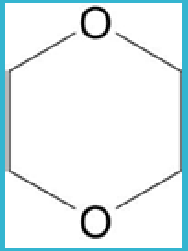
Successful Bioremediation of 1,4-Dioxane and 1,2-Dichloroethane in a Dilute Plume



$C_4H_8O_2$

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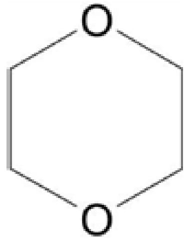
  - Confluence Environmental, Inc.
  - Microbial Insights & PACE Analytical
  - H&A field staff

Challenges in Treating 1,4-D Contaminated Groundwater

- The presence of 1,4-D in a chlorinated solvent plume often requires a costly pump-and-treat remedy.
- 1,4-D in groundwater is generally less than 100 μg/L.
- Biodegradation of 1,4-D at such low concentrations may not support metabolic growth.



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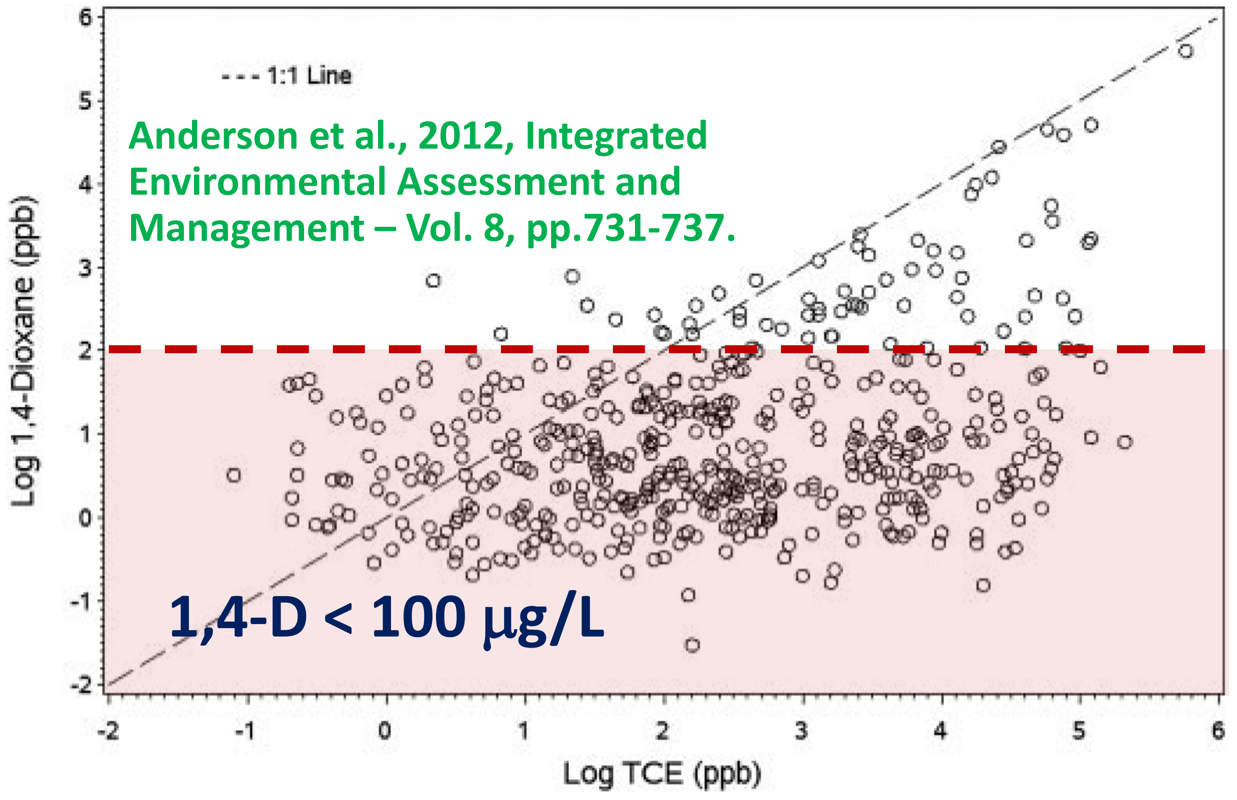

Note: 1,4-D = 1,4-dioxane

What is Aerobic Cometabolic Biodegradation (ACB)?

- Contaminants are oxidized by an enzyme produced during microbial metabolism of another compound with oxygen.
- Contaminant degradation is fortuitous and cannot support microbial growth.

Laboratory and Field studies so far show:

- The process can potentially degrade a wide variety of compounds, such as TCE, cDCE, VC, 1,4-D, MTBE, NDMA, …
- In many instances, it can degrade target chemicals to sub-ppb levels (< 1ppb).
- The process is typically able to convert target chemicals to non-toxic compounds.

Note: 1,4-D = 1,4-dioxane; ACB = aerobic cometabolic biodegradation

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Advantages of using ACB to Treat 1,4-Dioxane and CVOCs in a Dilute Plume In Situ

- Concurrent degradation of many contaminants: 1,4-D, many CVOCs, PAHs, etc.
- Low toxicity of target contaminants and degradation products: ACB can generate toxic intermediates resulting in cell damage; however, when the total concentration of target chemicals is low, the toxicity effects may be much more tolerable.
- Less likely to result in water quality degradation: Substrates used for ACB can be quickly mineralized, do not increase TDS in groundwater, and generally do not result in secondary water quality impacts.

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Field Site and Remedial System

Field Demonstration Site

- Location: The Operable Unit D (OU D) at the Former McClellan Air Force Base, Sacramento County, California
- The depth to groundwater (GW) is approximately 100 feet below ground surface.
- A stable 1,4-D and 1,2-DCA plume is present at low concentrations in the top 10 feet of the shallow GW.

