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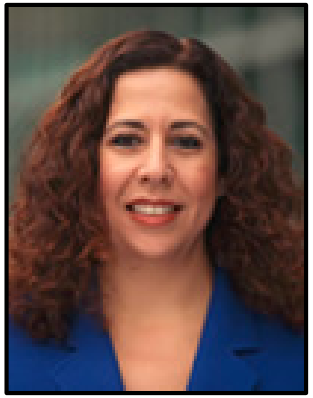
Advances in the Treatment of 1,4-Dioxane in Mixed Contaminant Plumes

June 18, 2020

SERDP DOD • EPA • DOE | ESTCP

Welcome and Introductions



Rula A. Deeb, Ph.D.
Webinar Coordinator

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Webinar Agenda

- **Webinar Logistics** (5 minutes)
  Dr. Rula Deeb, Geosyntec Consultants
- **Overview of SERDP and ESTCP** (5 minutes)
  Dr. Andrea Leeson, SERDP and ESTCP
- **Synergistic Reductive Dechlorination of 1,1,1-Trichloroethane and Trichloroethene and Aerobic Biodegradation of 1,4-Dioxane** (25 minutes + Q&A)
  Dr. Bruce Rittmann, Arizona State University
- **Bioelectrochemical Treatment of 1,4-Dioxane in the Presence of Chlorinated Solvents** (25 minutes + Q&A)
  Dr. Jens Blotevogel, Colorado State University
- **Final Q&A session**

Zoom Instructions

- Download Zoom
  - https://zoom.us/download
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- Find the Q&A button on your control bar and type in your question(s)
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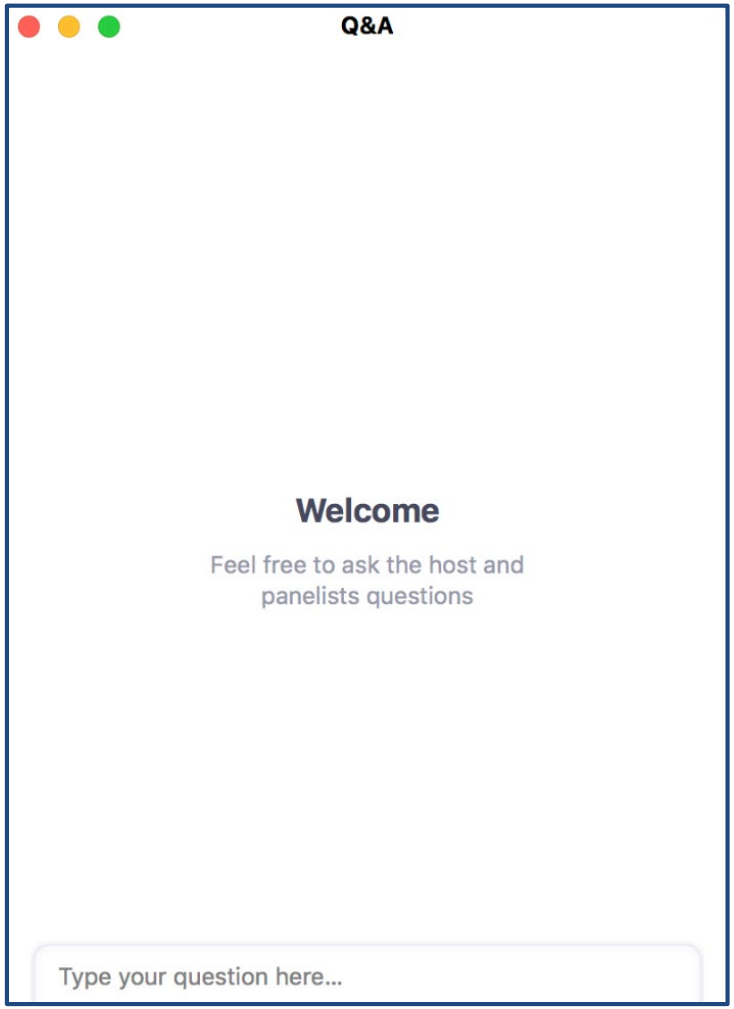

SERDP and ESTCP Overview

Andrea Leeson, Ph.D.
SERDP and ESTCP

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DoD's Environmental Technology Programs

Science and Technology

- Statutory program established 1991
- DoD, DOE, EPA partnership
  - Advanced technology development to address near-term needs
  - Fundamental research to impact real world environmental management

Demonstration and Validation

- Demonstrate innovative cost-effective environmental and energy technologies
  - Transition technology out of the lab
  - Establish cost and performance
  - Partner with end user and regulator
  - Technology transfer
    - Accelerate commercialization or broader adoption
    - Direct technology insertion

Environmental Drivers

Sustaining Ranges, Facilities and Operations

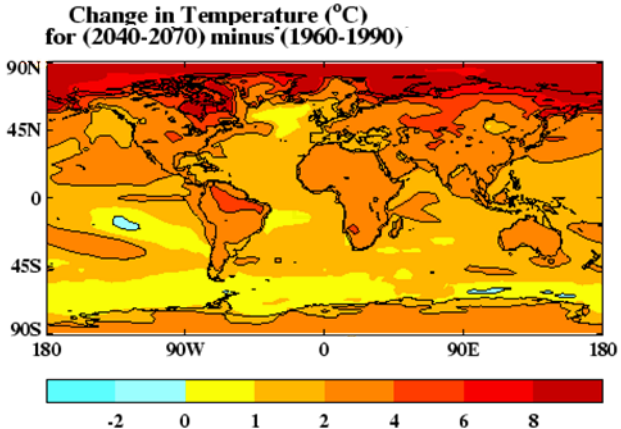
Maritime Sustainability
Threatened and Endangered Species

Toxic Air Emissions and Dust

UXO and Munitions Constituents

Noise

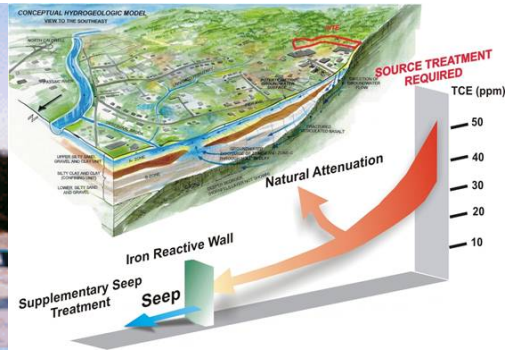
Sustainable FOB



Environmental Drivers

Reducing Current and Future Liability

Contamination from Past Practices



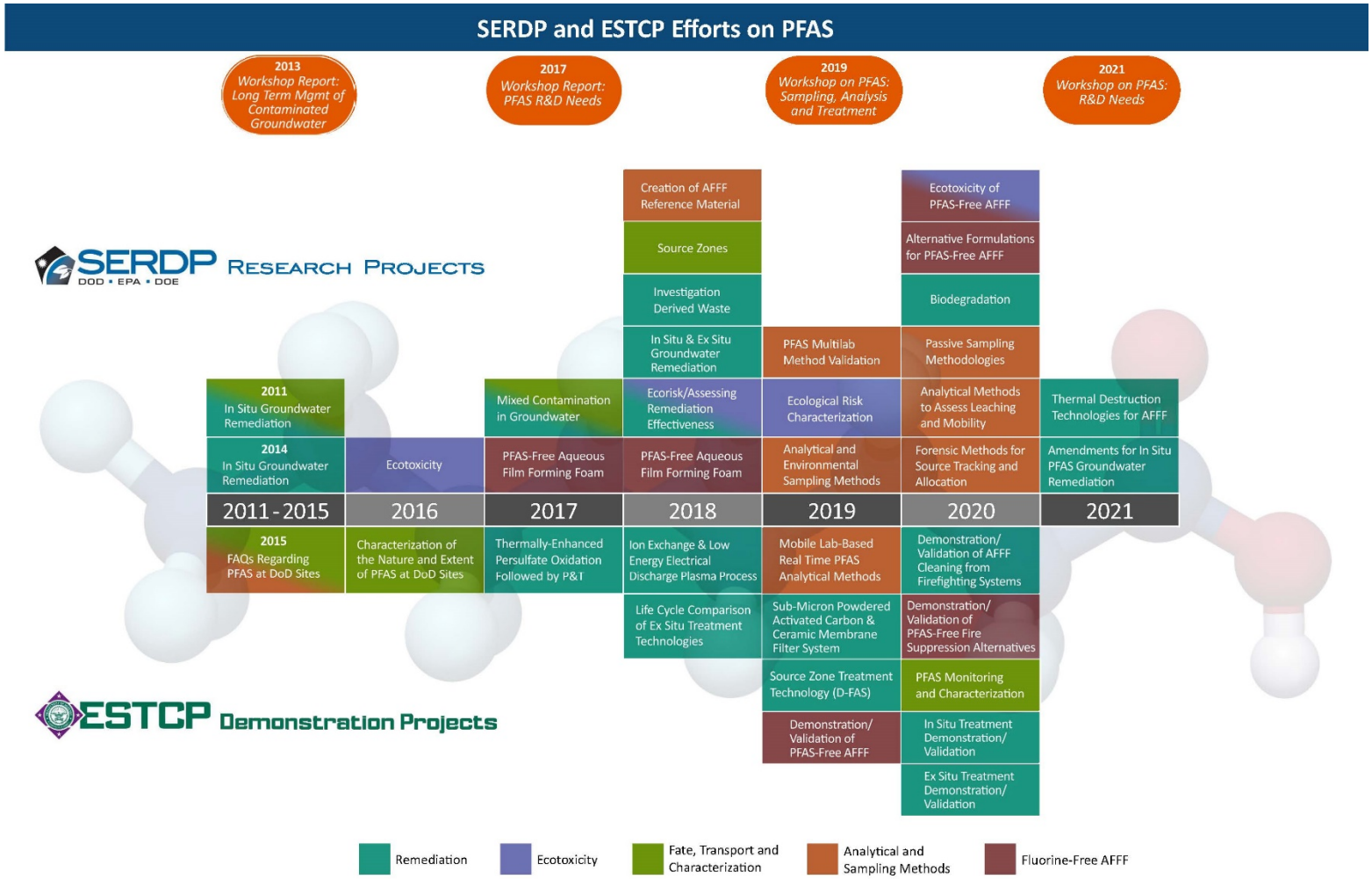
- Groundwater, soils and sediments
- Large UXO liability
- Emerging contaminants

Pollution Prevention to Control Life Cycle Costs

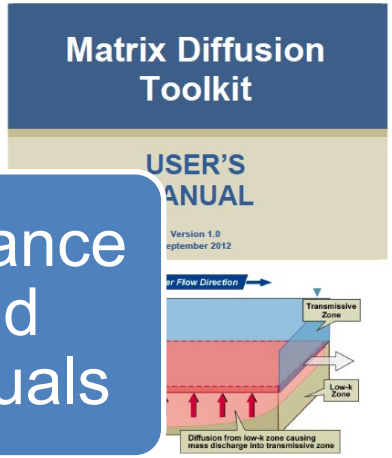
- Elimination of pollutants and hazardous materials in manufacturing, maintenance, and operations
- Achieve compliance through pollution prevention

PFAS Online Resource

https://map.serdp-estcp.org/Featured-Initiatives/Per-and-Polyfluoroalkyl-Substances-PFASs/pfas_efforts.pdf



www.serdp-estcp.org



Webinars

In Person Training

EnviroWiki

Videos

Technology Transfer

Guidance and Manuals

SERDP and ESTCP Webinar Series

Date	Topic
July 9, 2020	Securing DoD Control Systems and Infrastructure from Cyber Threats
July 23, 2020	Predicting PFAS Fate and Transport in Subsurface Environments, and Treatment
August 20, 2020	Addressing Threatened and Endangered Species on DoD Lands
September 10, 2020	Advances in Cold Spray Repair Technologies and Application of Waterjet to Large and Medium Caliber Gun Barrel Refurbishment
September 24, 2020	Munitions Response
October 8, 2020 October 22, 2020	Managing AFFF Impacts to Subsurface Environments and Assessment of Commercially Available Fluorine-Free Foams (**Parts 1** & **2)**

For upcoming webinars, please visit

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Save the Date!

SERDP • ESTCP
SYMPOSIUM

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

December 1-3, 2020
Washington, DC

Poster abstracts due July 15

Synergistic Reductive Dechlorination of 1,1,1-Trichloroethane and Trichloroethene and Aerobic Biodegradation of 1,4-Dioxane

Bruce Rittmann, Ph.D.
Arizona State University

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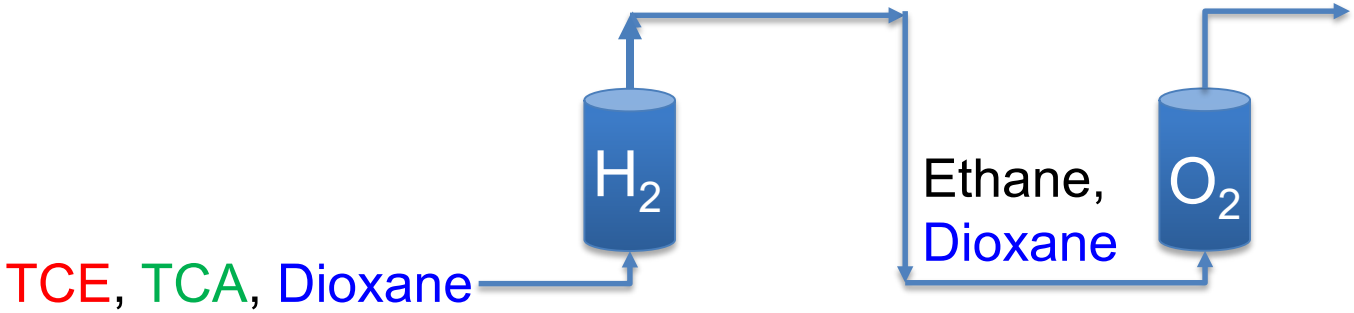
Outline

- The problem
- Overarching objectives
- Membrane-film reactors
- Reductive dechlorination of TCE and TCA
- Aerobic biodegradation of 1,4-dioxane
- The synergistic two-stage system
- Conclusions
- Ongoing research
- Benefits to DoD

The Problem

- Groundwater co-contaminated with 1,4-dioxane and TCA and/or TCE is common
  - 1,4-dioxane was widely used as a stabilizer for chlorinated solvents
- MCLs established by U.S. EPA for TCA and TCE
- State drinking water and groundwater guidelines for 1,4-dioxane
  - Range: 0.25 to 1 µg/L

Overarching Technical Objectives



1. Reduce TCE and TCA to ethane in a H_2-based first stage
2. Enhance co-metabolism of 1,4-dioxane by using ethane as the primary donor substrate in an O_2-based second stage
3. Run the two stages in series for complete removals of TCE, TCA, and dioxane

