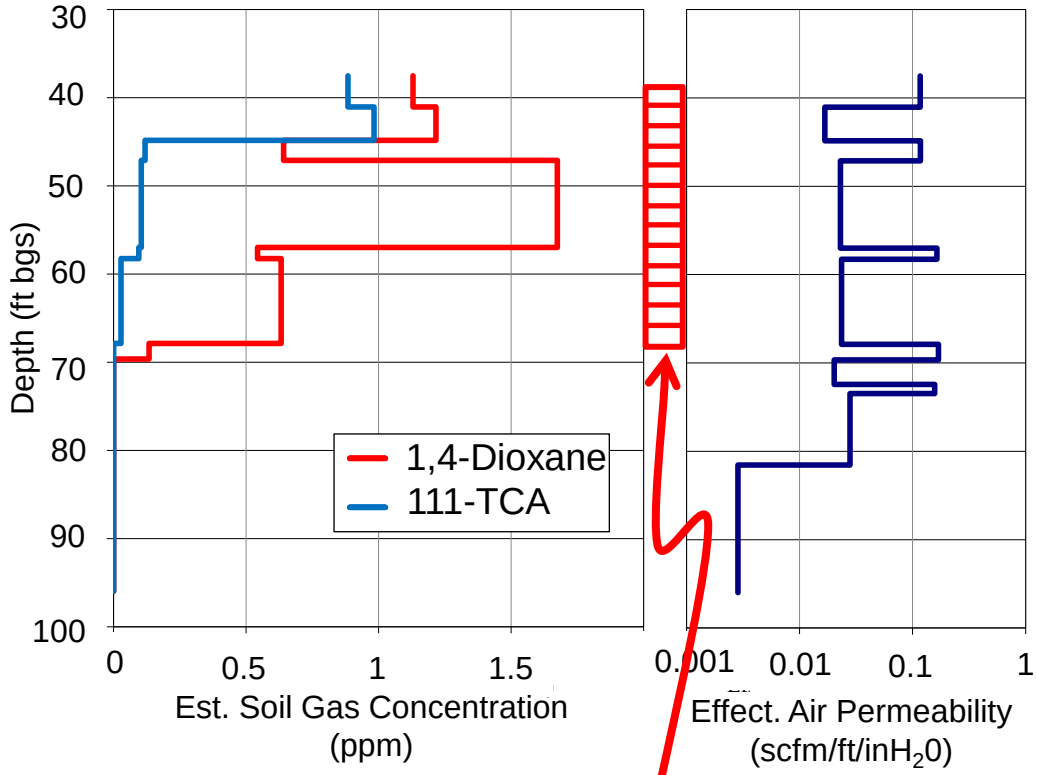
PneuLog Analysis of SVE Well

Concentrations and Effective Permeability





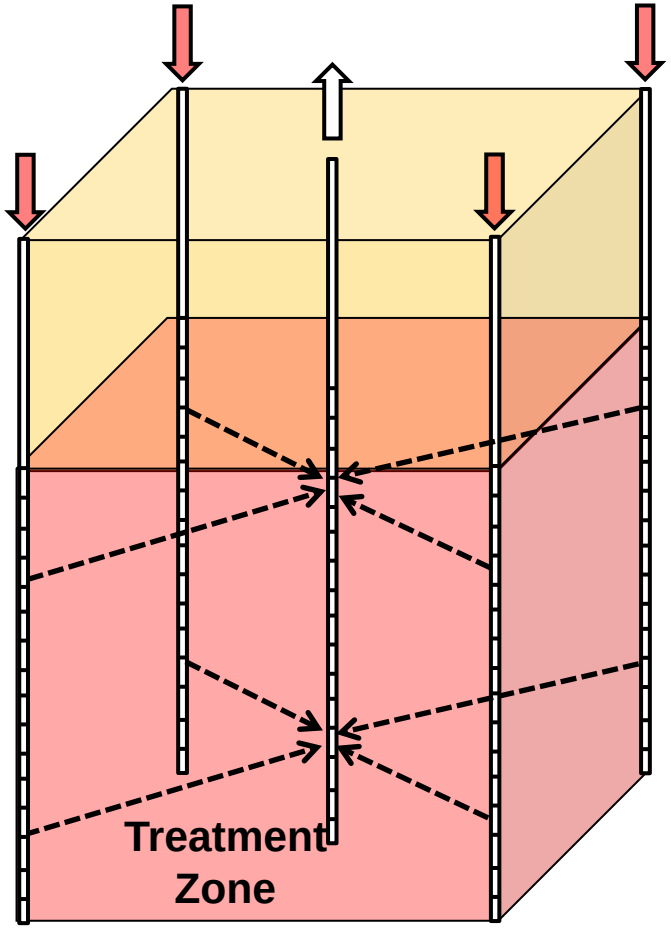
PneuLog by Praxis Environmental



XSVE Well VES-105
Screened Interval 38 to 68 ft bgs

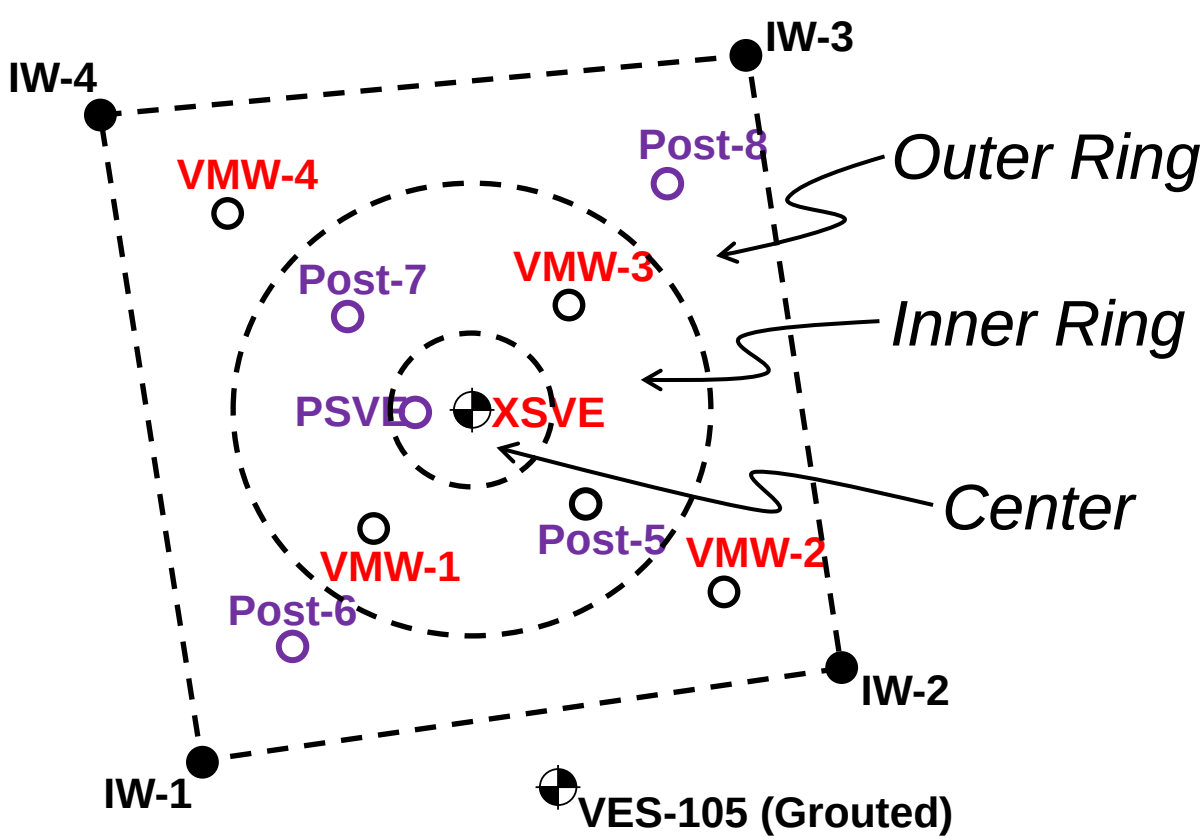
XSVE Demonstration Design