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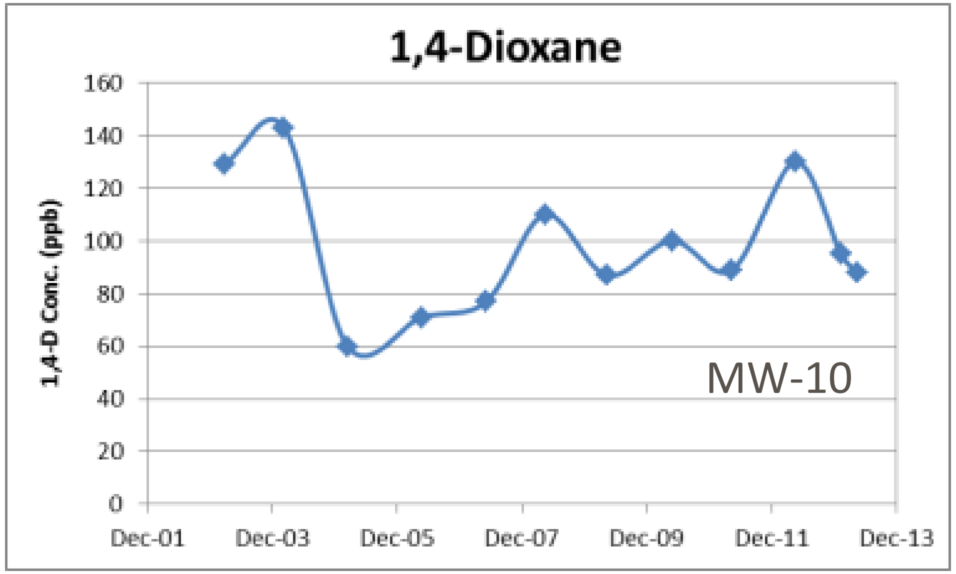
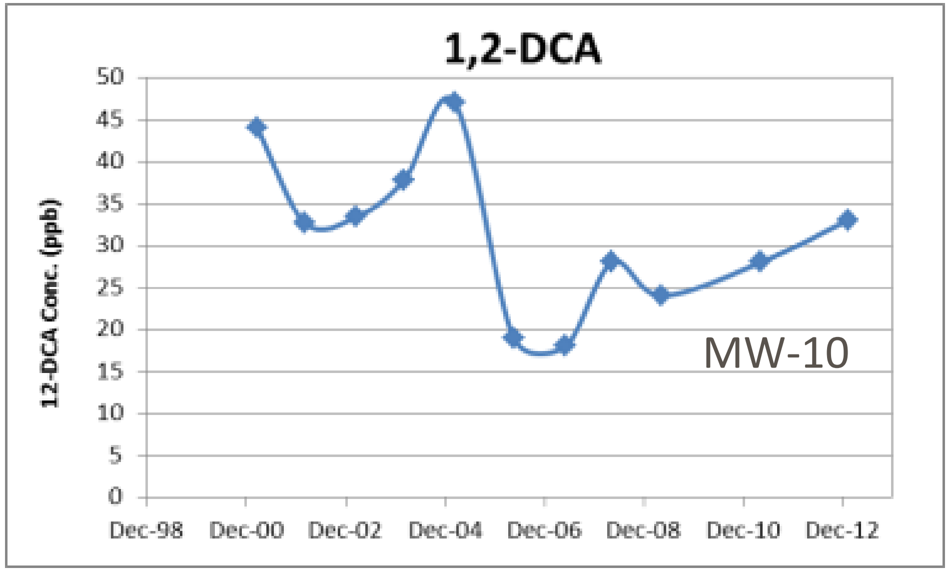
Key Contaminants and Their Concentrations in the Pilot Test Area (Before Recirculation)





COC \ Well	Cleanup Goals (ppb)	IACB-1	MACB-1	MACB-2	MACB-3
			GW sampling on 5/1/15		
1,4-Dioxane	6.1	62	46	47	45
1,2-DCA	0.5	12	8.2	8.4	9.7
1,1-DCE	6	<1	<1	<1	<1
TCE	5	2.5	2.3	2.3	2.7

> 90% treatment efficiency needed!!

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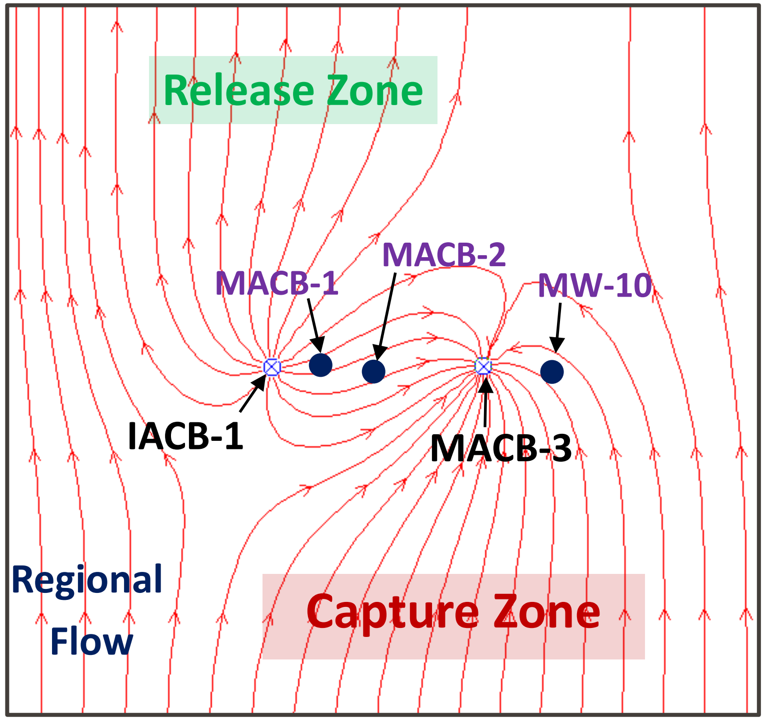
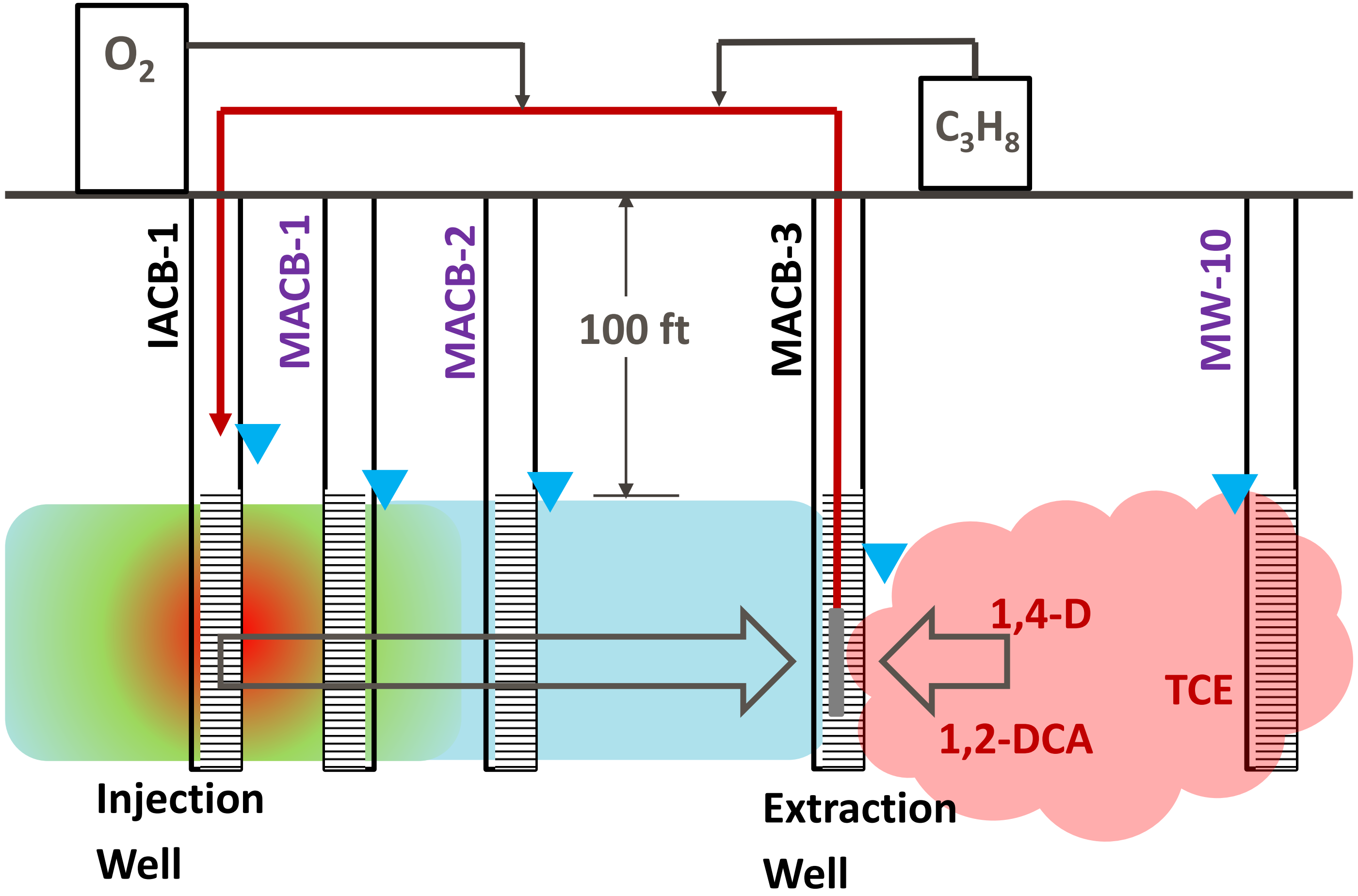
Remediation Approach