Foundation Information

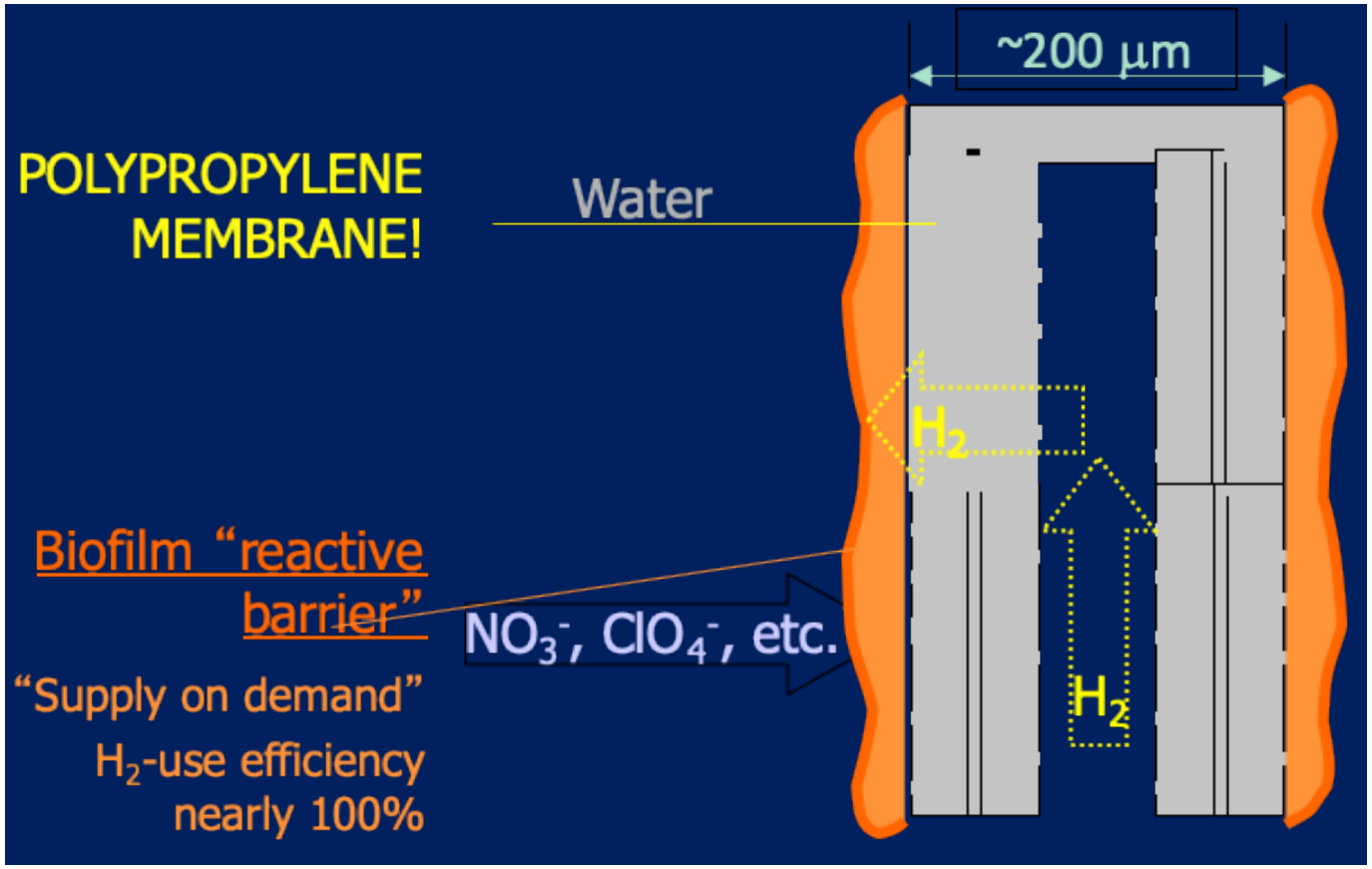
- Membrane-film reactors
  - Direct delivery of a gaseous reactant to a catalyst on the surface of a gas-transfer membrane

Foundation Information

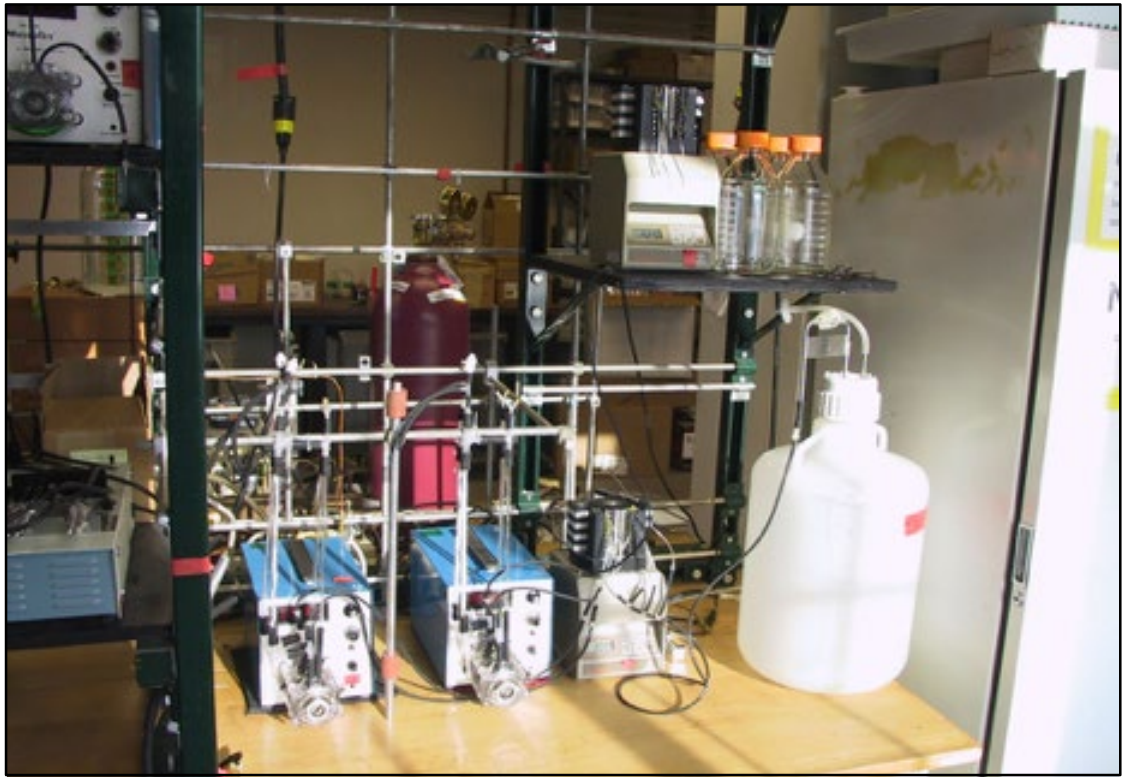
- The H_2-based Membrane Biofilm Reactor (H_2-MBfR)
  - A long-standing process to reduce oxidized contaminants in water (e.g., nitrate, perchlorate, selenate, chromate, and chlorinated solvent)

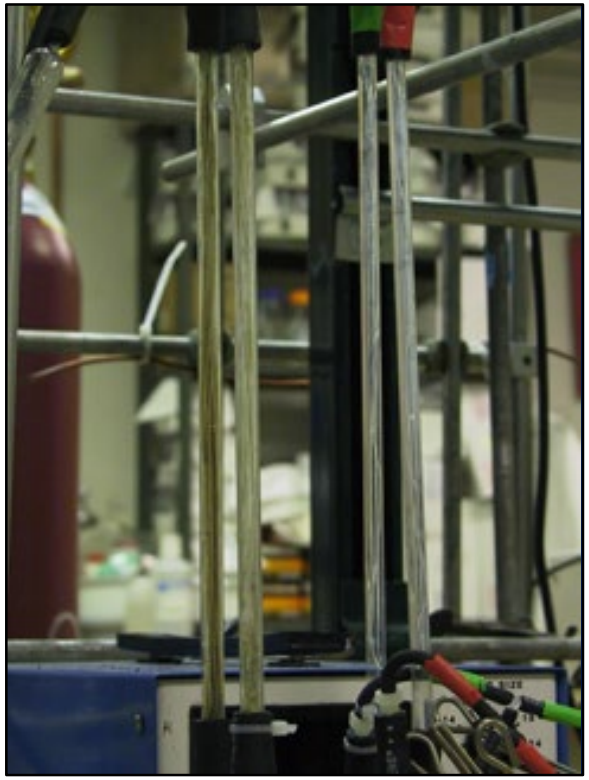
The H_2-Based MBfR

Basis: Biofilm on a bubble-less gas-transfer fiber



Pictures of MBfRs for Bench-Scale Studies





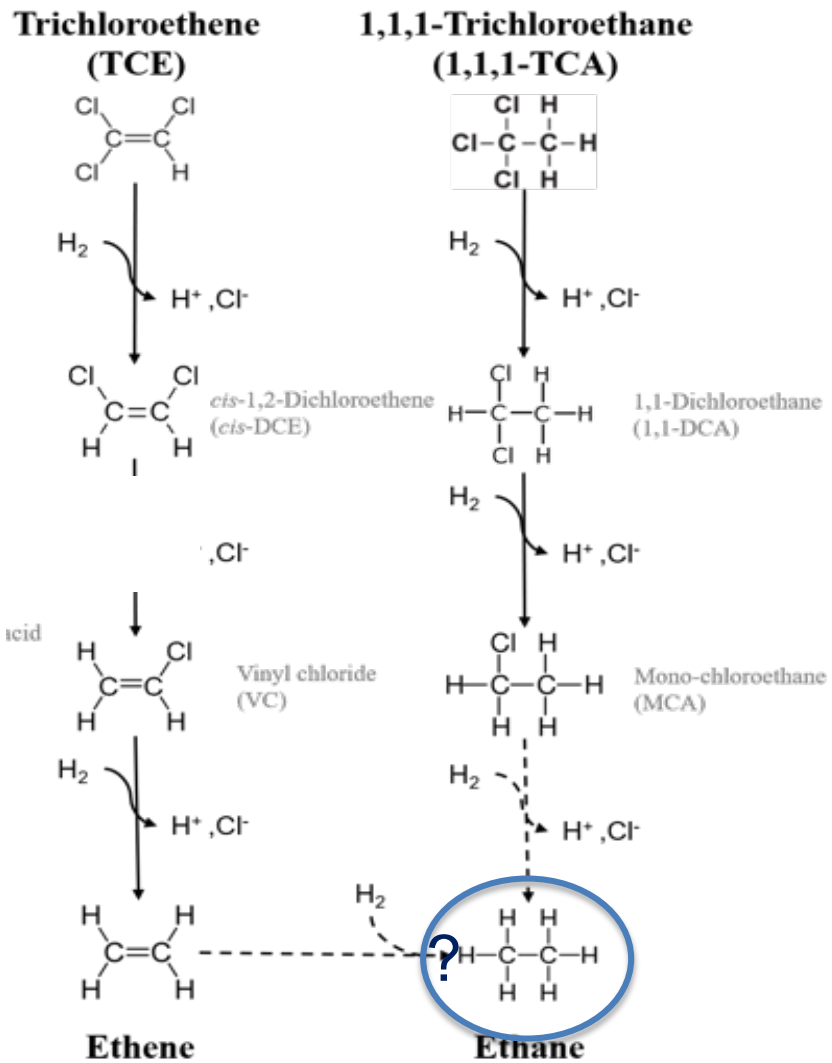
Full-Scale MBfRs for Nitrate Reduction – APTwater

Rancho Cucamonga, CA

La Cresenta, CA

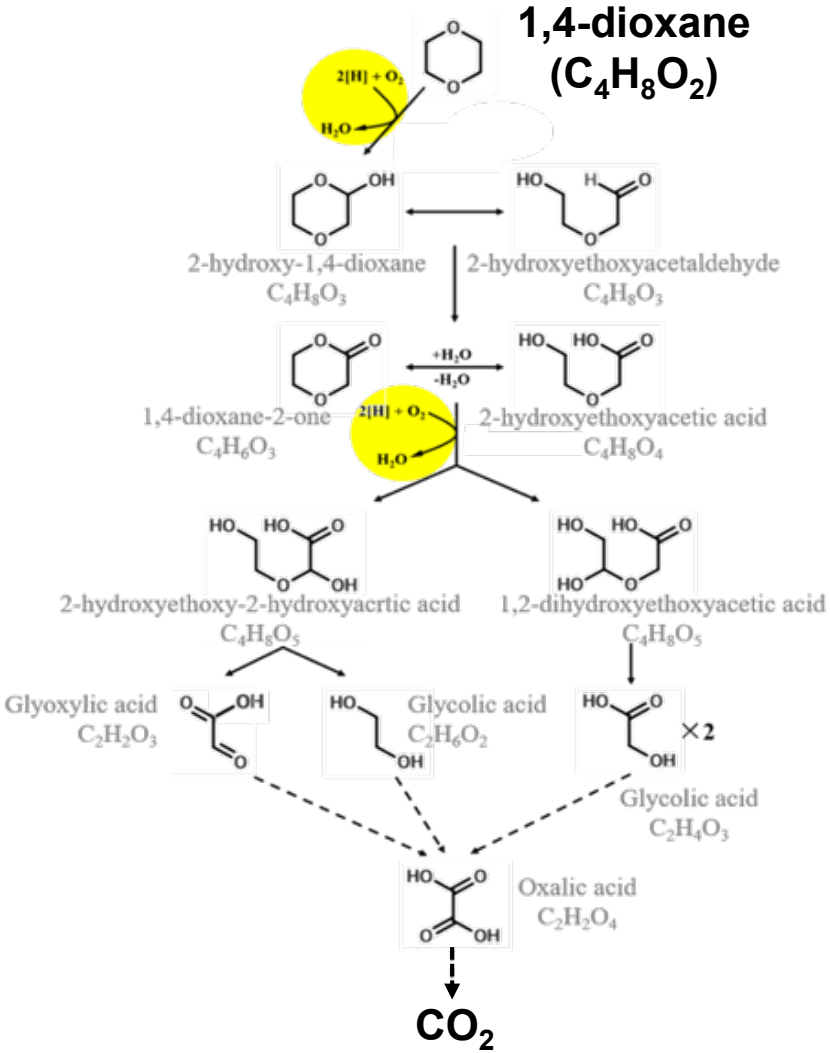
Foundation for Reductive Dechlorination

- Can be accomplished microbially or catalytically

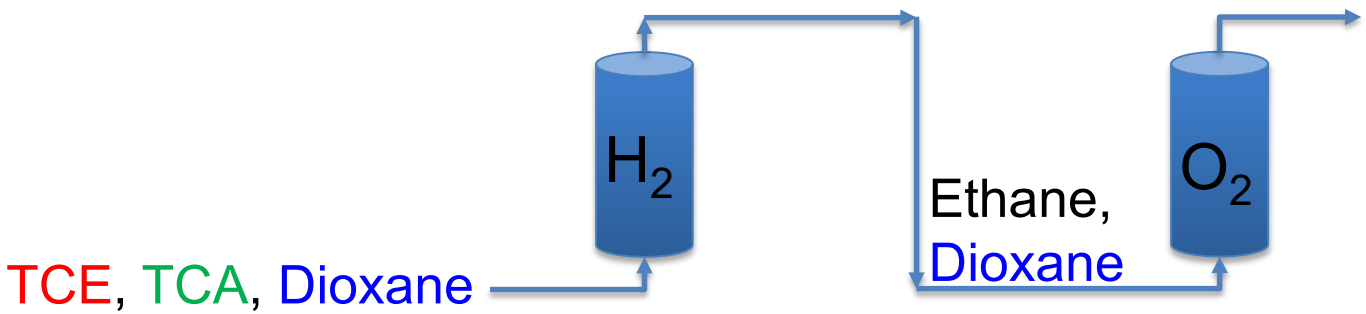


Foundation for Aerobic 1,4-Dioxane Biodegradation

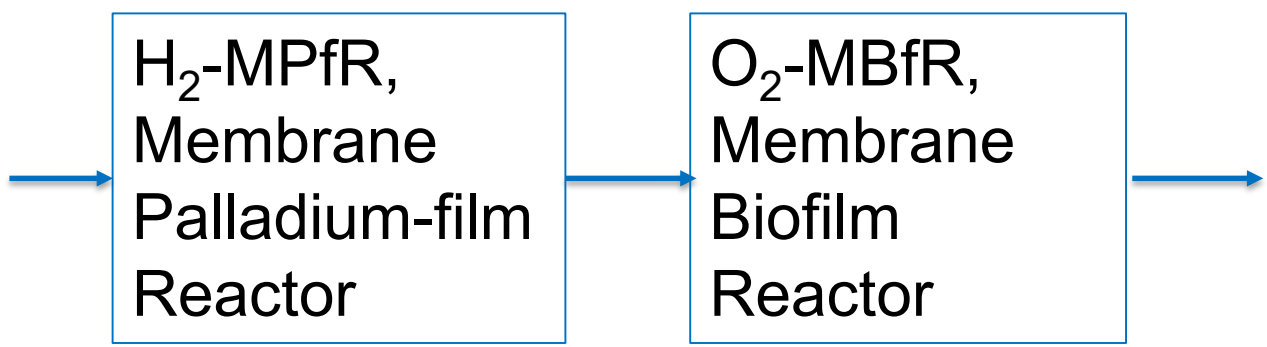
- Yellow highlights the initial monooxygenation reactions
- Ethane oxidation is the source of 2[H] and stimulates the expression of the mono-oxygenases