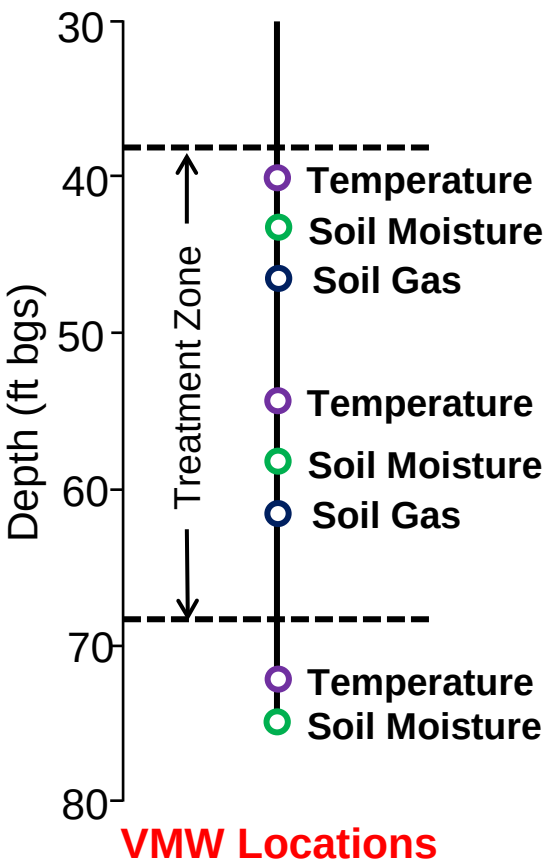
- Four injection wells at 20 ft corners
  - ~100 cfm each; ~100 to 120˚C
- One extraction well in center
  - ~100 cfm
- Wells constructed for elevated temperature
  - Steel casings, concrete grout
- Screened interval 38 to 68 ft
- Existing vapor treatment system
- Condensate collection