The GW recirculation approach was used to add propane and oxygen intermittently into recirculated GW in order to create an underground ACB bio-reactor.





Substrate Addition for Biostimulation

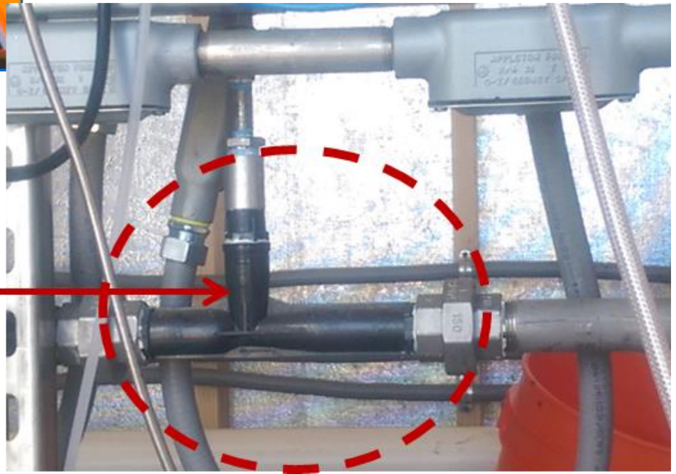
Gaseous Substrates

- HD-10 propane gas tank
  - propane (85-100%)
  - butane & heavier (0-2.5%)
  - ethane (0-5%)
  - propylene (0-10%)
  - ethyl mercaptan (<0.0025%)

- 99.5% Pure Oxygen (Welding Grade)

<u>Note</u>: H_2O_2 was used for bioclogging control and also served as a secondary source of oxygen.

Gas Injection Method



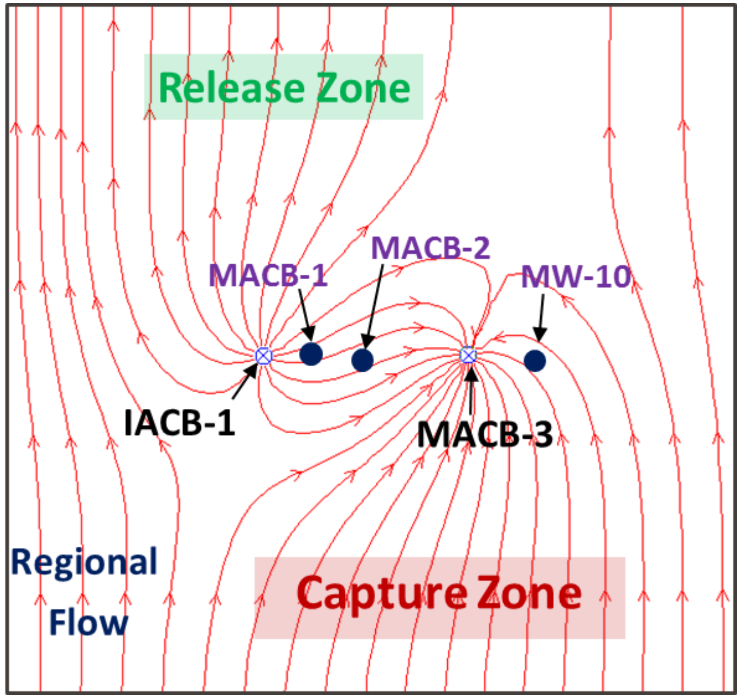
Field Demonstration Study and Results

Recirculation Baseline Conditions (8/26/15 - 9/17/15)

Baseline and Bromide Tracer Testing Phase	1,4-D Sampling Date	µg/L IACB-1	(EPA 8260B SIM; RL = 3 ppb) MACB-1	MACB-2	MACB-3	MW-10
No Flow	5/1/2015	62	46	47	45	58
Recirculation Rate 1.75 gpm (Bromide Tracer)	8/26/2015	60	68	61	77	50
	8/28/2015	71	64	60	63	57
	8/31/2015	66	67	66	65	68
Recirculation Rate 2 gpm	9/8/2015	57	56	56	--	47
	9/11/2015	56	57	57	--	47
	9/14/2015	53	56	56	--	50
	9/17/2015	61	62	60	--	46