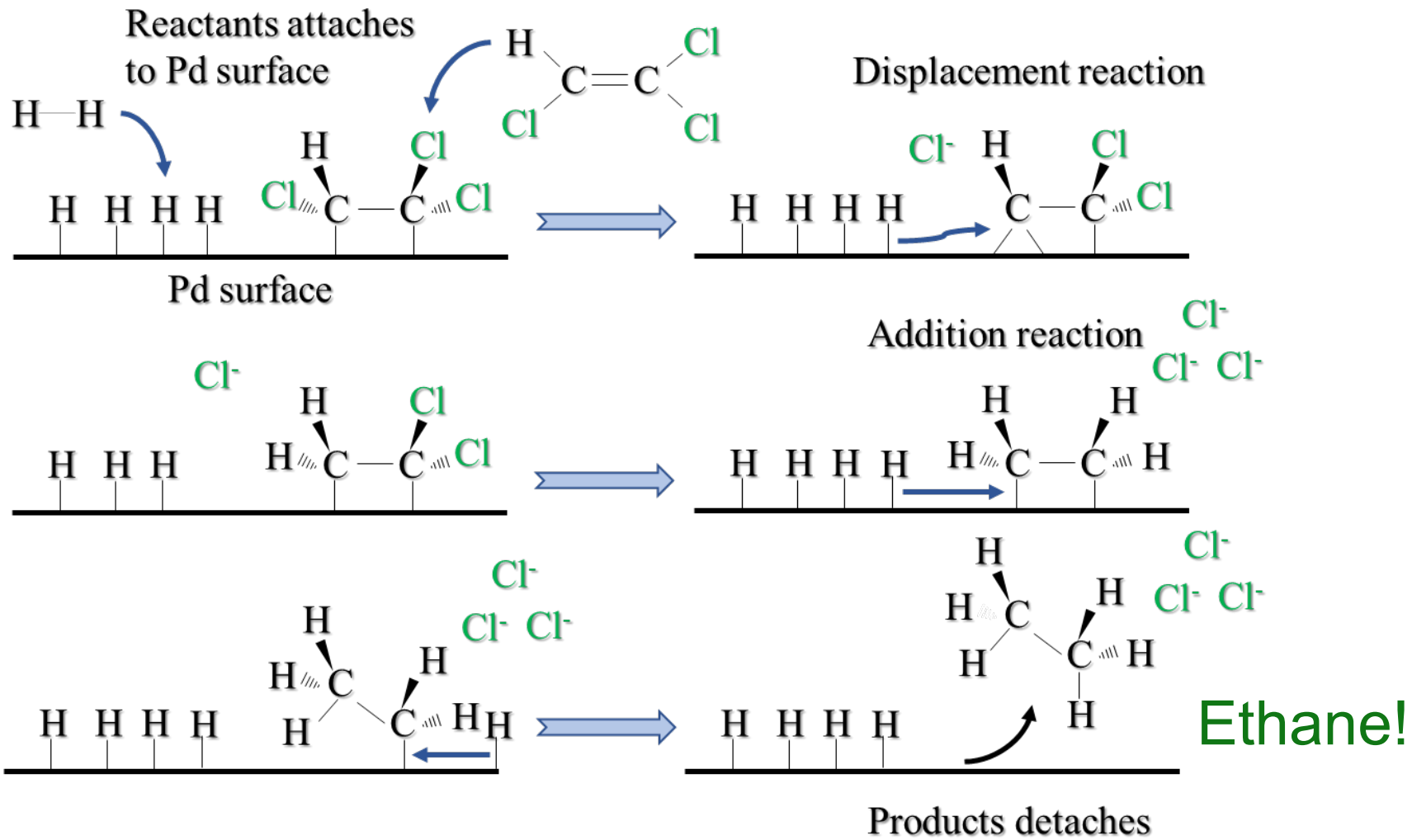
Technical Approach



What worked well

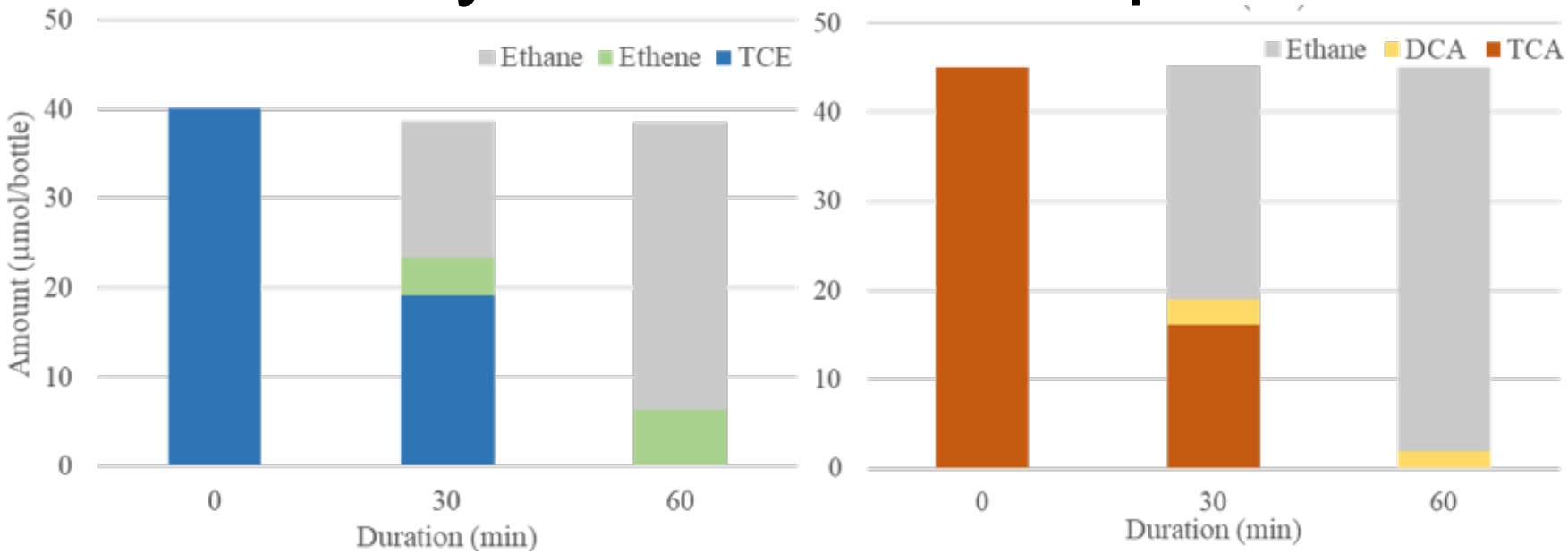


Pd-Catalyzed TCE Hydrodechlorination



Note: *Pd = Palladium*

Initial Proof of Hydrodechlorination to Ethane by Palladium Nanoparticles

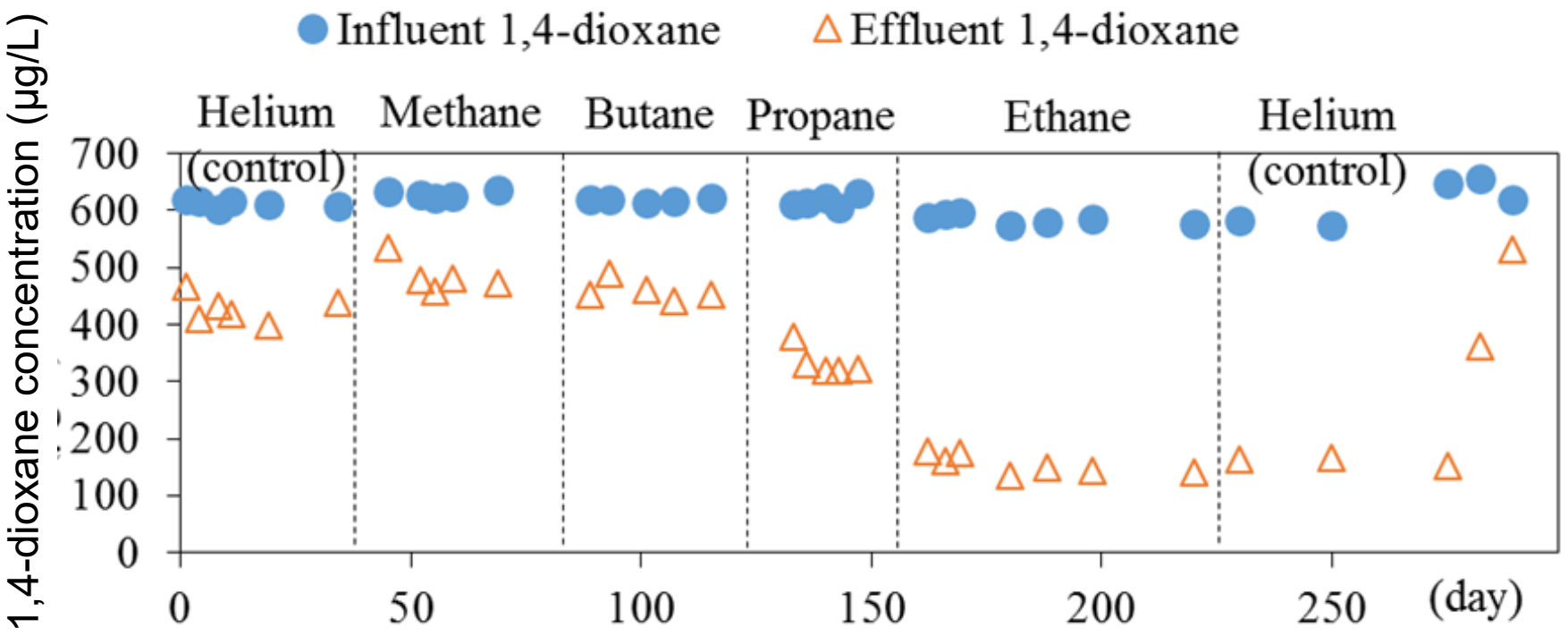


- TCE and TCA reductions catalyzed by suspended PdNPs in batch tests
- Almost all to ethane!
- The missing mass for TCE was MCA and DCA (< 3 µmole each)