Site Layout and Zones

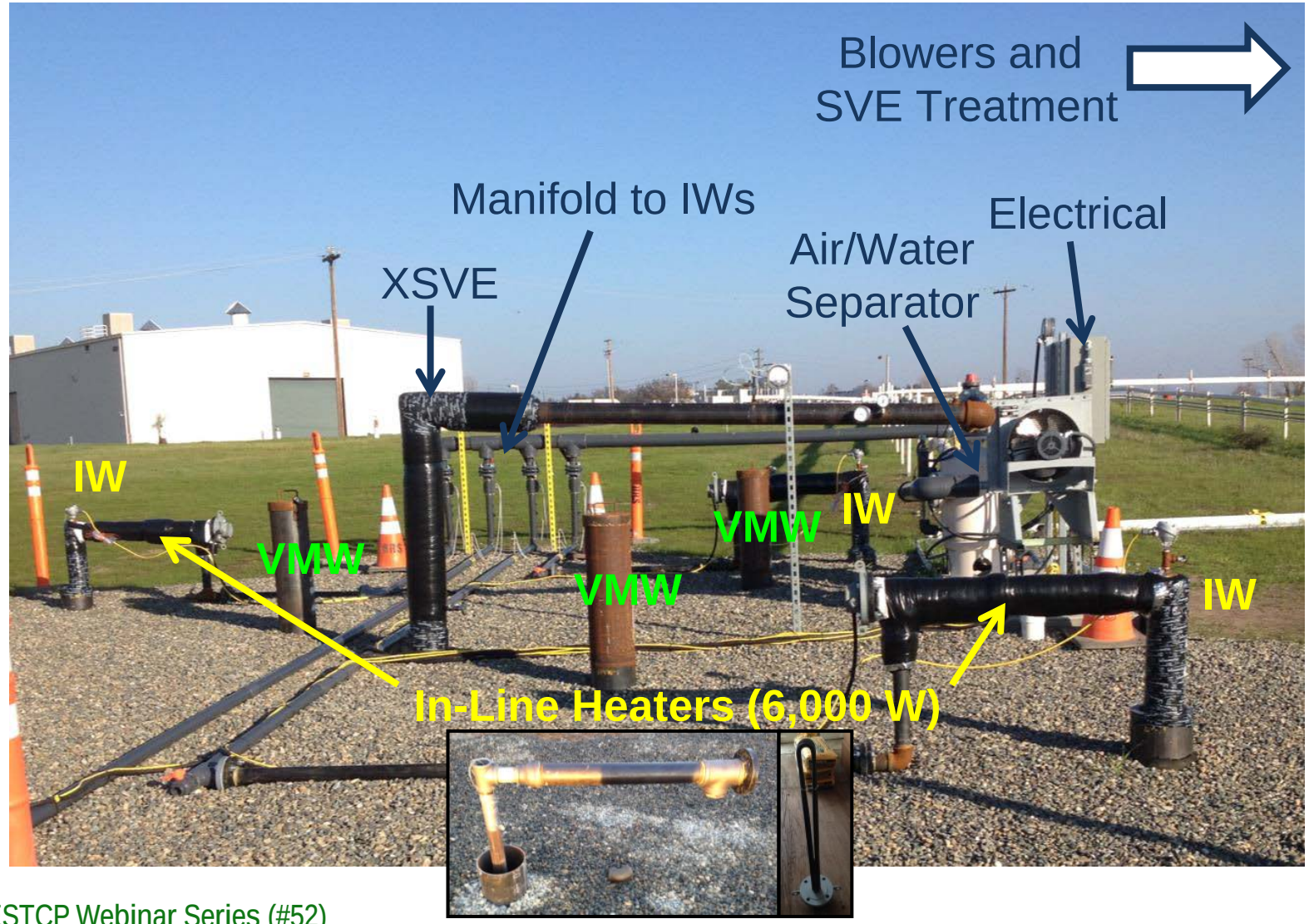
Center, Inner Ring, Outer Ring





Composite soil sampling: 5 initial borings, 5 final borings

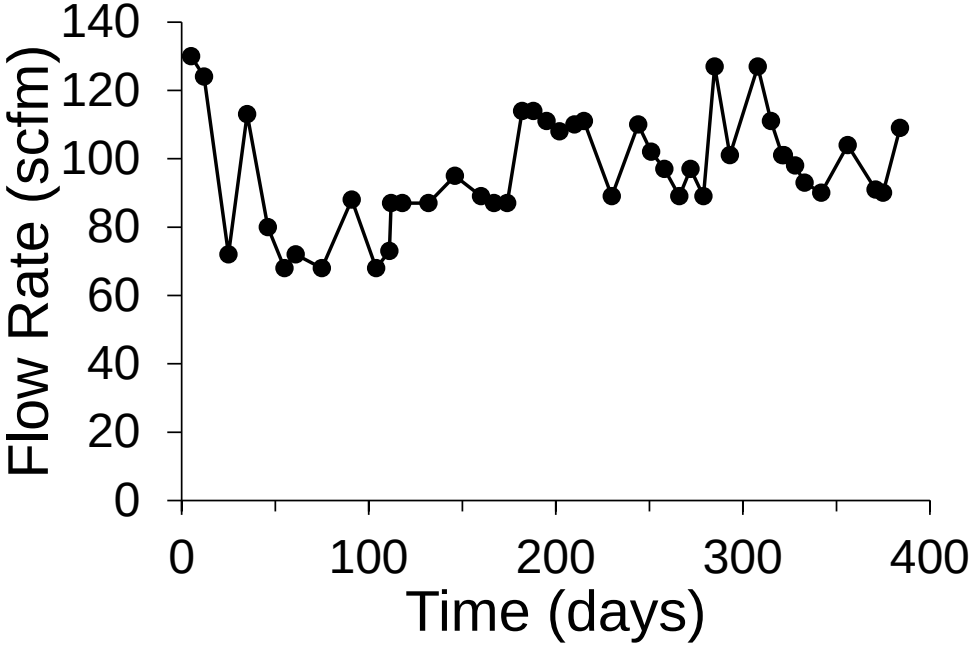
XSVE System


Blowers and
SVE Treatment
Manifold to IWs
Electrical
Air/Water
Separator
XSVE
IW
VMW
VMW
VMW
IW
IW
In-Line Heaters (6,000 W)