Average concentration = 66 ug/L
1,4-D mass flux = 437 µg/min

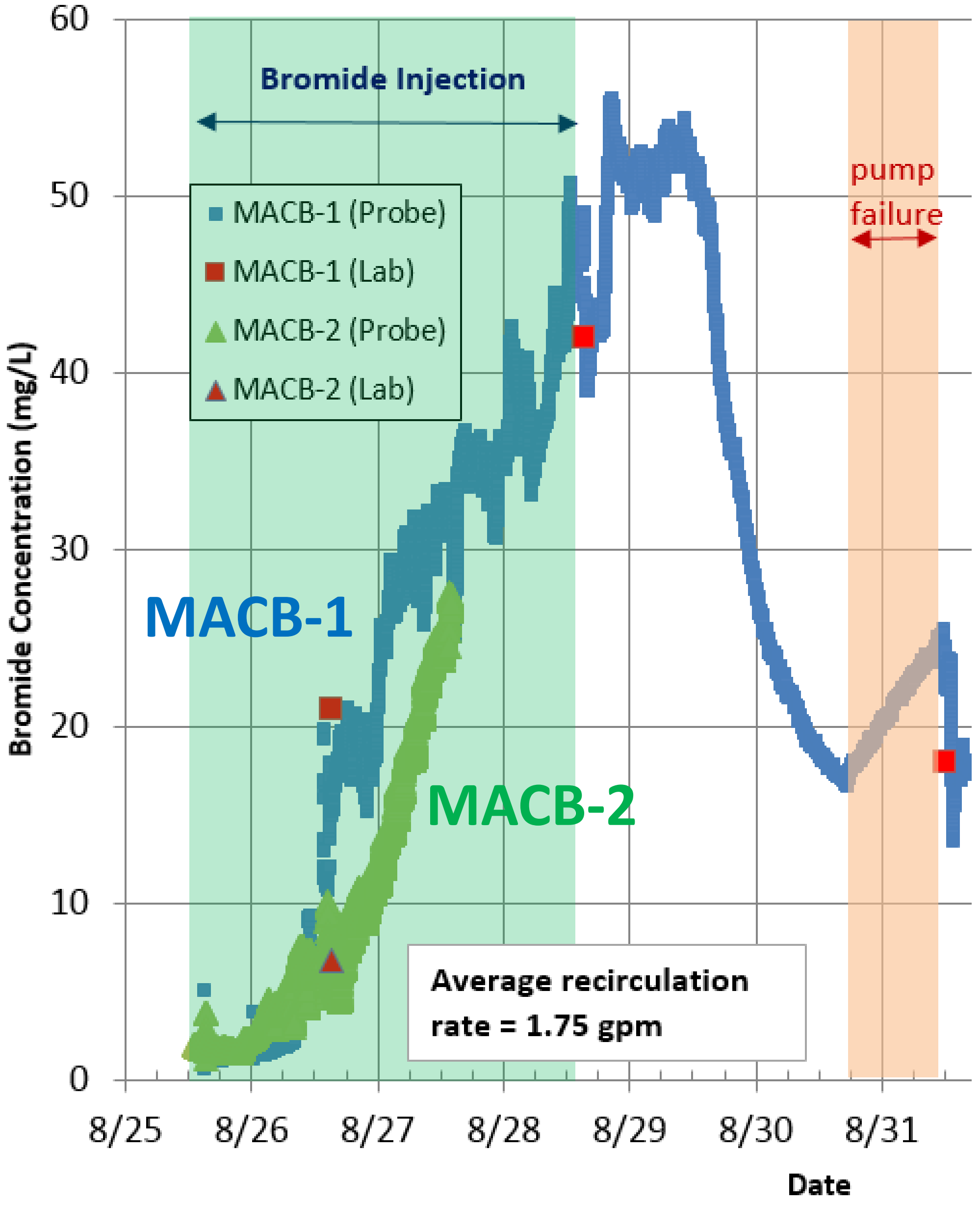
Average concentration = 57.5 ug/L
1,4-D mass flux = 435 µg/min



- **1,4-D mass flux captured by the recirculation system is steady under two different pumping rates.**

Bromide Tracer Test

- A constant mass loading rate of bromide was added to recirculated GW.
- Br probes were placed in MACB-1 and MACB-2.
- Travel times from the injection well to
  - MACB-1 (3 feet away): ~ 1.5 days
  - MACB-2 (6 feet away): ~ 2 days



System Operation and Optimization for Biostimulation

Period 1: High Propane, Low Oxygen – propane injection only

Period 2: Unstable Operation (oxygen added)

Period 3: High Propane, Sufficient Oxygen

Injection Modes	Injection Frequency (C_3H_8 / O_2)
1. High frequency pulses:	3mins / constant, Daily (18 min cycle)
2. Short propane/oxygen pulses:	0.5hr / 2.5hrs, Daily (3 hr cycle)
3. Long pulses:	1.5hrs / 4.5hrs, Daily (6 hr cycle)
4. Extended pulses:	3.0hrs / 9.0hrs, Daily (12 hr cycle)
5. Prolonged pulses:	5.0hrs / 17hrs, Daily (24 hr cycle)
6. Low frequency pulses:	6.0hrs / 16hrs, Monday & Friday each week