Note: *PdNPs = Palladium nanoparticles*

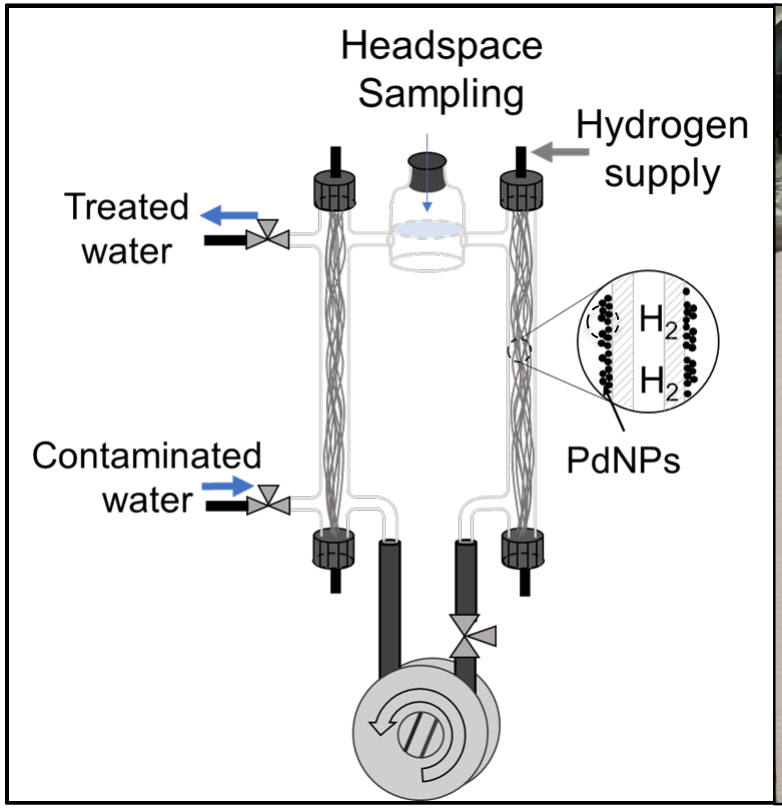
Ethane vs. Other Alkanes

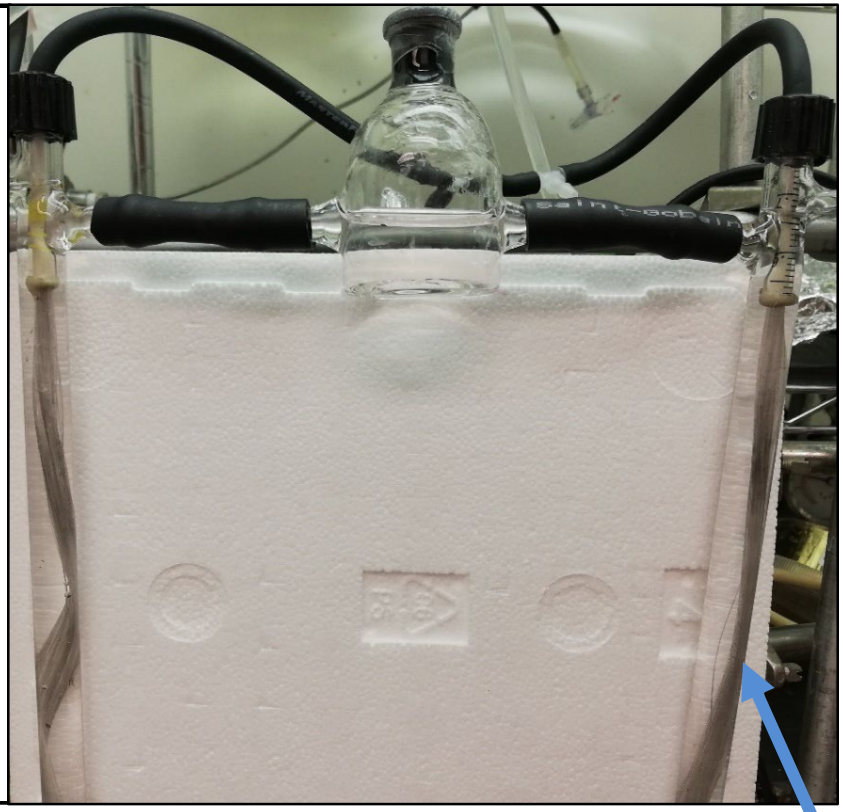
1,4-dioxane biodegradation in the MBfR



TCE AND TCA REDUCTIONS IN THE H_2-MPfR

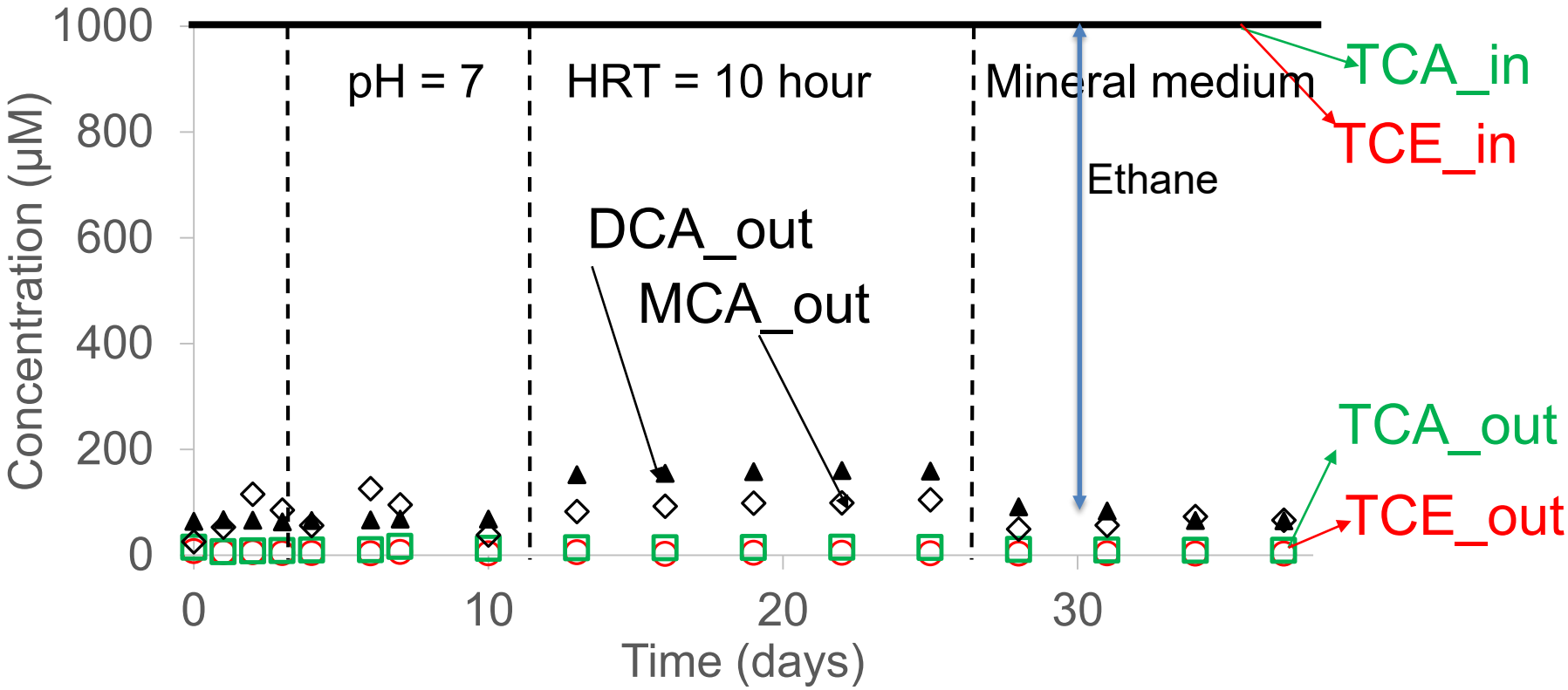
TCE and TCA Reductions in the H_2-MPfR





***In situ* Pd reduction and coating (black)**

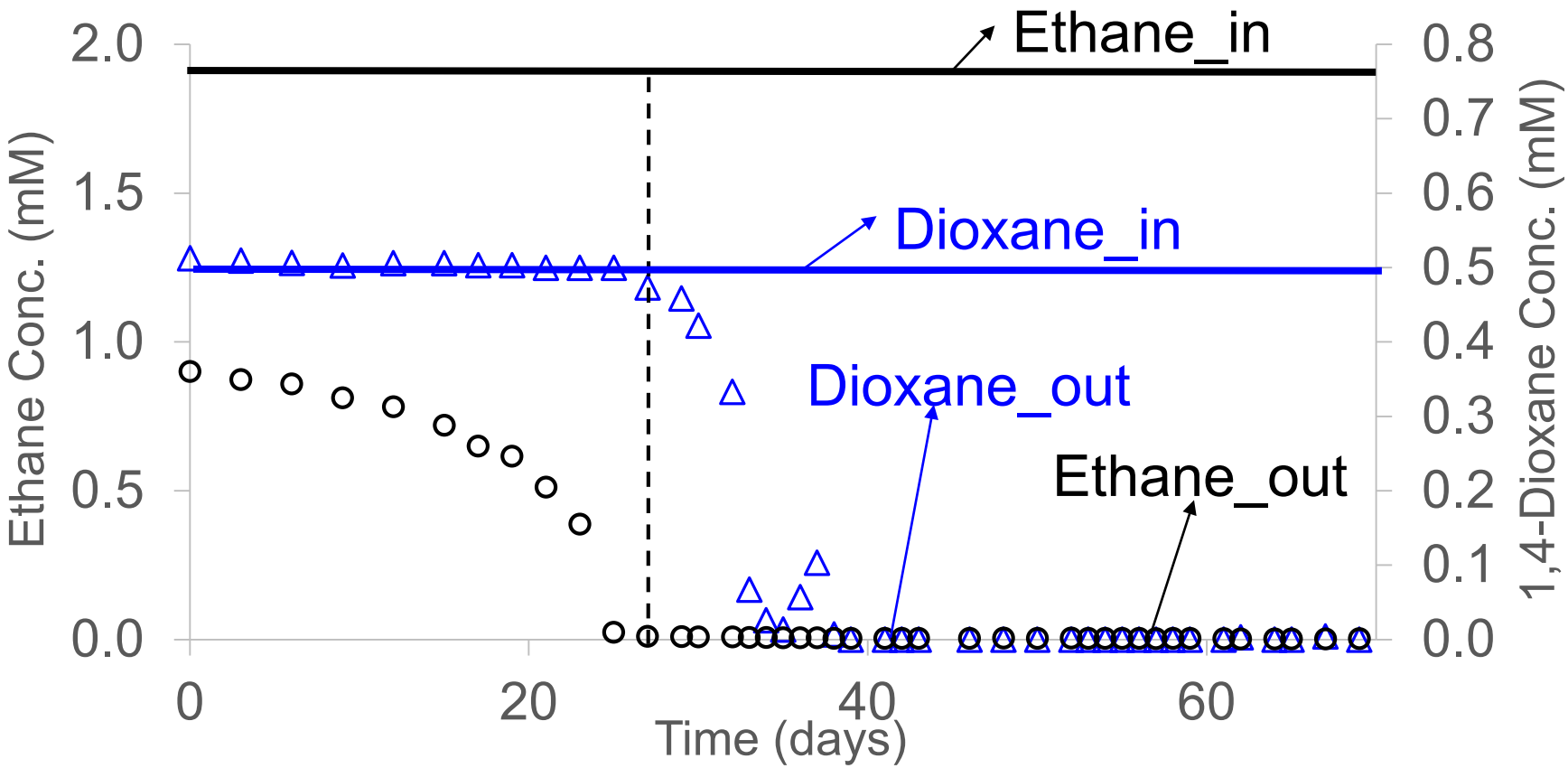
Results for TCE and TCA in the H_2-MPfR



- Continuous-flow (loading = 50 - 75 mmol/m^2-day)
- Key findings: >96% removals, >93% to ethane = Success!

1,4-DIOXANE BIODEGRADATION IN THE O_2-MBfR

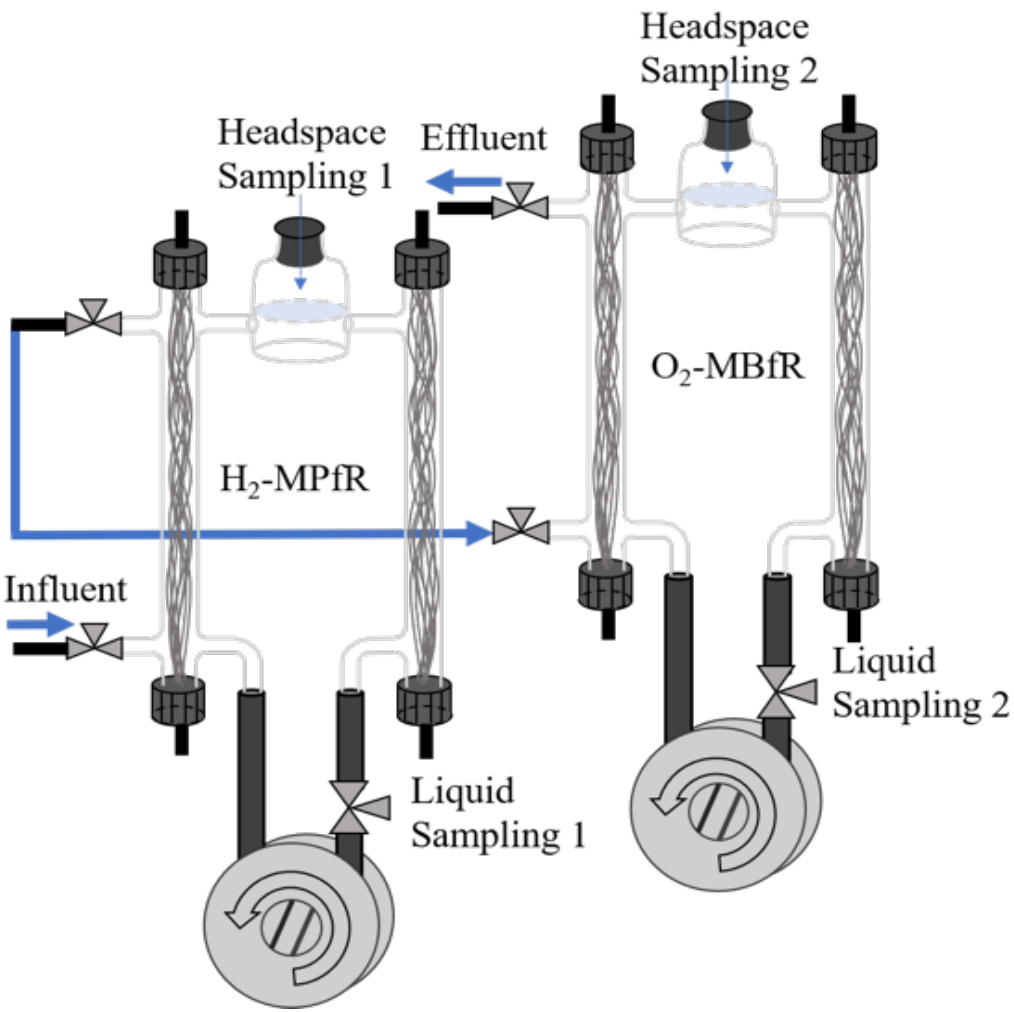
Results for Dioxane in the O_2-MBfR



- Continuous-flow (loading = 3.4 mmol/m^2-day)
- >99% removal, dioxane < detection limit (20 ppb) = Success!

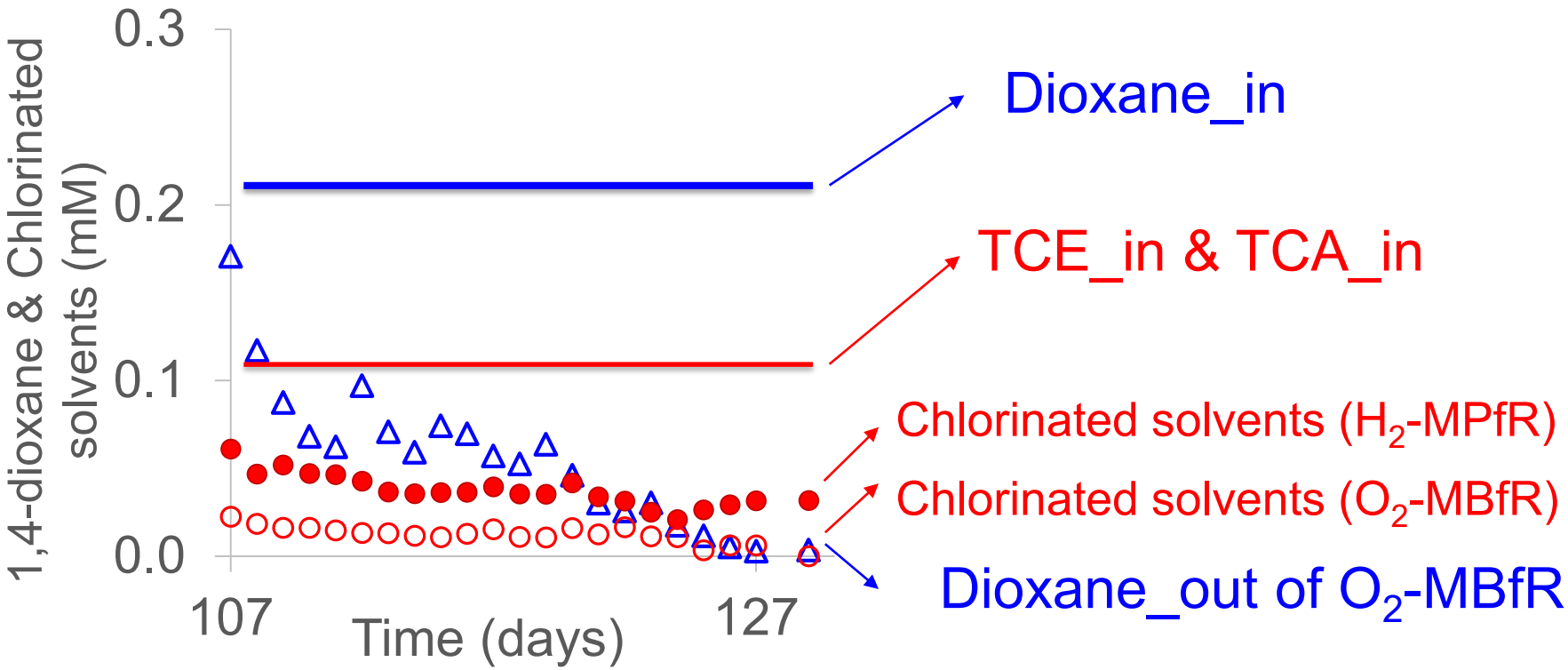
SYNERGISTIC TWO-STAGE SYSTEM

Two Stages in Series
H_2-MPfR → O_2-MBfR



Results from Two Stages in Series

After 130 Days of Continuous Operation



- Continuous-flow (loading ~1 mmol/m^2-day)
- All contaminants concentrations < MCLs (chlorinated) or the dioxane detection limit. Success!