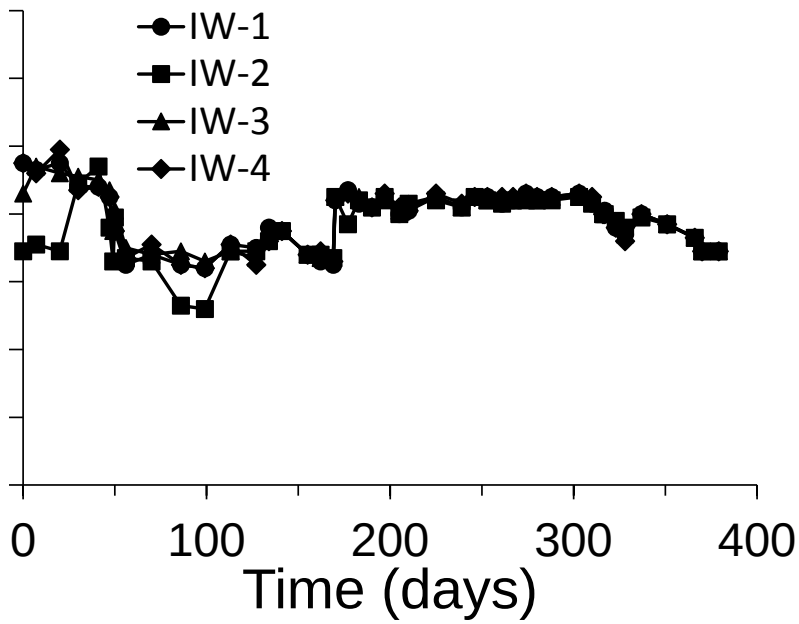
XSVE Operation

Flow Rates

Extraction well
~100 cfm range

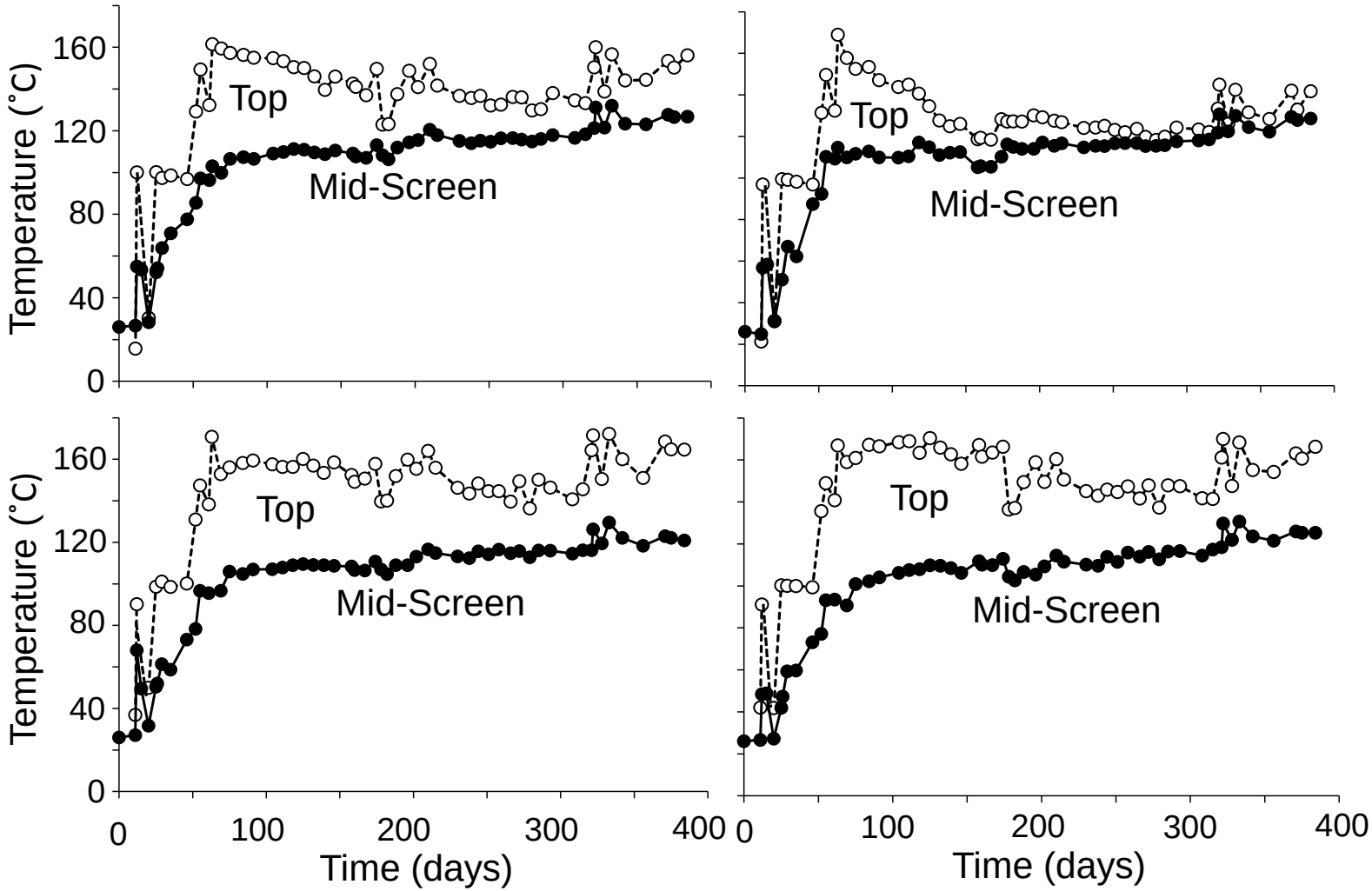


Injection wells
~80 cfm range each



XSVE Operation

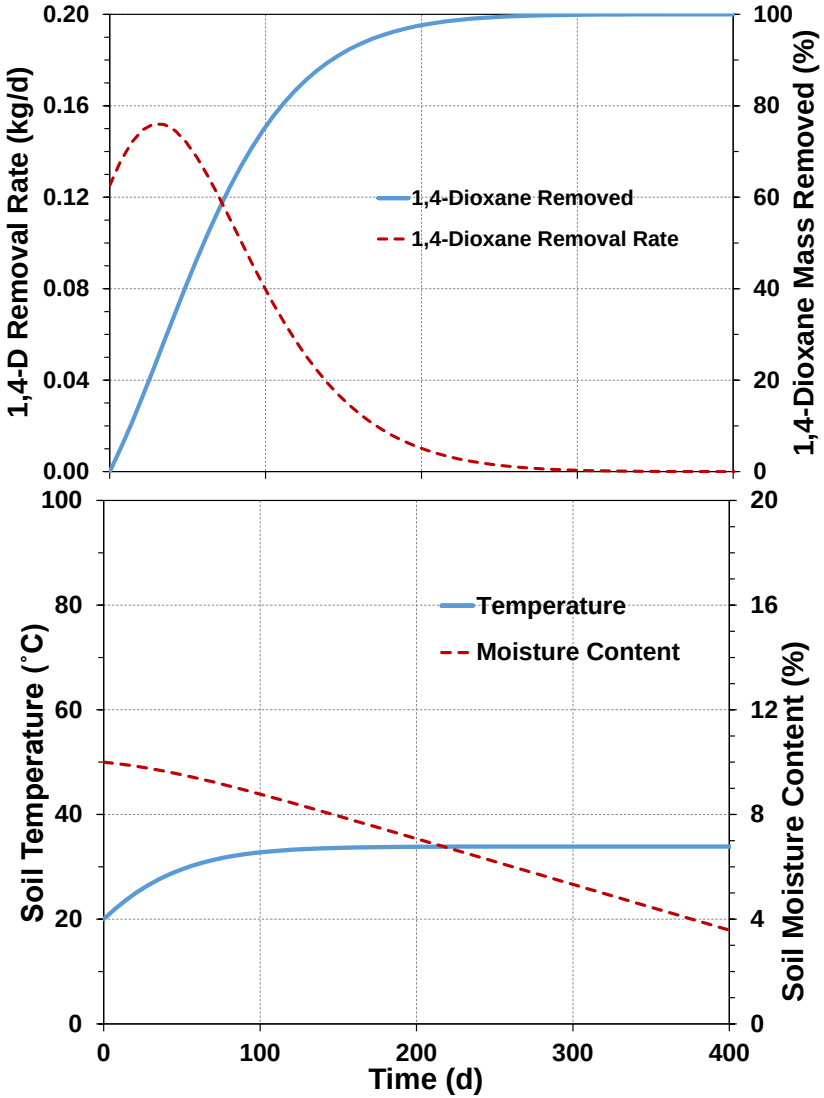
Injection Well Temperatures



Note: Mid-screens ~100-120˚C

HypeVent Model of XSVE for 1,4-Dioxane

- Mass and energy balance
- Fully mixed system
- Screening level model
- Incorporates T-dependent Henry's for 1,4-dioxane
- 1,4-dioxane removal
- Soil temperature
- Soil moisture content