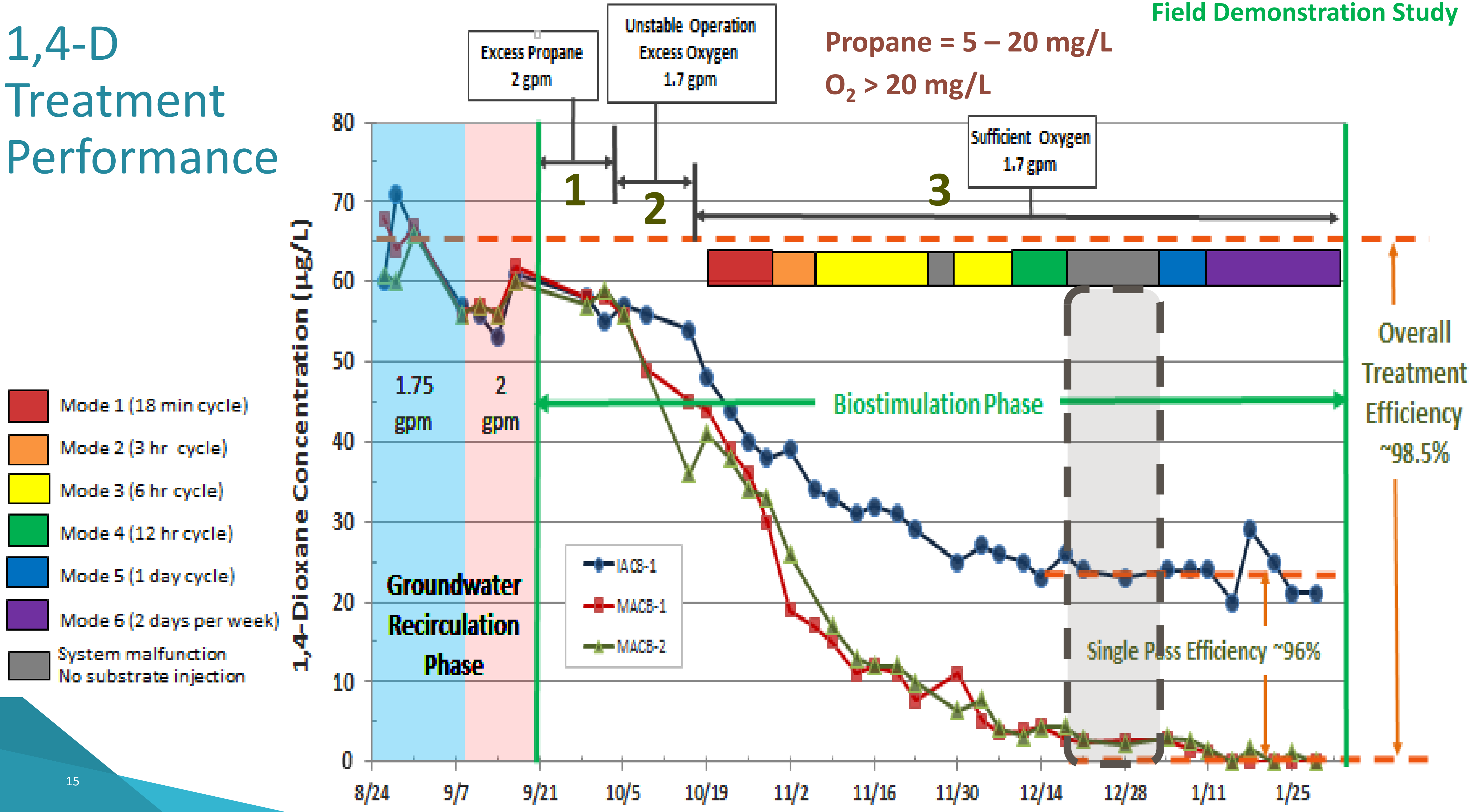
Propane = 5 – 20 mg/L

O_2 > 20 mg/L

Longer and more concentrated propane pulses is expected to help increase the propane-oxidizing activity away from the injection well

1,4-D Treatment Performance

Field Demonstration Study



1,4-D Treatment Efficiency

Field Demonstration Study

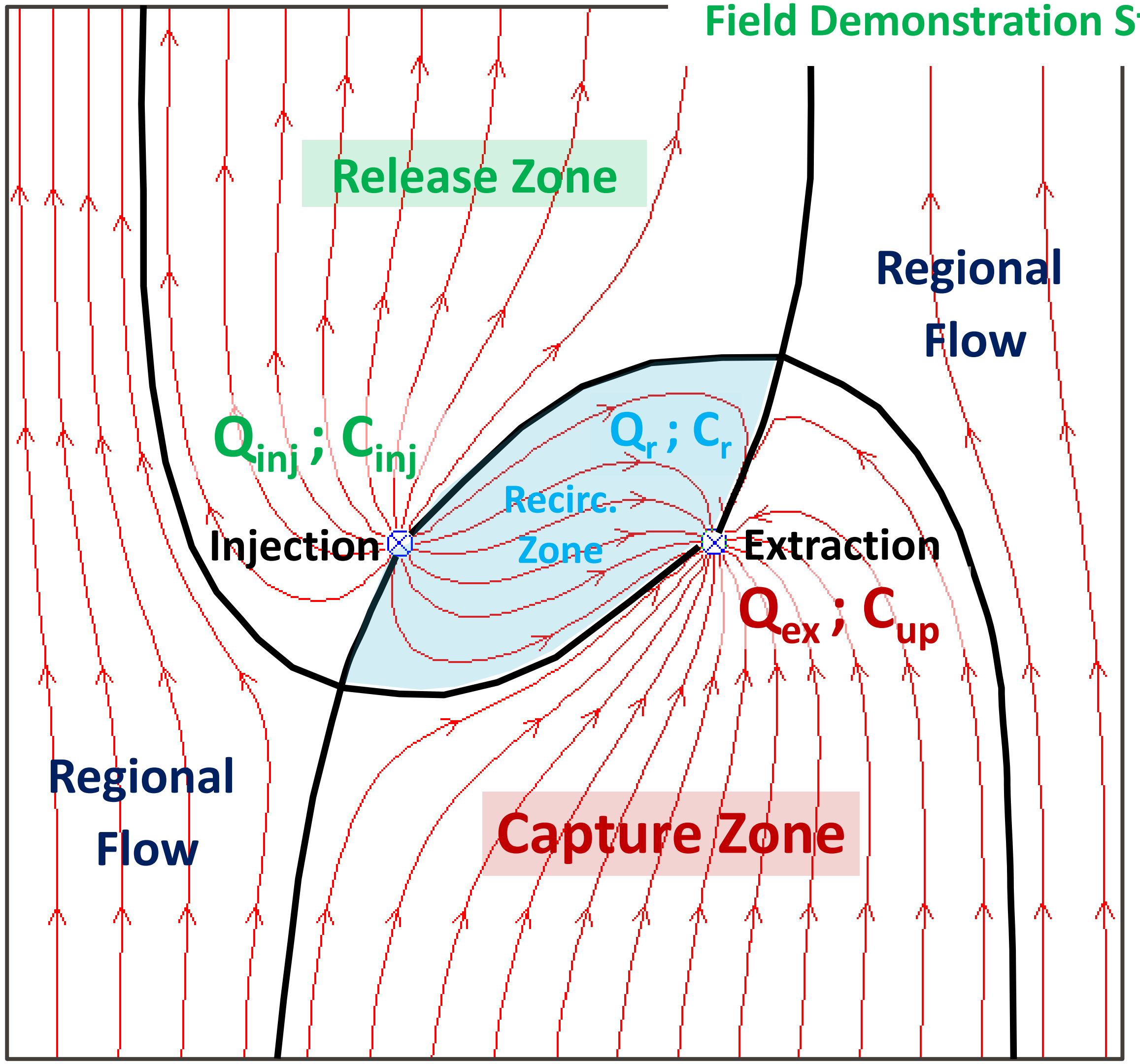
Single pass efficiency (η) = 1 - C_r / C_{inj} (96%)

Overall efficiency = 1- C_r/C_{up} (~ 99%)

$$\eta_{overall} = \frac{\eta}{1 - I(1-\eta)}$$

Recirculation Ratio (Q_r / Q_{inj})

The recirculation ratio is estimated to be ~ 72%.



C_{up} = background 1,4-D concentration in GW

C_{inj} = 1,4-D concentration in injected GW

C_r = 1,4-D concentration at the end of recirculation zone

The formula is adopted from Goltz, M.N. and Christ, J.A., 2012, Recirculation Systems, and the figure was adopted from Luo, J., 2012, Travel-time based reactive transport modeling for in situ subsurface reactor; both are from the book - In Delivery and Mixing in the Subsurface (Springer New York).

Treatment Efficiency for 1,4-D and Co-contaminants

Chemical	C_{up} (ppb)	C_{inj} (ppb)	C_r (ppb) #	Site-Specific Cleanup Goal	Single Pass Efficiency	Overall Efficiency
1,4-D	66	21	0.77	**6.1**	~ 96%	~ 99%
1,2-DCA	11.7	2.9	< 0.18*	**0.5**	~ 97%	~ 99%
1,1-DCE	1.3	0.3	< 0.2*	**6**	~ 67%	~ 92%
TCE	3.9	1.5	0.24	**5**	~ 84%	~ 93%

* When C_r is below the method detection limit (MDL), ½ MDL is used for C_r

\# Estimated from concentrations observed in MACB-1 and MACB-2 near the end of system optimization.

Bulk First-Order Biodegradation Rate Constant & Half Life

$$\eta = 1 - e^{-(k \times T)}$$

- η = single pass efficiency
- e = exponential function
- k = 1st order rate constant
- T = residence time in the bioactive zone

This Field Study

- Assuming η = 90% and T = 1.5 day, the first-order rate constant k = 1.5 day^{-1} or the half life = 0.45 day.