Conclusions

- The two-stage system synergistically removed TCE, TCA, and dioxane to below all MCLs or detection limit (for 1,4-dioxane)
- As the first stage for TCE and TCA reduction, the H_2-MPfR was efficient for nearly complete TCE and TCA reduction to ethane
- Ethane from the H_2-MPfR significantly stimulated dioxane biodegradation in the O_2-MBfR via two mechanisms:
  - Inducing the mono-oxygenase and providing the electron donor

Ongoing Research

- Current SERDP scope of work
  - Focus on the O_2-MBfR and 1,4-dioxane
  - Better define need for ethane in the O_2-MBfR
    - Coordinated experiments and modeling at ASU and FSU
- For longer term, develop synergistic system for pilot testing
- In parallel, using the H_2-MPfR for reductions of PFOA, RDX, and HMX
  - It works for all of them!
  - Full mineralization is possible when coupled to an MBfR

Benefits to DoD

- The synergistic system provides a single treatment solution for TCE, TCA, and 1,4-dioxane
- The only inputs are H_2 and O_2, which can be generated on-site and on-demand
- The system has no need for hazardous chemicals, extreme conditions, or large energy input
- The system builds directly on an existing technology base

Acknowledgements

- ASU co-PIs
  - Dr. Chen Zhou and Dr. Rosa Krajmalnik-Brown
- FSU co-PI
  - Dr. Youneng Tang
- ASU researchers
  - Mr. Yihao Luo and Dr. Min Long
- FSU researchers
  - Mr. Boya Wang, Ms. Yi Xiong, and Mr. Ermias Tesfamarian
- APTwater collaborator
  - Mr. David Friese

For additional information, please visit
https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/ER-2721

Speaker Contact Information

rittmann@asu.edu; 480-727-0434

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Q&A Session 1

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Bioelectrochemical Treatment of 1,4-Dioxane in the Presence of Chlorinated Solvents

Jens Blotevogel, Ph.D.
Colorado State University

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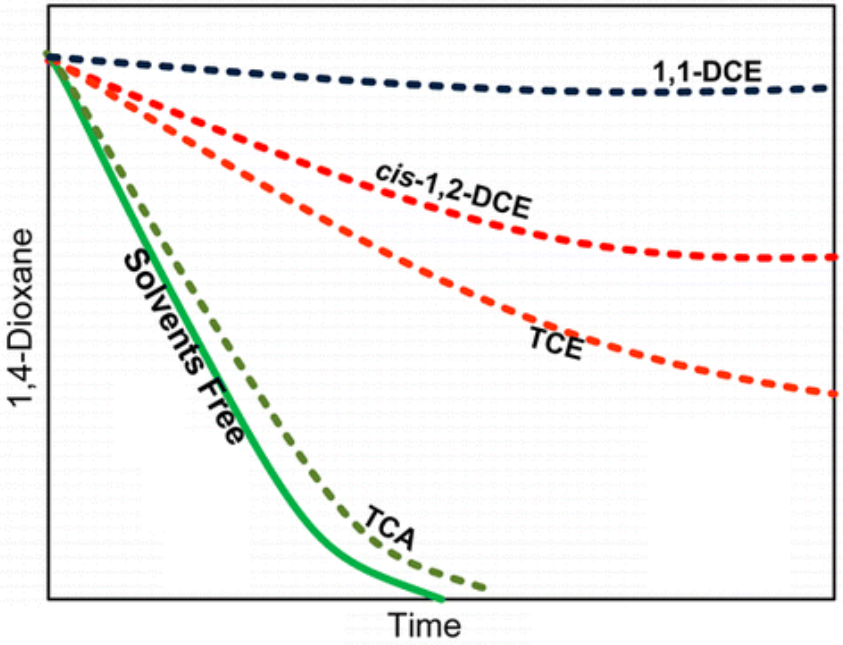
Agenda

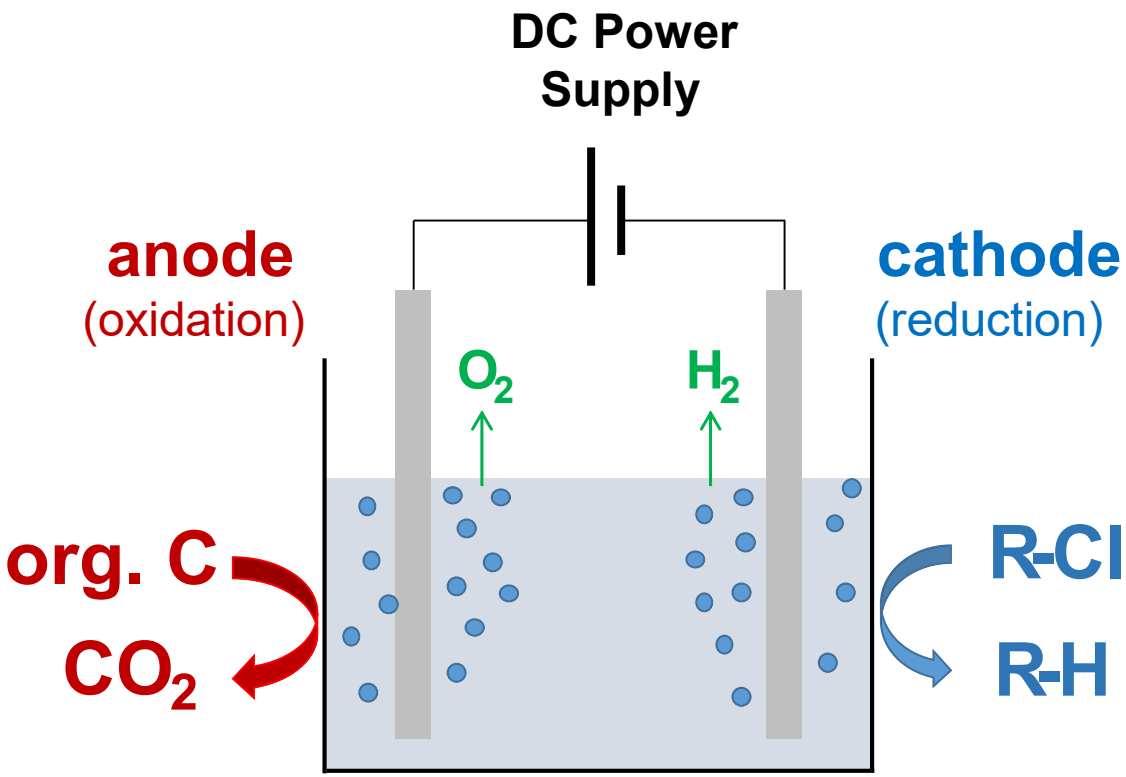
- Problem statement
- Technology description
- Bench-scale performance
- Technology scale-up
- Conclusions
- Benefits to DoD

1,4-Dioxane Biodegradation is Inhibited by Chlorinated Solvents

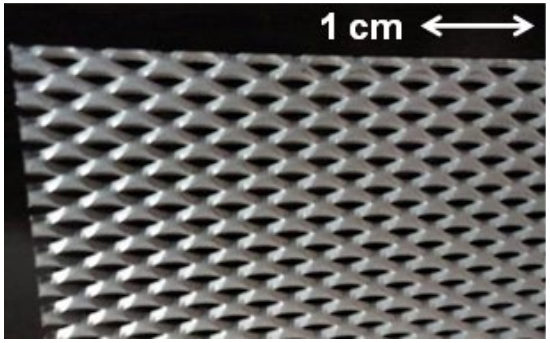
- Aerobic cometabolic
  - Organic co-substrate
- Aerobic metabolic
  - *Pseudonocardia dioxanivorans* CB1190
    - Microaerophilic
    - Survives anoxic periods
    - pH 5-8 for growth
- Biodegradation to below MCLs is challenging



Electrochemical Oxidation Can Degrade Virtually Any Organic Contaminant



$2\ H_2O \rightarrow O_2 + 4H^+ + 4e^-$ $\qquad$ $2H^+ + 2e^- \rightarrow H_2$

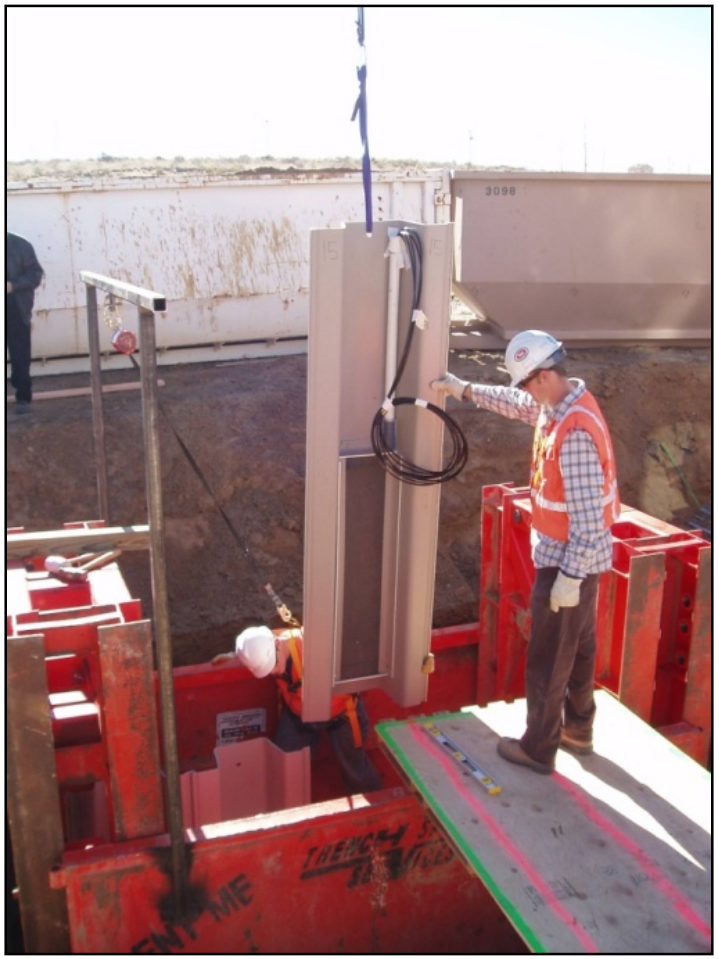


Dimensionally **S**table **A**nodes

- Ti / SnO_2-X*
- Ti / IrO_2-Ta_2O_5
- Ti / Ti_nO_{2n-1}
- Nb / BDD

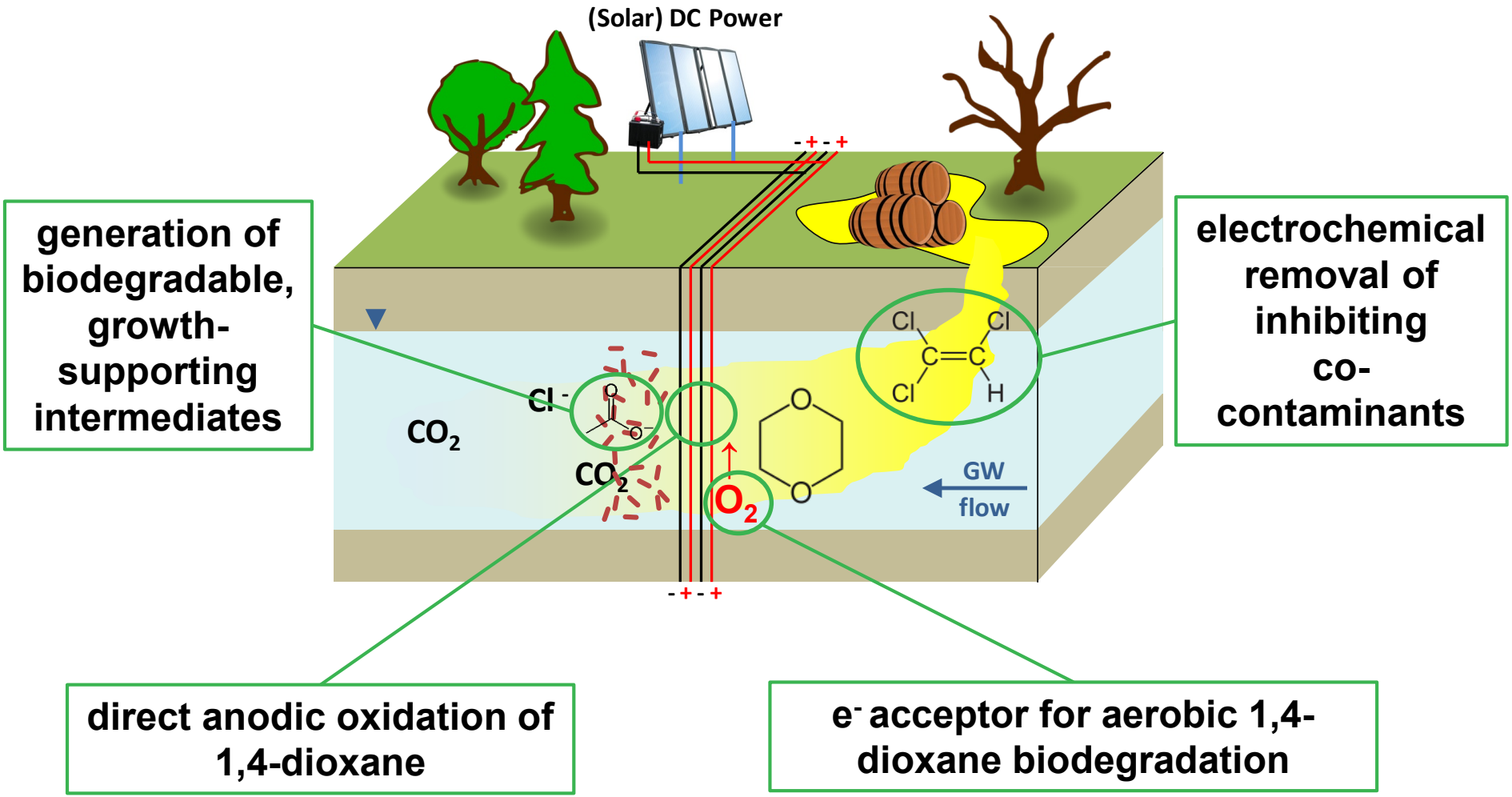
**used in this study*

Mesh Electrodes Enable Installation as Permeable Reactive Barrier (e^-barrier)