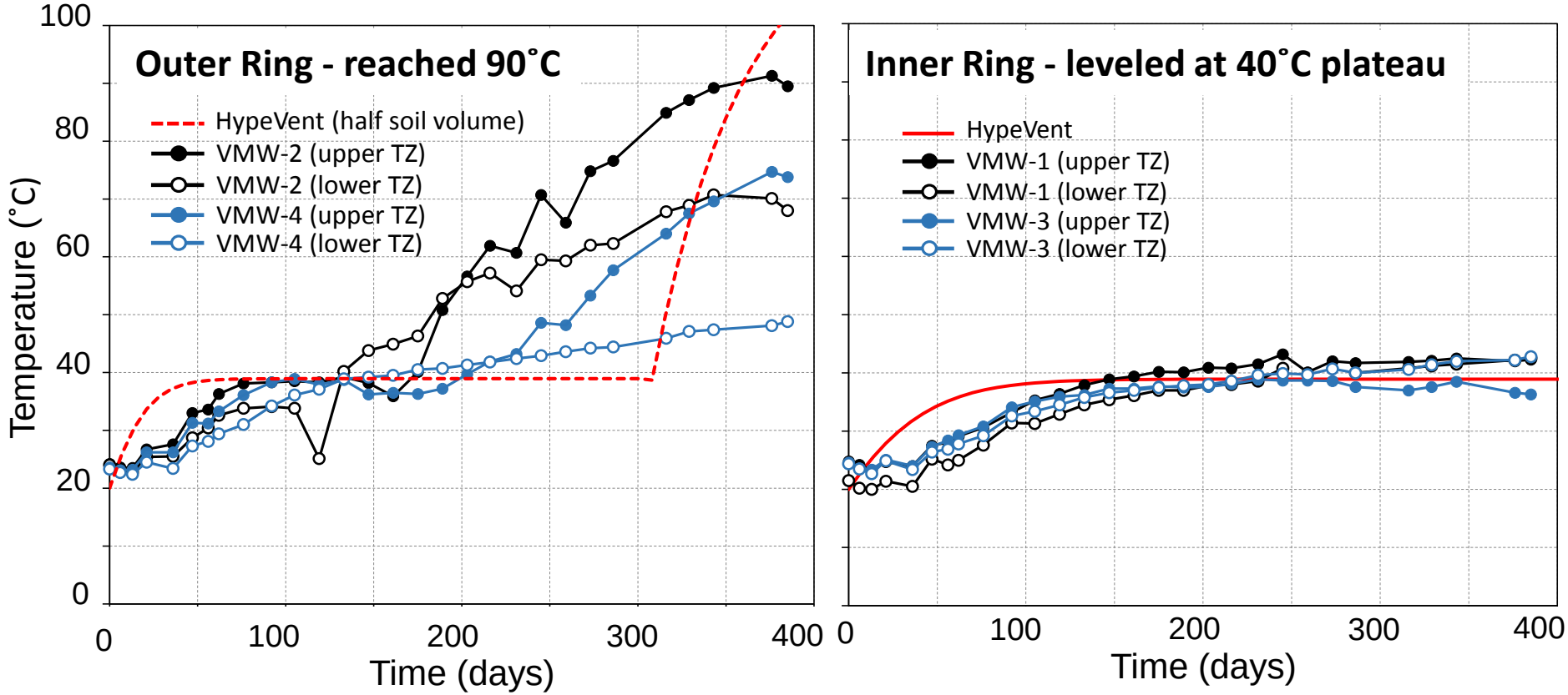


Dr. Paul Johnson, Colorado School of Mines

Field Results and HypeVent Model

Soil Temperature

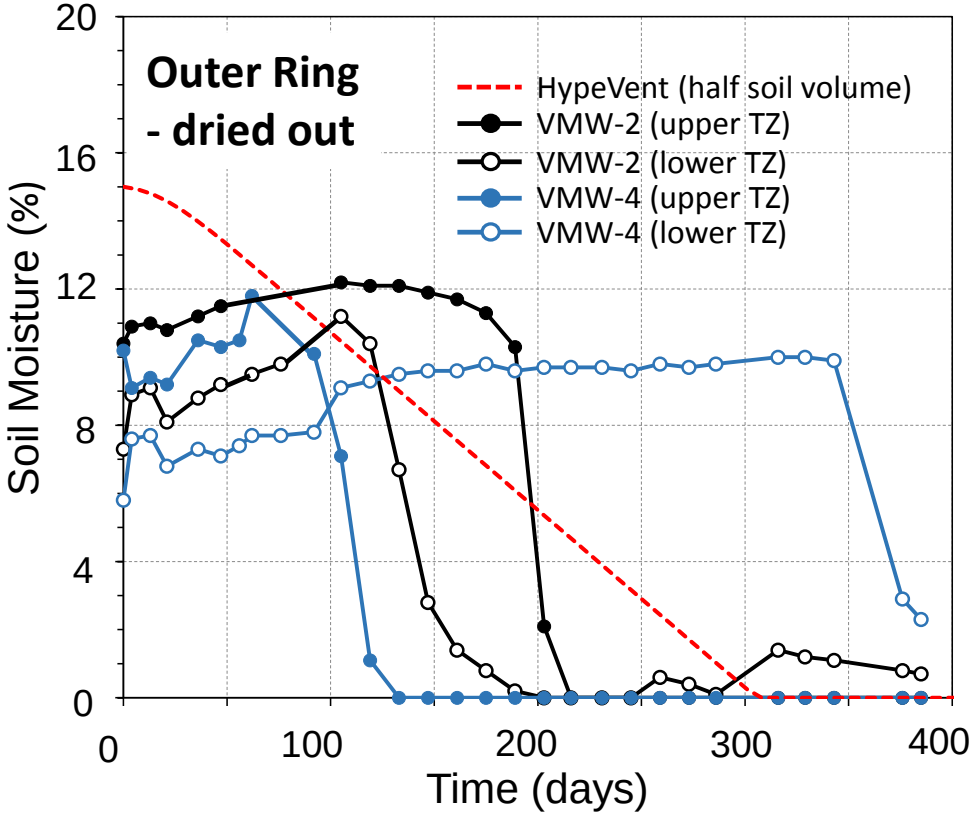
- HypeVent worked well as screening level model