Other Field Studies	Site Location	Primary Substrate Target Chemical	Estimated Half Life (day)
McCarty et al. (1998)	Edwards AFB, CA	Toluene TCE*	~ 1
Kuo et al. (2004)	Taiwan	Toluene TCE*	~ 0.4
Hopkins et al. (1993)	Moffett Field, CA	Phenol TCE*	~ 0.4
Lippincott et al. (2015) #	Vandenberg AFB, CA	Propane 1,4-D	~ 20

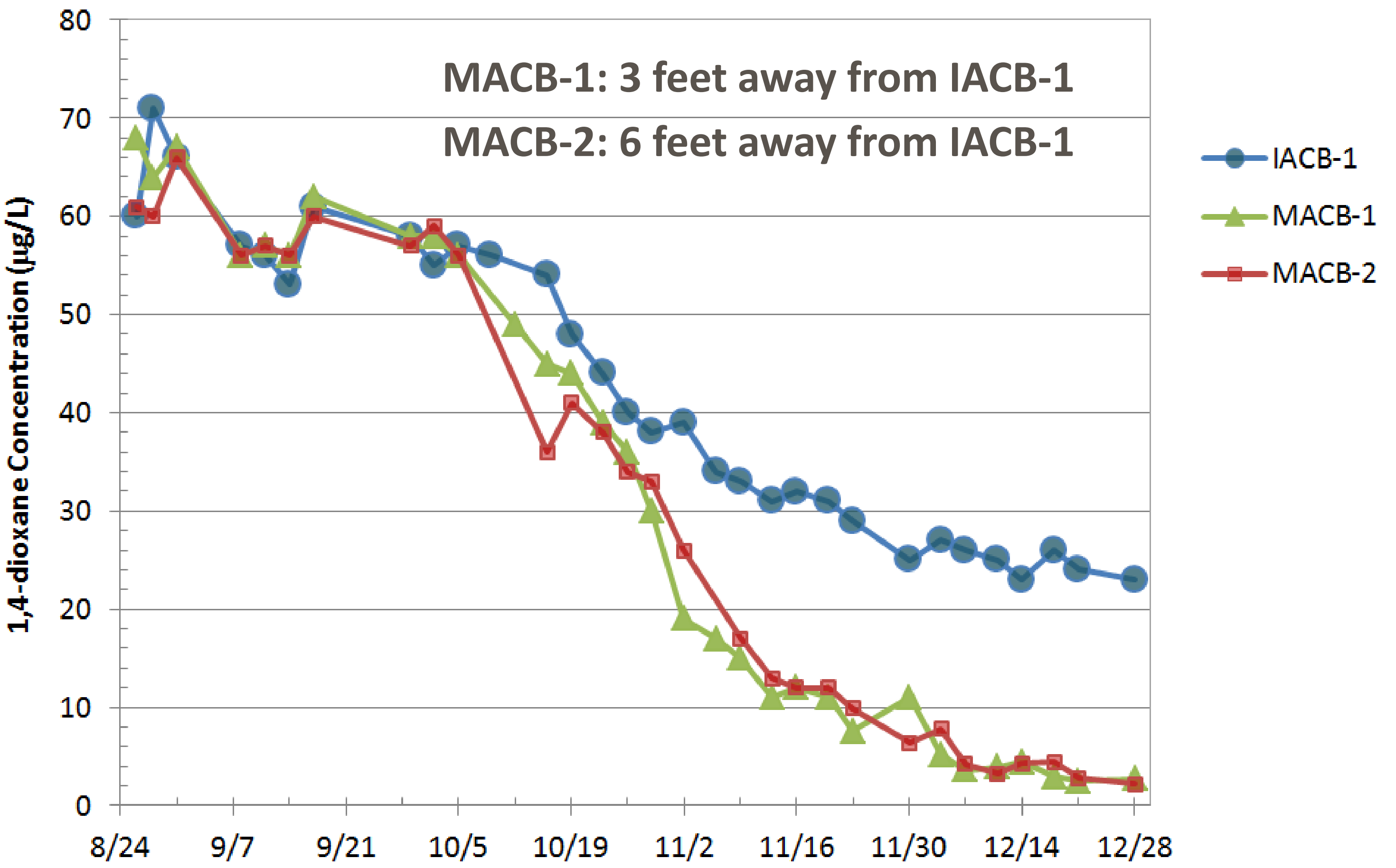
** For TCE studies, the residence time does not take into account the retardation effects. Substrates were solubilized before injection.*

 # The study uses sparging to deliver substrates.

Literature Cited:
McCarty et al. 1998. Full-scale evaluation of in situ cometabolic degradation of trichloroethylene in groundwater through toluene injection. ES&T.
Kuo et al. 2004. Pilot studies for in-situ aerobic cometabolism of trichloroethylene using toluene-vapor as the primary substrate. Water Research.
Hopkins et al. 1993. Trichloroethylene concentration effects on pilot field-scale in-situ groundwater bioremediation by phenol-oxidizing microorganisms. ES&T.
Lippincott et al. 2015. Bioaugmentation and Propane Biosparging for In Situ Biodegradation of 1, 4-Dioxane. Groundwater Monitoring & Remediation.

The Size of the Reaction Zone

- Most of cometabolic degradation of 1,4-D occurs within 3 feet from the injection well (between IACB-1 and MACB-1)



Notes:

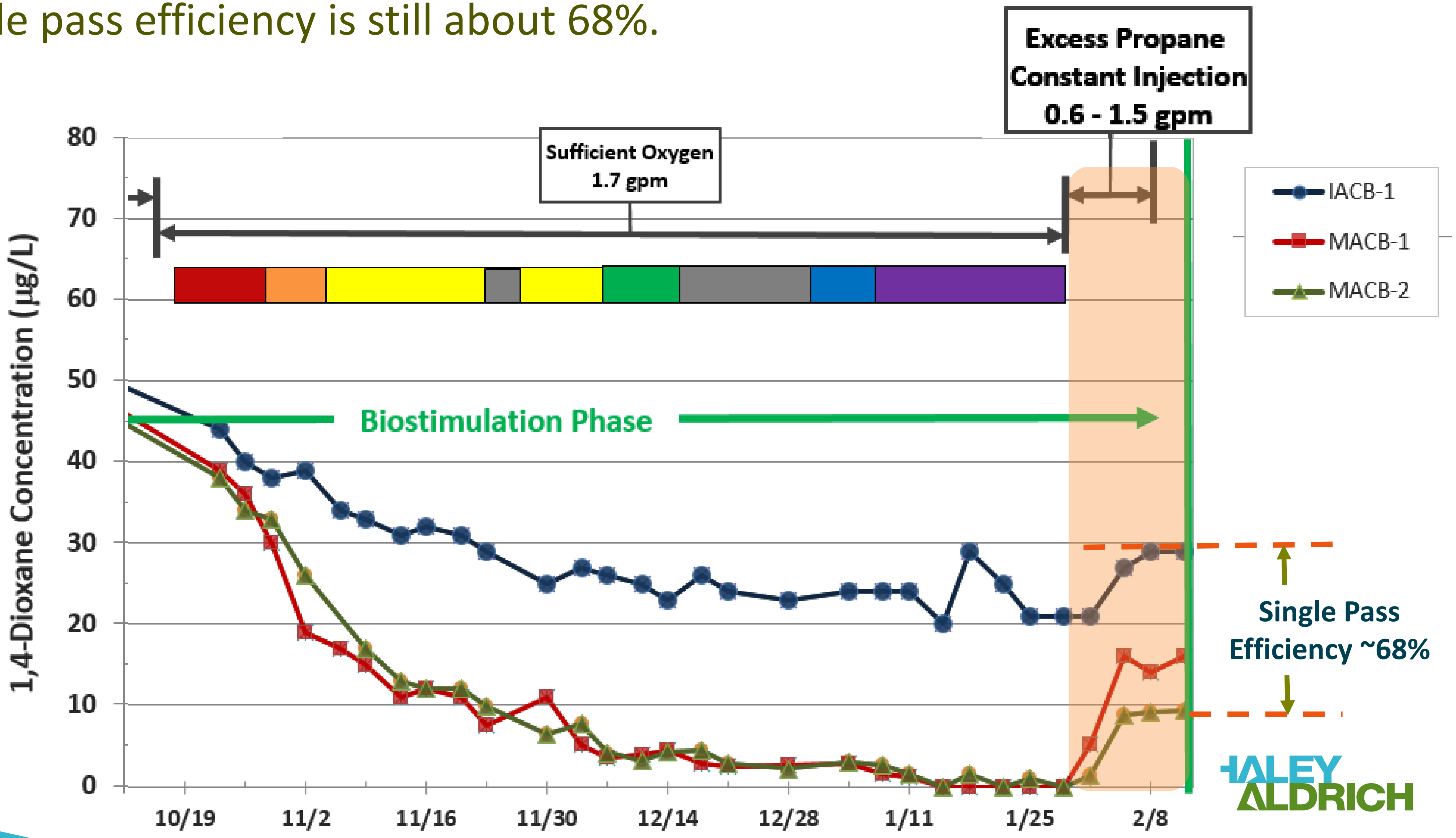
1. The TCE cometabolic field test at the Edwards AFB shows that most degradation occurs within 15 feet from the injection well (McCarty et al., 1998).

2. The cometabolic field test at the Moffett site shows that most degradation occurs within 3.3 feet from the injection well (Semprini et al., 2005).

McCarty et al. 1998. Full-scale evaluation of in situ cometabolic degradation of trichloroethylene in groundwater through toluene injection. ES&T.
Semprini et al. 2005. Development of Effective Aerobic Cometabolic Systems for the In Situ Transformation of Problematic Chlorinated Solvent Mixtures, SERDP Final Report: ER-1127.

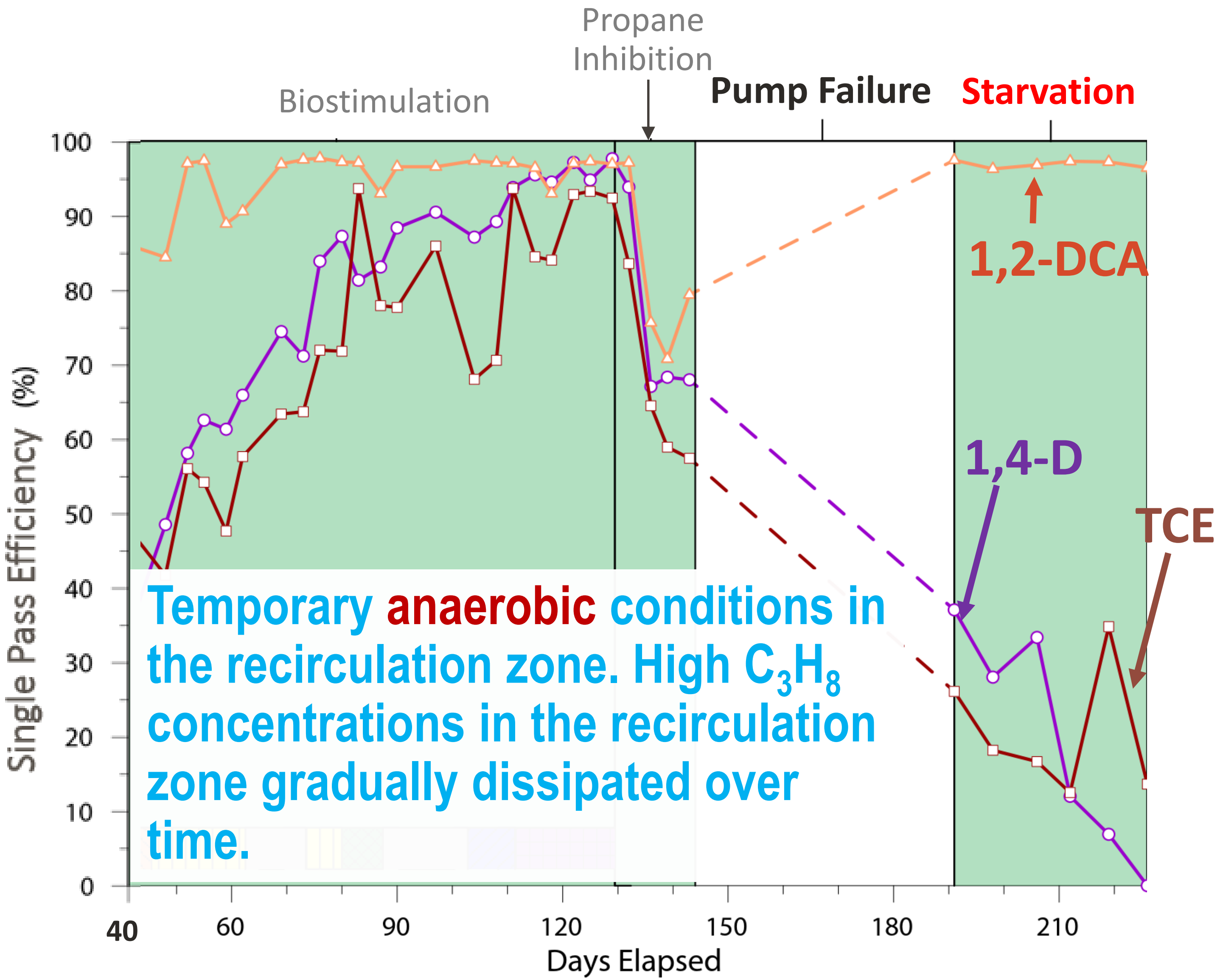
Constant Injection of High Propane Concentration

Under high propane levels (>20 mg/L) and low oxygen levels (DO < 1.5 mg/L), the single pass efficiency is still about 68%.