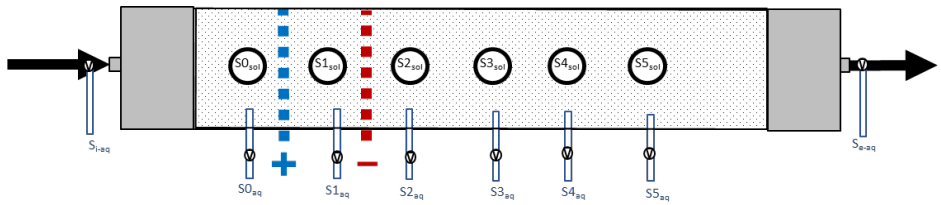


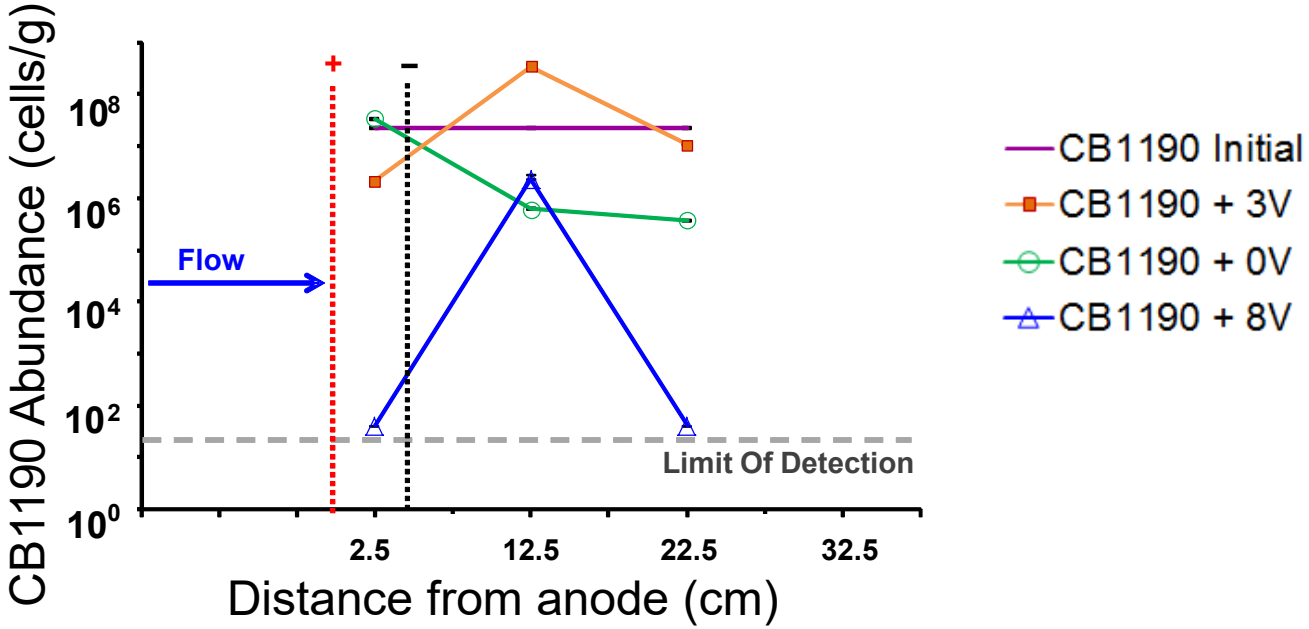
ESTCP ER-0112
ESTCP ER-0519
PI Tom Sale (CSU)