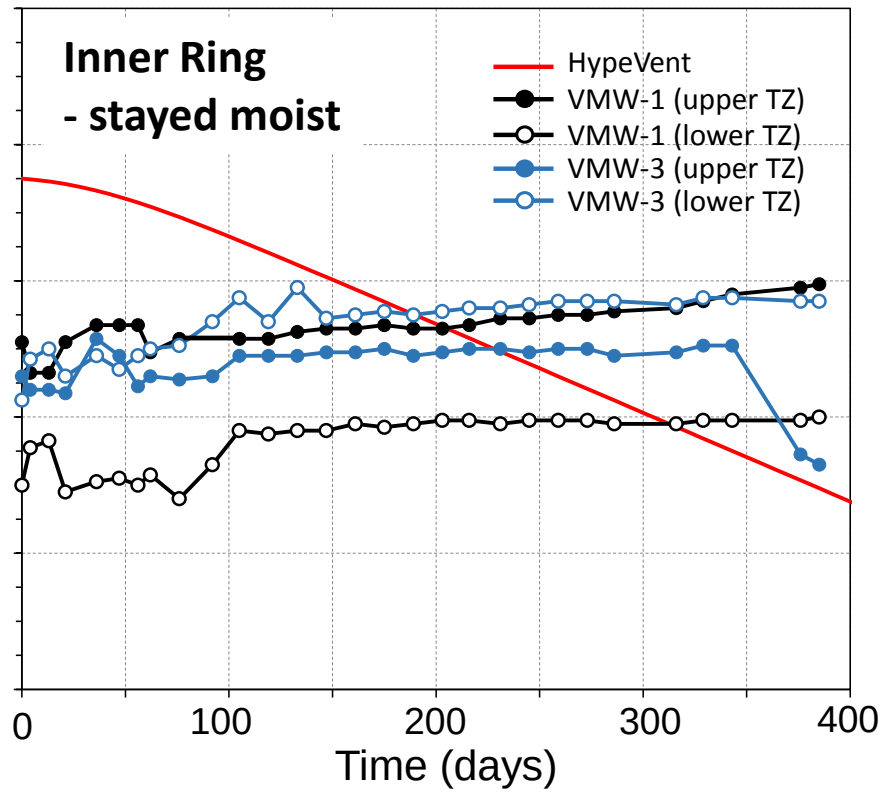


Field Results and HypeVent Model

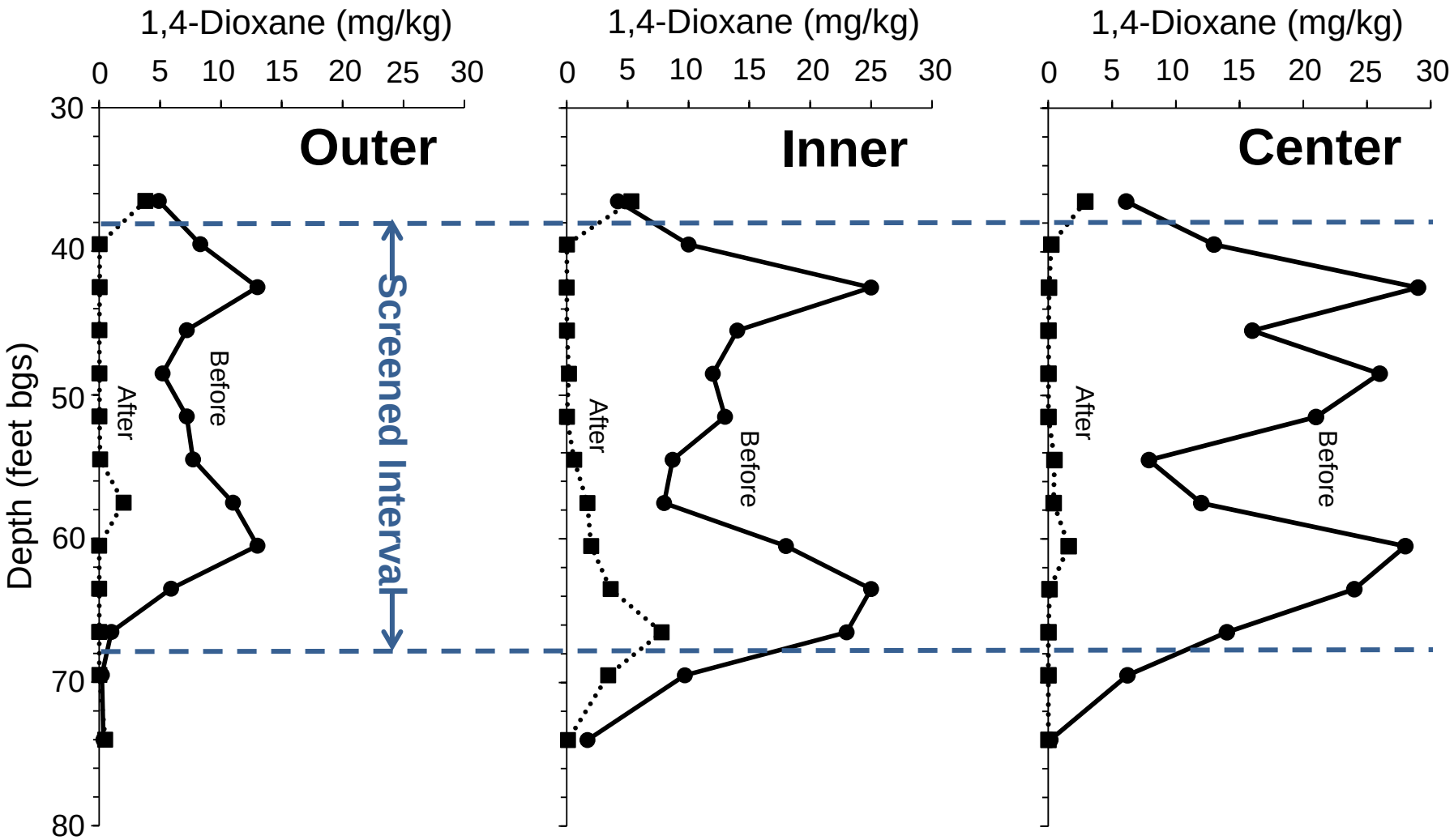
Soil Moisture

- HypeVent worked well as screening level model