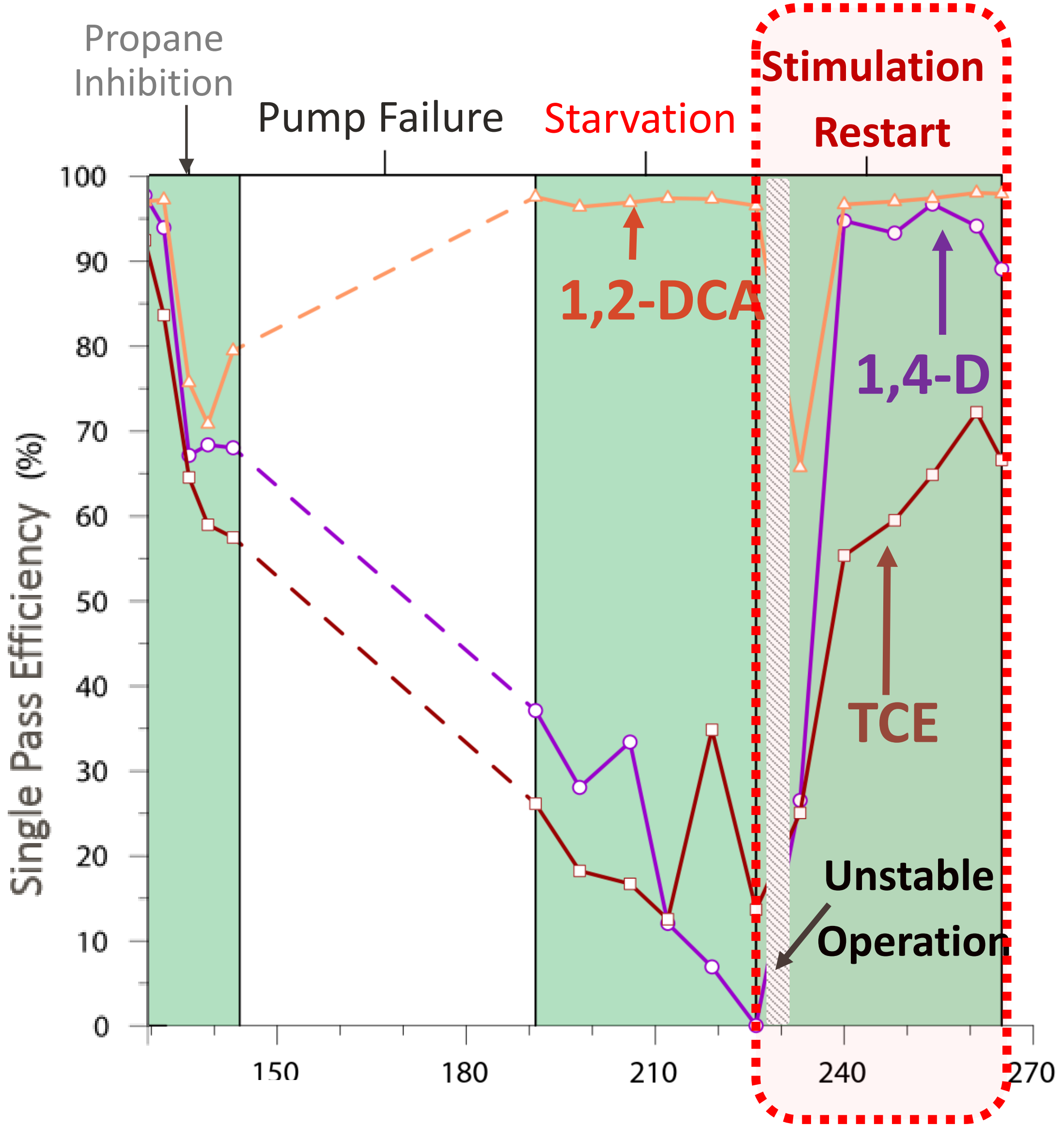
Starvation Test (No Propane Addition)

- During this period, propane levels dropped from 30 to <1 ug/L.
- 1,2-DCA treatment remained steady.
- 1,4-D and TCE treatment efficiencies decreased over time.



Re-Stimulation

- After a brief period of unstable operation, 1,4-D single pass treatment efficiency quickly recovered to above 90%.
- TCE treatment efficiency recovered significantly slower.
- Some biodegradation activity for TCE that was lost during the starvation period could not recover as fast as that for 1,4-D.



Microbial Community Profiling Results

Next generation sequencing (by PACE Analytical, Inc.) was used to assess the microbial community structures in aquifer solids, solids in microbial samplers, & GW samples.

Solid samples:

- Before propane and oxygen addition, native sediments contain a variety of aerobic bacteria together with facultative/anaerobic bacteria.
- Pseudomonas and Acidovorax (genus) was dominant in the solid microbial samples either before or during biostimulation.
- Mycobacterium (genus) increased significantly over time.

GW samples:

- At the species level, the microbial community structures were similar in MACB-1 (within bioactive zone) and MW-10 (background well) during the early stage of biostimulation.
- Several potential types of bacteria in GW samples were related to propane oxidation, such as *Pseudomonas, Mycobacterium, Rhodocyclus, and Herbaspirillum.* ***Mycobacterium also increased significantly over time*****.**
- After the propane inhibition period and pump failure period, some metal reducing bacteria types, such as geobacter and anaeromyxobacter became dominant in GW.

Microbial Functional Genes Results (qPCR)

- Groundwater samples collected from MACB-1, MACB-2, and MW-10 during the **Re-Stimulation Period** were analyzed by Microbial Insights.
- The total eubacteria concentrations were between 10^5 and 10^6 cells/mL. Propane and oxygen addition did not result in significant increase in total bacterial biomass in groundwater.
- Concentrations of soluble methane monooxygenase (SMMO) and dioxane monooxygenase (DXMO) remained low throughout the test (< 10^3 cell/mL), consistent with no methane addition and low 1,4-D levels that cannot support metabolic 1,4-D biodegradation.
- Levels of propane monooxygenase (PMO) increased in MACB-1 and MACB-2; however, the PMO levels were less than 1/100 of the total eubacteria levels. The PMO assay may not fully capture the activity of all propanotrophs.

Concluding Remarks

- ✓Aerobic cometabolic biodegradation can treat a dilute plume of 1,4-D and 1,2-DCA to the level below 1 and 0.5 ppb, respectively.
- ✓Treatment efficiency can reach more than 95%.
- ✓High propane concentrations (~20 mg/L) do not appear to drastically inhibit 1,4-dioxane cometabolic biodegradation.
- ✓The stimulated ACB activity appears very resilient and robust because a two-week starvation does not affect the system performance.
- ✓After system upset and one-month starvation, the cometabolic activity can still be re-stimulated quickly.
- ✓Microbial community profiling reflects the change in redox conditions during the field testing.
- ✓Mycobacterium may be the key bacterial group responsible for observed biodegradation.

Thank you!

Questions?