Synergistic Benefits of Bioelectrochemical Treatment

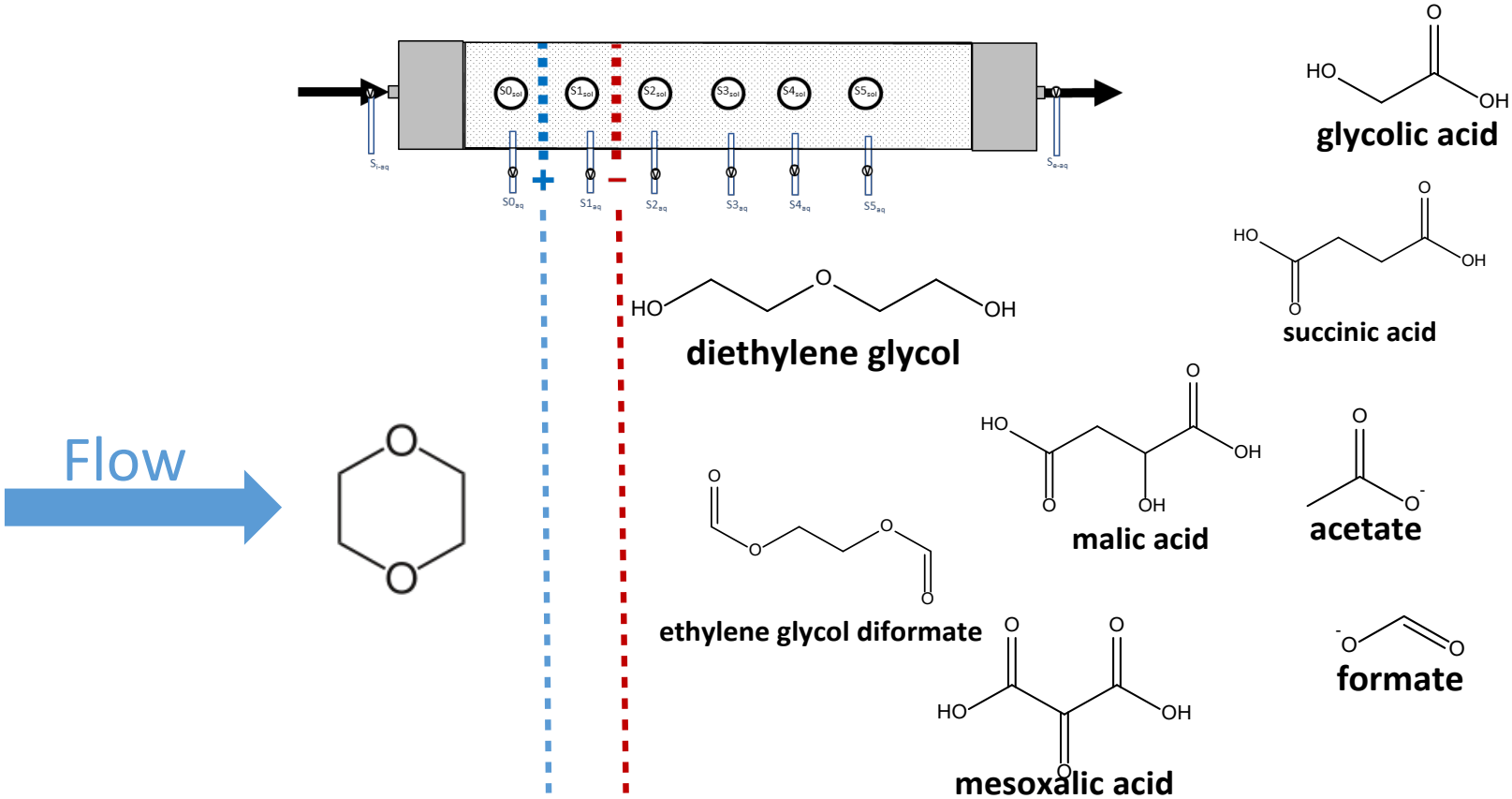


"Sweet Spot" of Bacterial Abundance ~10 cm Downstream of Anode

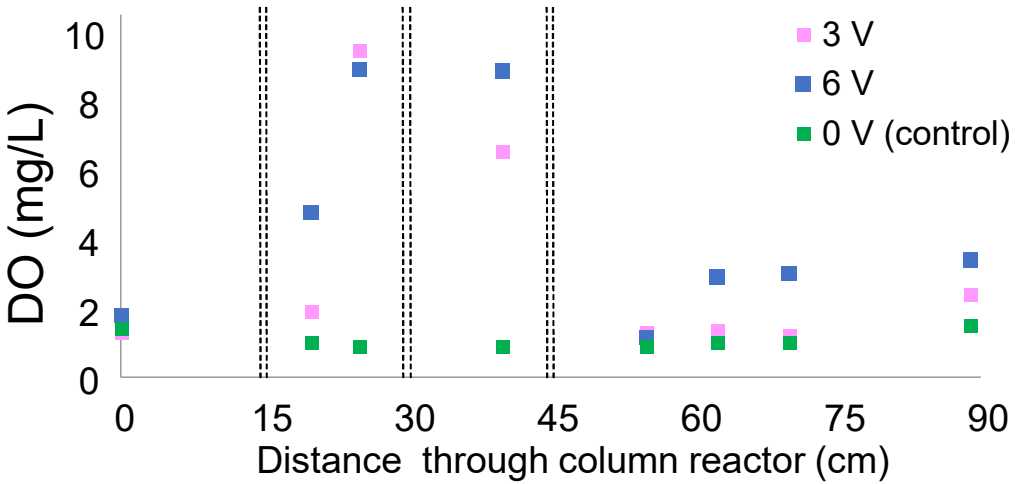


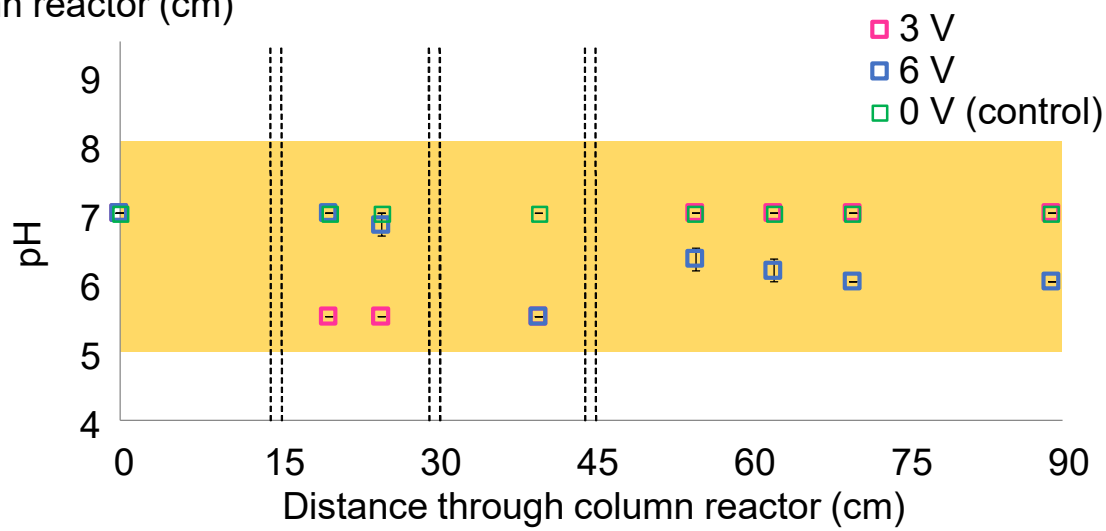


Incomplete 1,4-D Oxidation Generates Growth-Supporting Intermediates

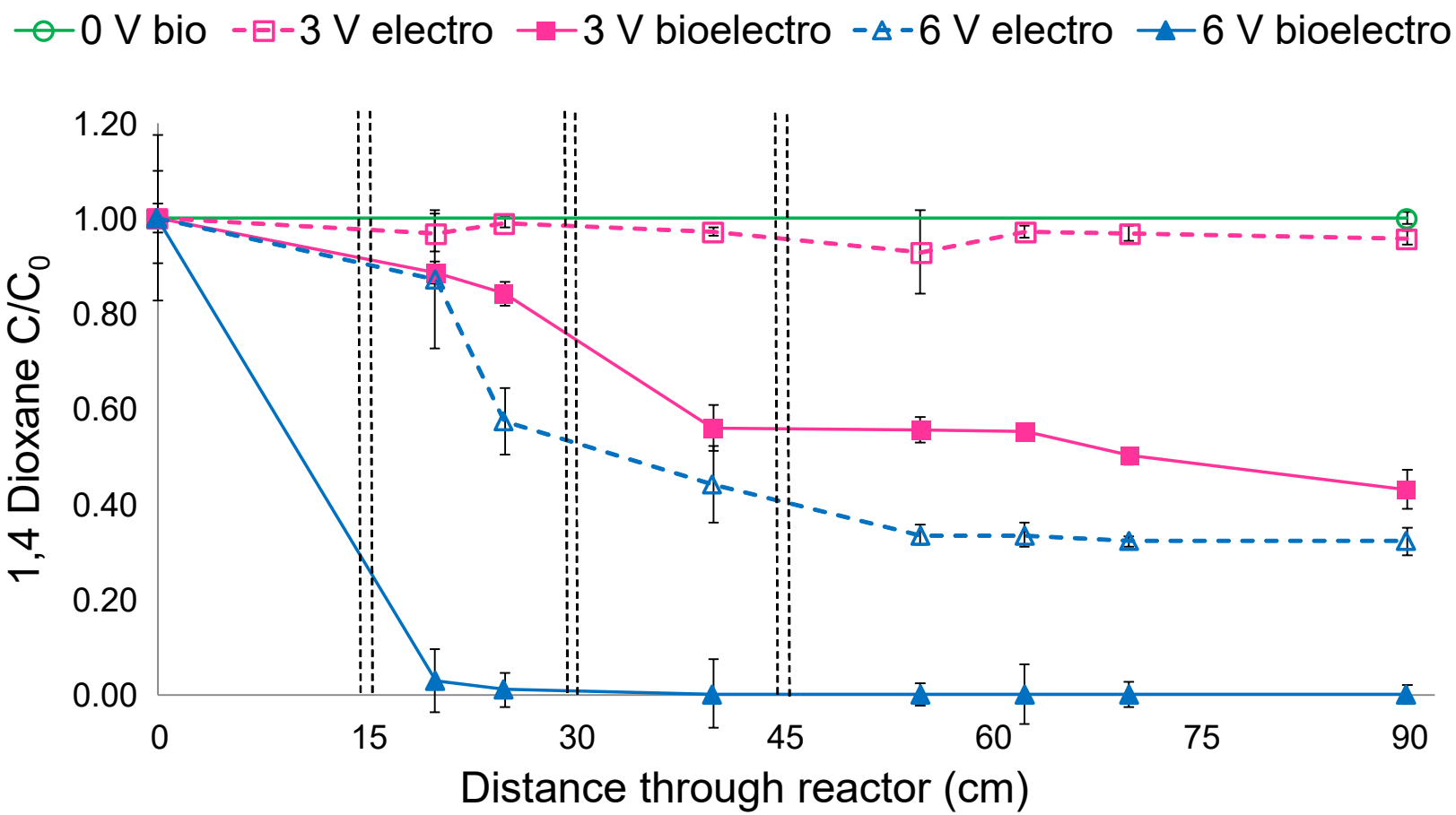


Water Electrolysis Increases Dissolved Oxygen (DO), pH Circumneutral

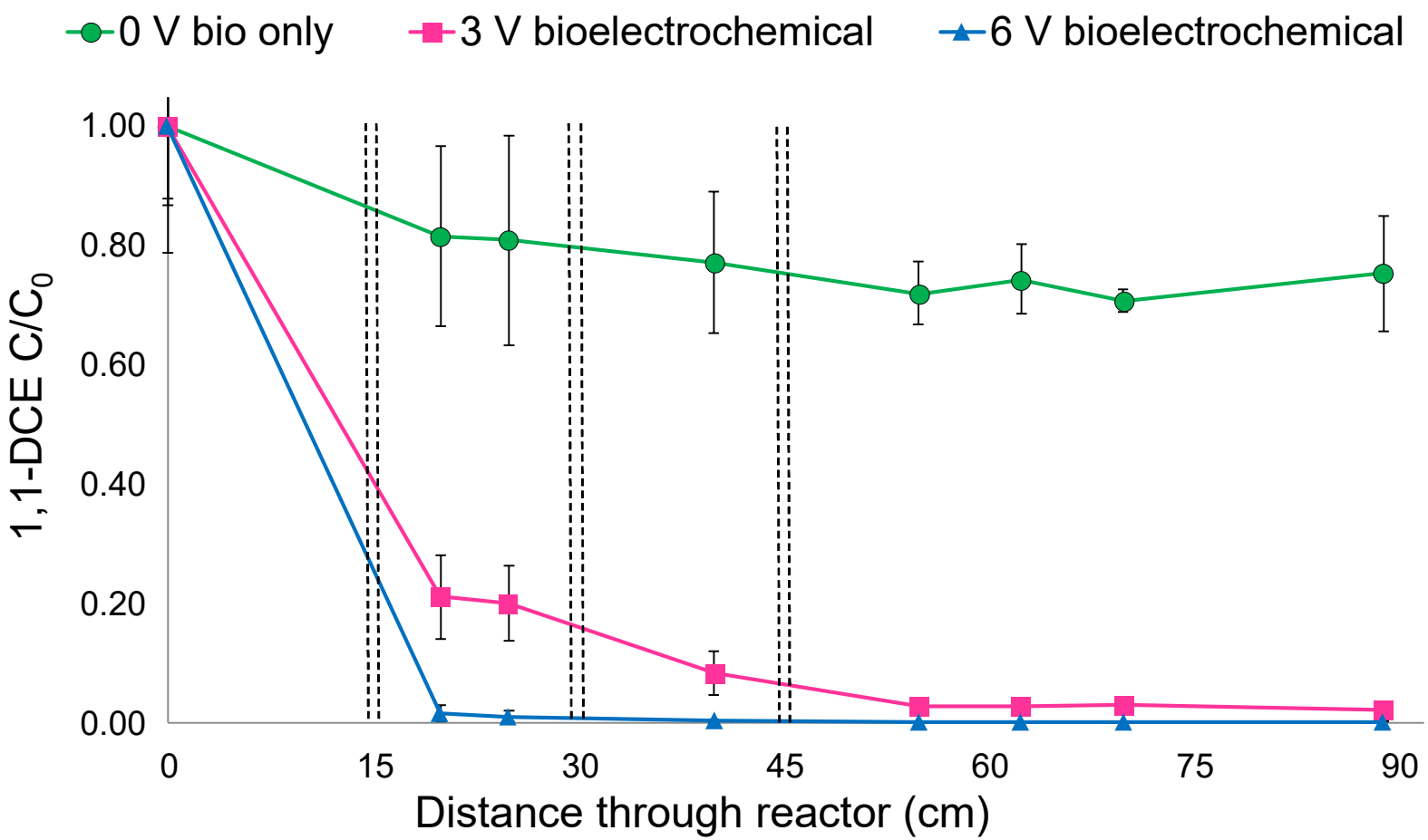




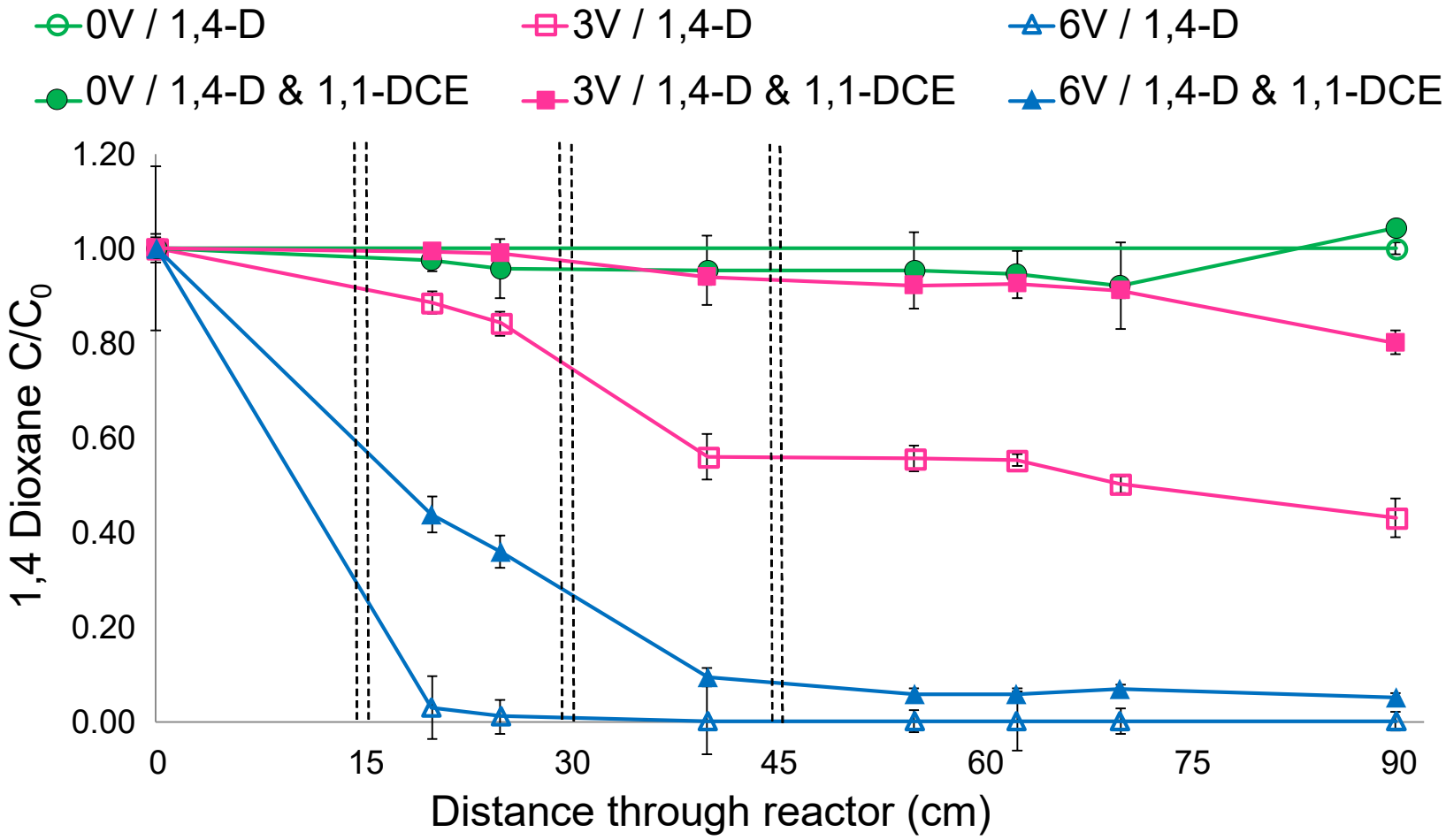
1,4-Dioxane Removed from >100,000 µg/L to below Detection Limit (3 µg/L)



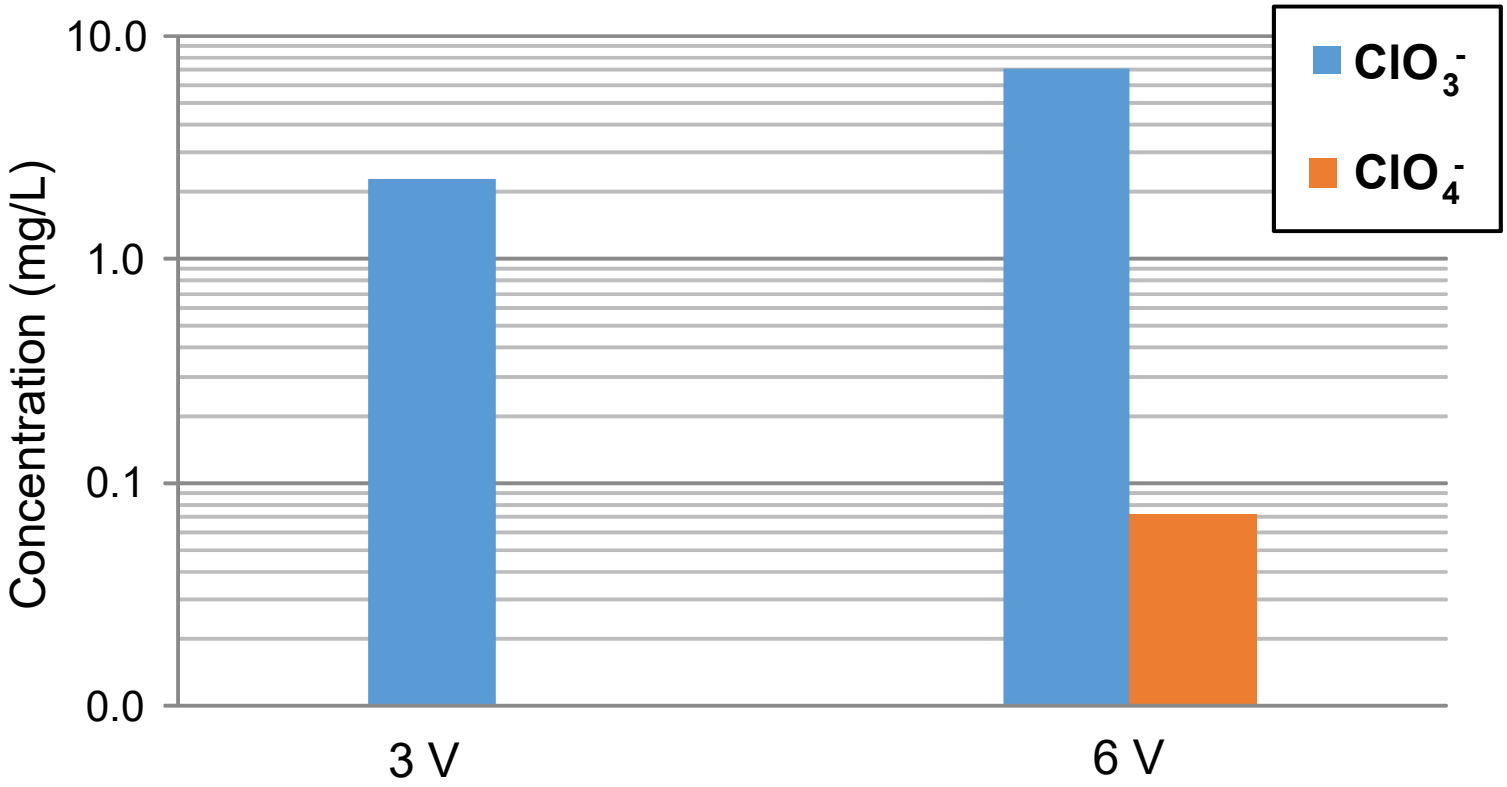
The Co-Contaminant and Strong Inhibitor 1,1-DCE is Removed by 99%



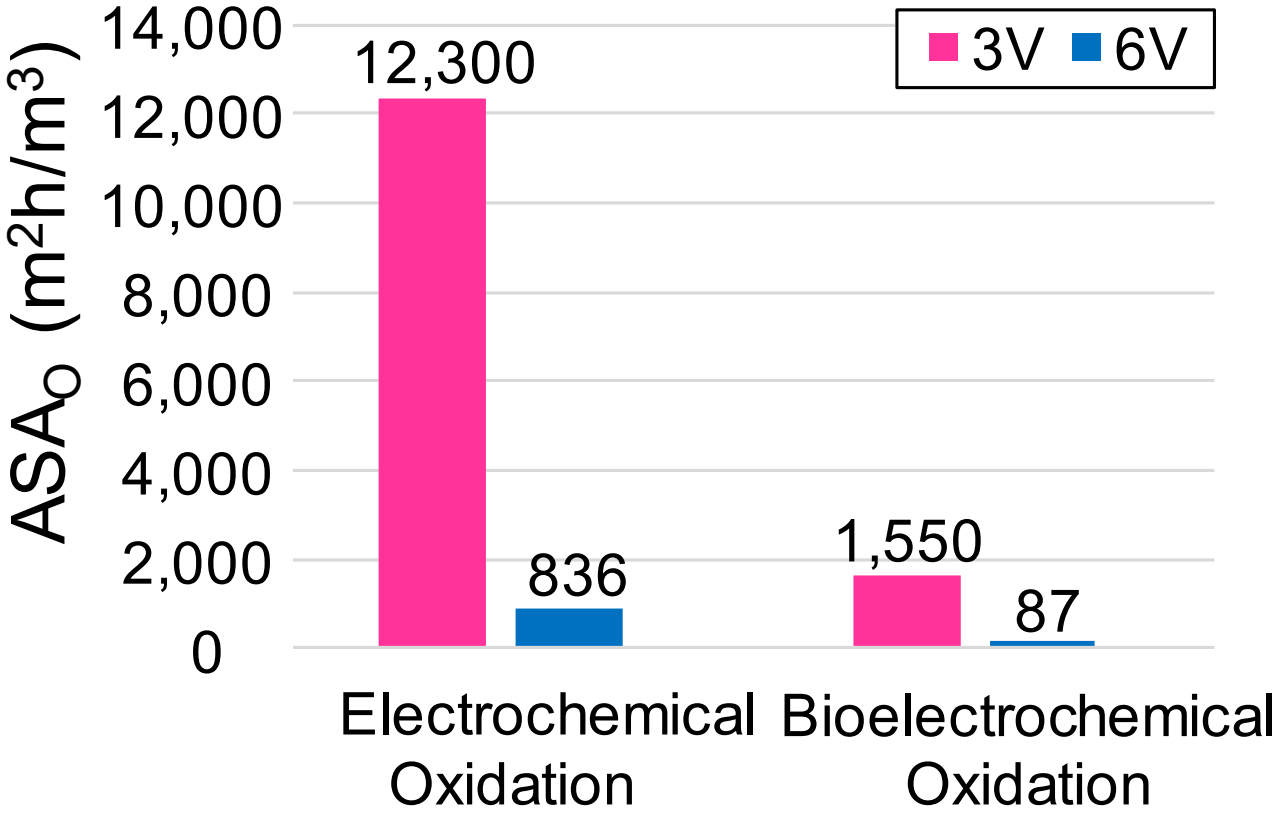
Despite ~99 % 1,1-DCE Removal, 1,4-D Biodegradation is Still Slowed