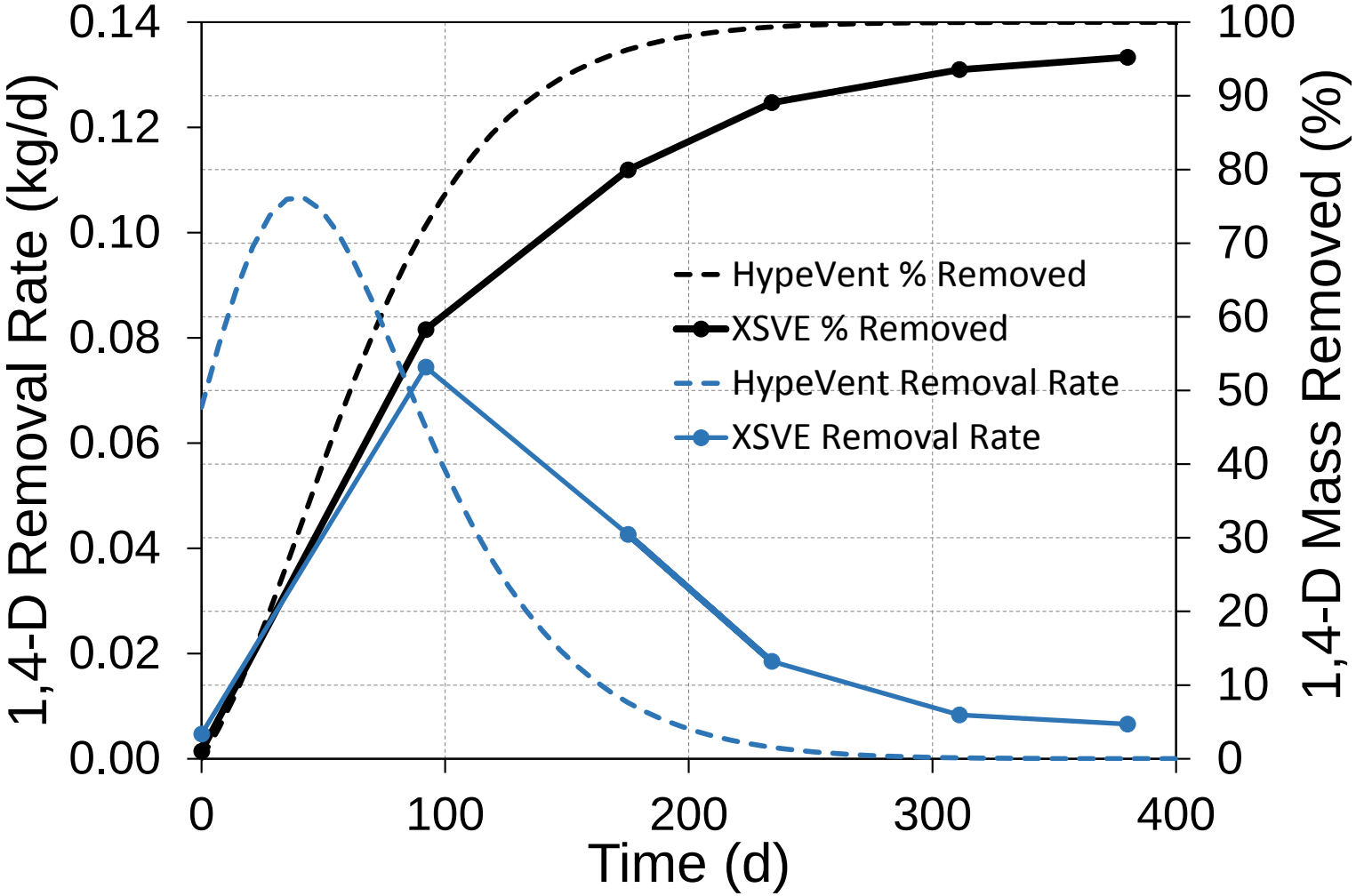
1,4-Dioxane in Soil



95% Loss

Field Results and HypeVent Model

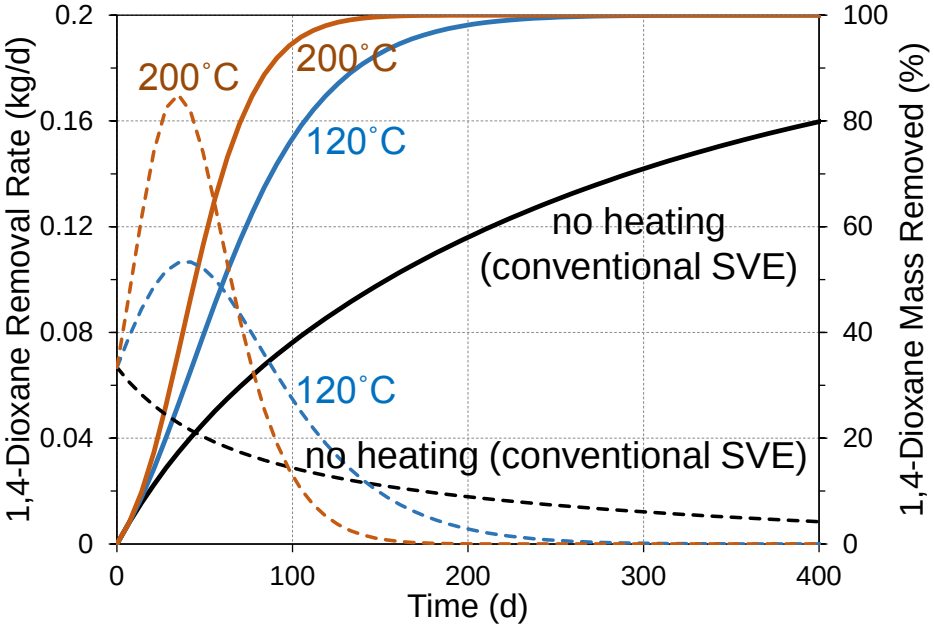
Reasonable Agreement on 1,4-Dioxane Removal