Less Oxidation by-Products are Formed at Lower Applied Potential

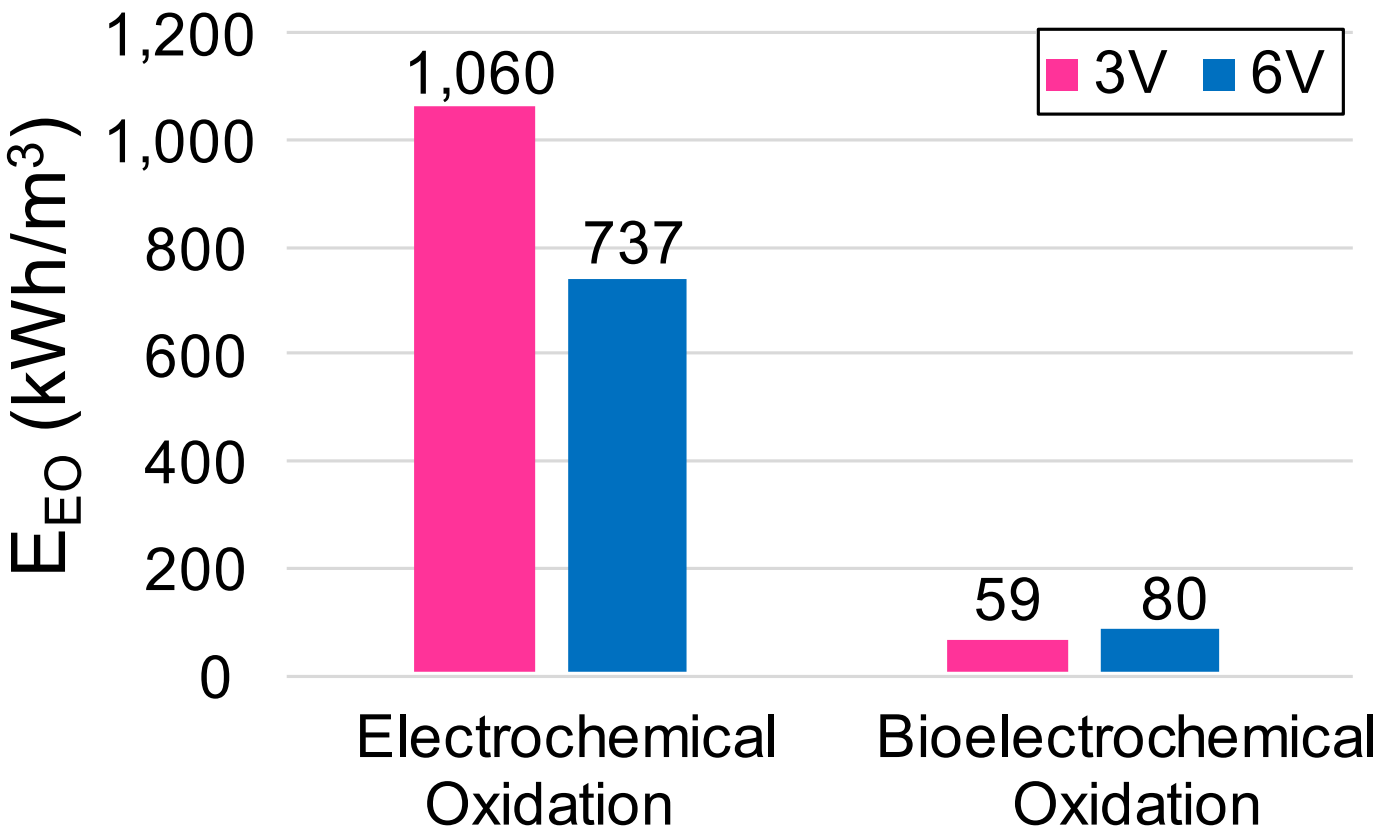


Bioelectrochemical Treatment Lowers Capital Costs (Electrodes)



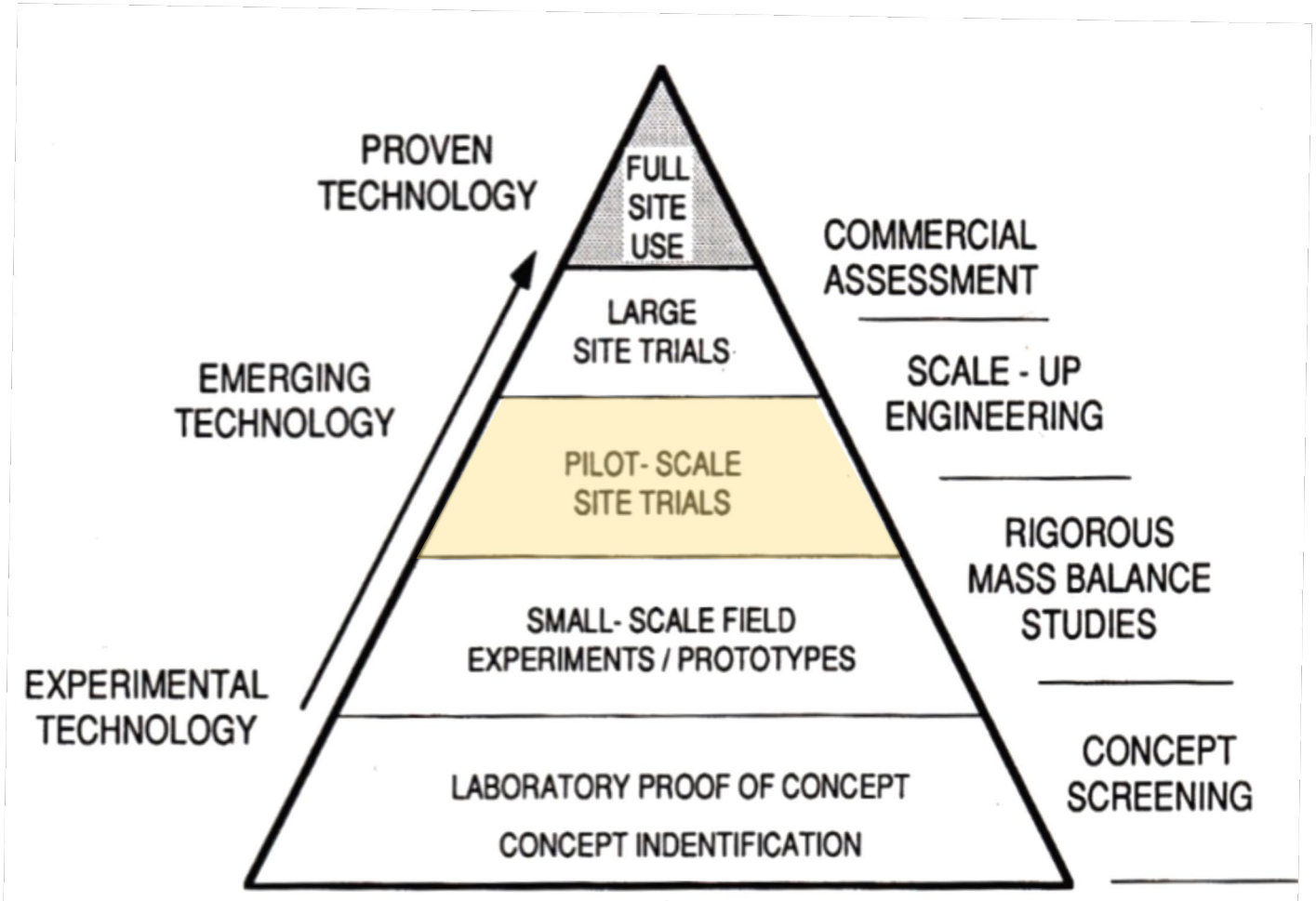
ASA$_O$ = anode surface area per order of magnitude of contaminant removed

Bioelectrochemical Treatment Lowers Operational Costs (Energy)



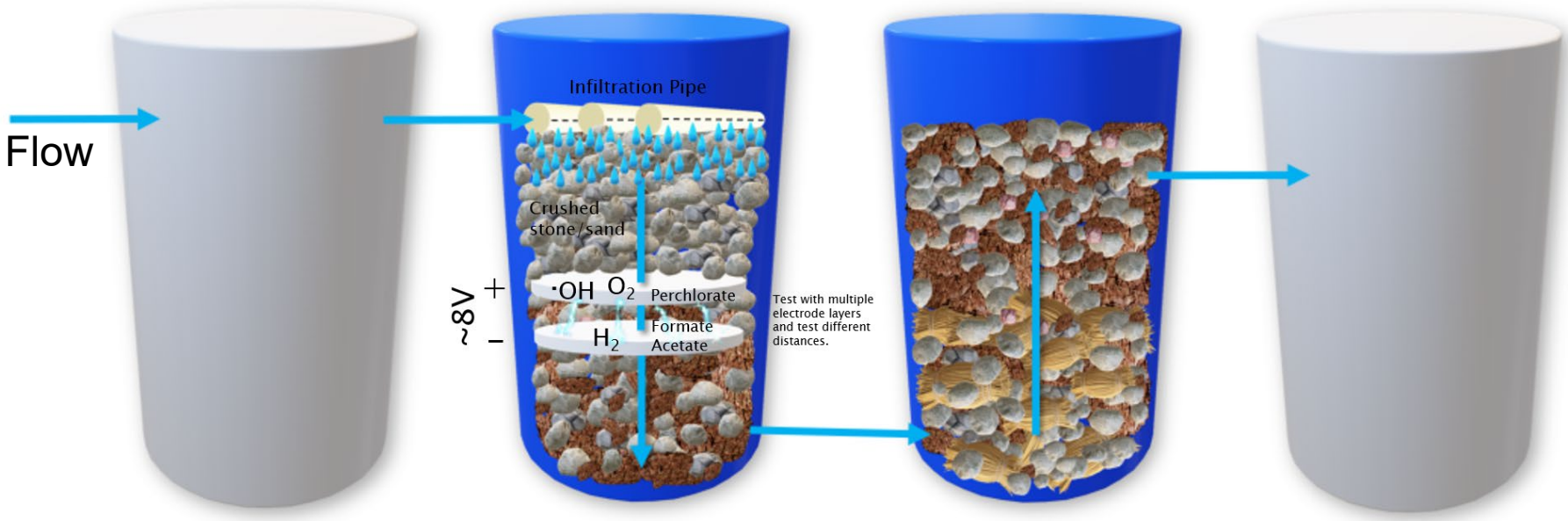
E_{EO} = electric energy per order of magnitude of contaminant removed

Scaling up Bioelectrochemical Treatment



***Source**: Pankow & Cherry 1996*

Electrobiogeochemical Reactor (e^-BGR)



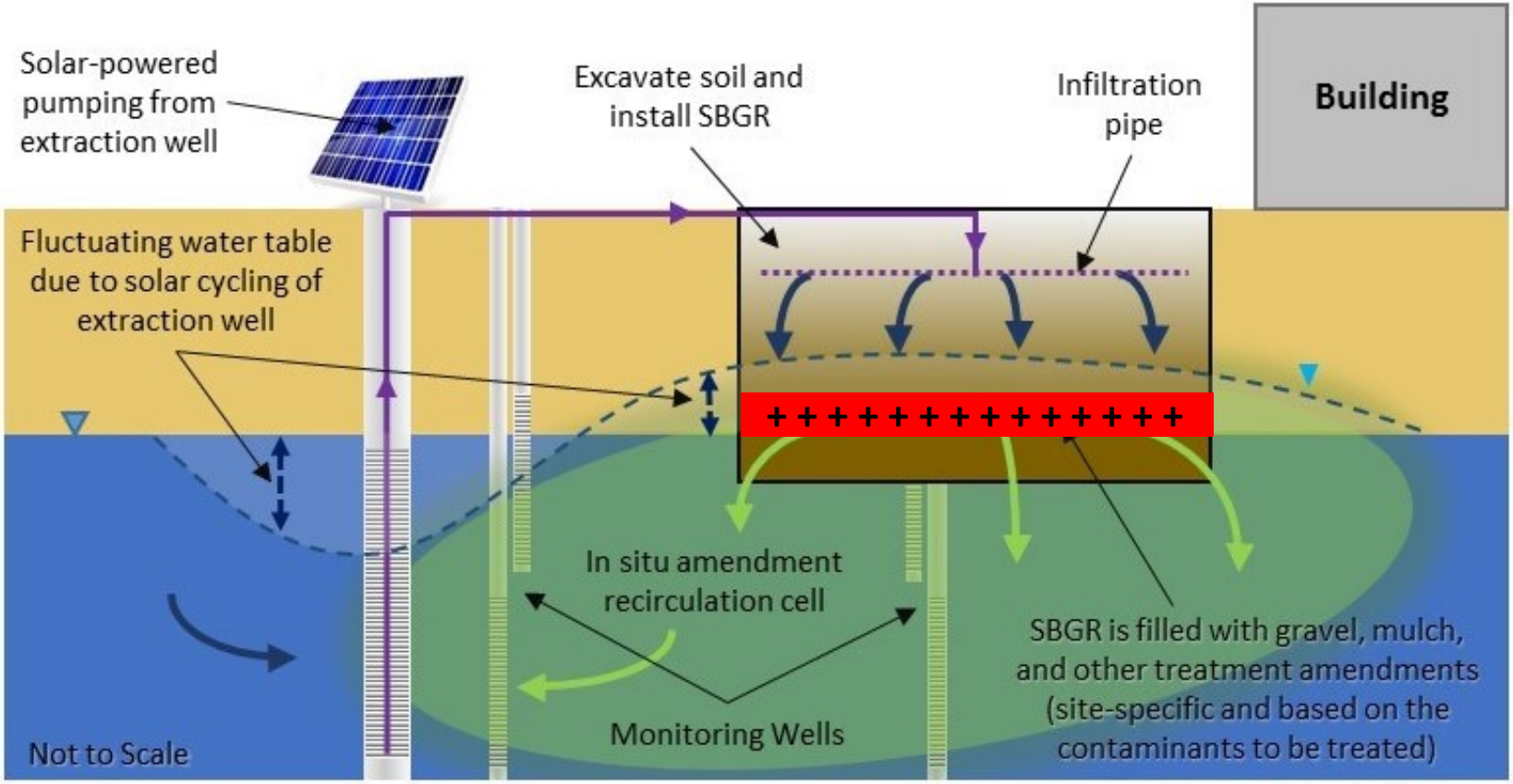
Equalization tank

Bioelectro-chemical oxidation

Anaerobic biogeochemical degradation

Holding tank

Electrobiogeochemical Reactor (e^-BGR)



Electrobiogeochemical reactor (e^-BGR)

Source: *Modified from Gamlin & Downey, Enviro Wiki*

Conclusions

- 1,4-dioxane removal to low/sub-ppb concentrations
- Synergistic treatment effects
  - Microbial utilization of generated O_2
  - Transformation of persistent contaminants into growth-supporting intermediates
  - Removal of inhibiting co-contaminants
- Reduced O&M costs
- Decreased by-product formation

Benefits to DoD

- Innovative technology to destroy 1,4-dioxane to below strict MCLs
- Effective where CVOCs co-occur
- Implementation ex situ or in situ
- Highly adjustable, active or passive
- Likely effective with other microorganisms
- Works for other persistent contaminants and mixtures

Acknowledgements

- ER-2718 project team
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  - Nasim Pica, CSU (now CDM Smith)
- Technology scale-up
  - Jeff Gamlin, Jacobs

For additional information, please visit

https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/ER-2718

Speaker Contact Information

jens.blotevogel@colostate.edu; 970-491-8880

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