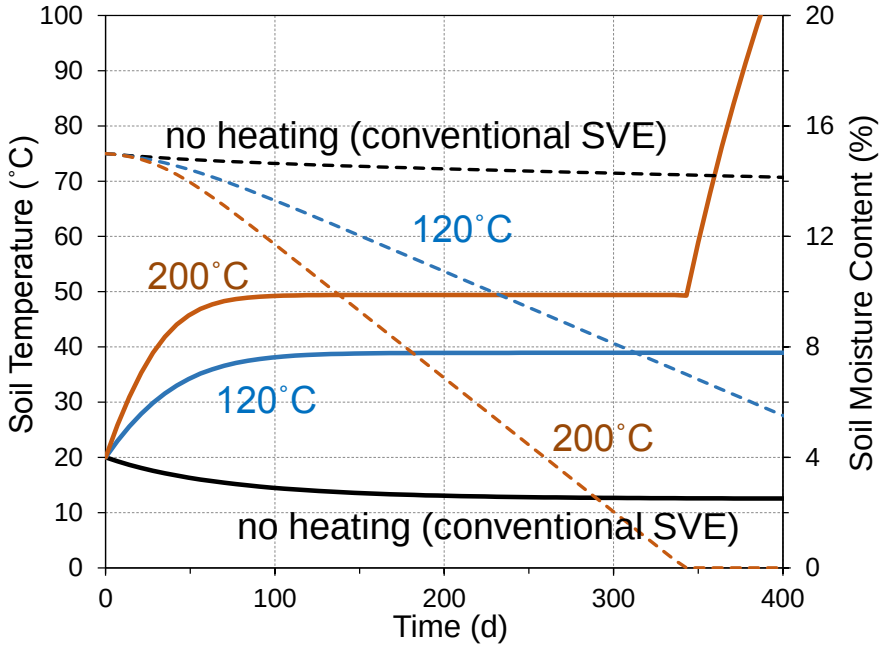


HypeVent Model Sensitivity Analysis

Injection Temperature of Ambient Air

- Injection temperature enhances 1,4-dioxane removal substantially over conventional SVE

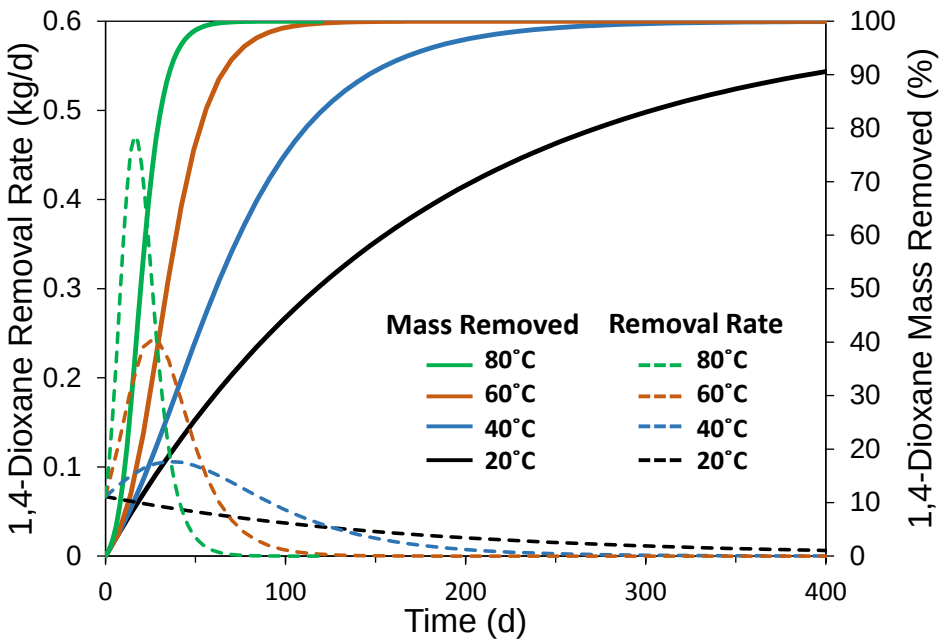


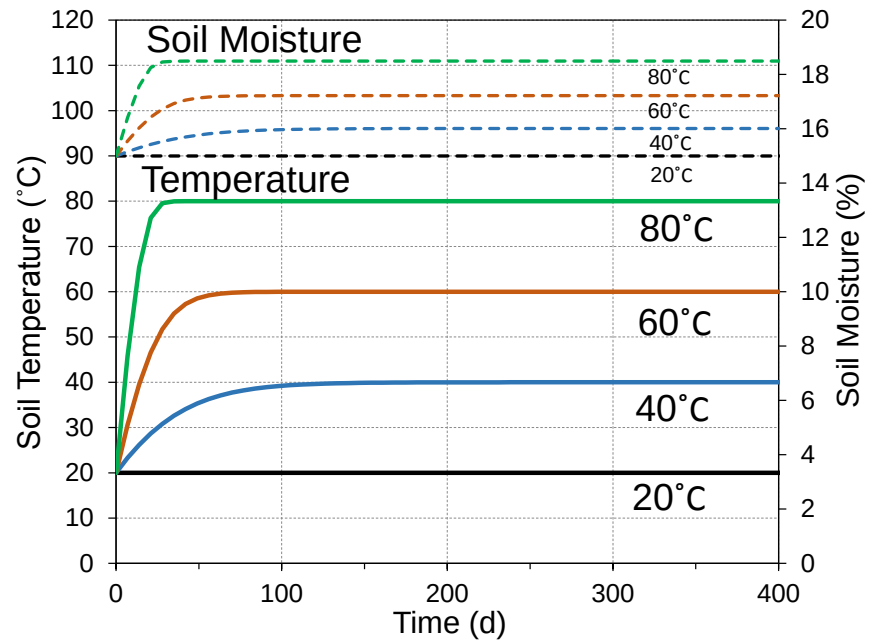


HypeVent Sensitivity Analysis

Varied Injection Temperature at 100% RH

- 100% RH heated injection may work
- Condensation – potential downward migration of 1,4-dioxane





Key Take-Home Messages

- Enhanced SVE (XSVE) successfully remediates 1,4-dioxane
  - ~95% mass removal in this study
  - Alternative to excavation
  - Provides DoD site viable remedial option for 1,4-dioxane in vadose zone
- High flow rates are required (i.e., focused extraction)
  - ~20,000 void volumes in this study
  - ~200 to ~5,000 void volumes for conventional SVE
- Heating helps
  - Estimated cost of heating ~$25/yd^3 in this study
  - More heat would speed up the process, but could increase costs
- HypeVent Model
  - Useful feasibility assessment and design tool

For additional information, please visit

https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Emerging-Issues/ER-201326

Speaker Contact Information

rob@hinchee.org; 850-984-4460

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Q&A Session 3

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The next webinar is on April 20, 2017

Solutions for Installations' Participation in Energy Markets

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