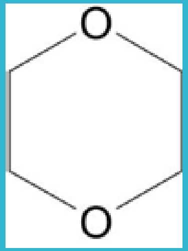
October 3-4, 2017

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



$C_4H_8O_2$

1,4-dioxane

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2017 GRA Conference
Sacramento, California

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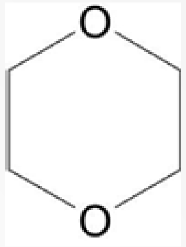
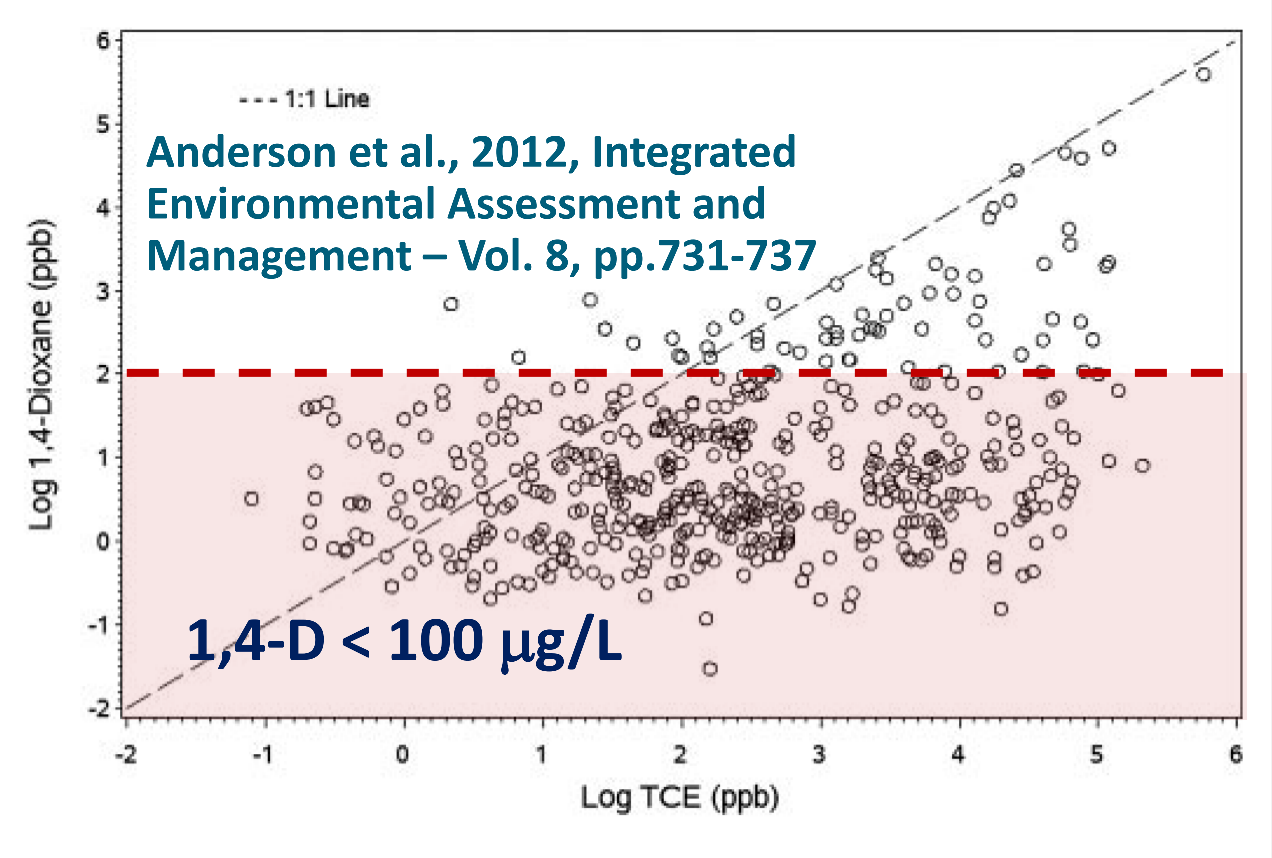
Challenges in Treating 1,4-D Contaminated Groundwater



$C_4H_8O_2$

- 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.



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

Brief History of ACB

- Extensive research started as early as 1980s for cVOCs (TCE, DCE, DCA) treatments.
- Several field tests in 1990s using methane, phenol, or toluene as a primary substrate.

However, ACB has not been widely used for bioremediation of cVOCs because anaerobic bioremediation becomes more popular.

ACB research remains active because some emerging contaminants (e.g., 1,4-dioxane) is very recalcitrant in anaerobic environments.

- More ACB research on emerging contaminants in 2000s (e.g., 1,4-dioxane, NDMA, and TNT)
- Field tests of treating 1,4-dioxane in 2010s.

ACB = Aerobic Cometabolic biodegradation

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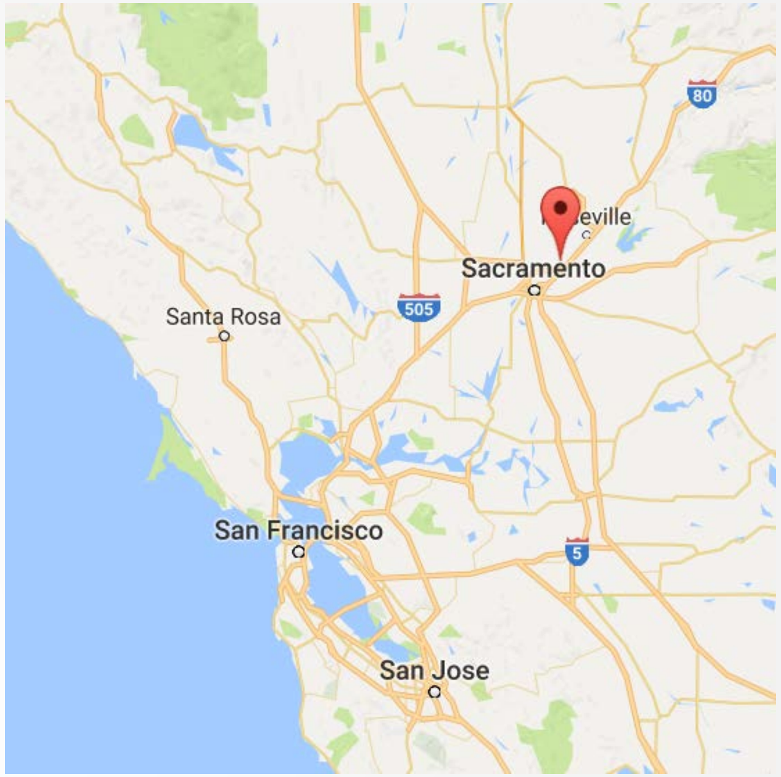
Advantages of using ACB to treat aerobic dilute plumes

- Potentially treat diverse contaminants concurrently (TCE, cDCE, VC, 1,1-DCA, 1,2-DCA, MTBE, TBA, 1,4-dioxane, NDMA, 1,2,3-TCP, RDX….)
- Can treat many contaminants to sub ug/L levels; therefore, may achieve cleanup goals for all target contaminants.
- Do not need to change aquifer geochemical conditions dramatically.
- Less likely to produce recalcitrant toxic daughter products.
- Less likely to result in secondary water quality degradation.



A Field Study (2015-2016)

ACB of 1,4-dioxane and 1,2-DCA
Former McClellan AFB, Sacramento, CA

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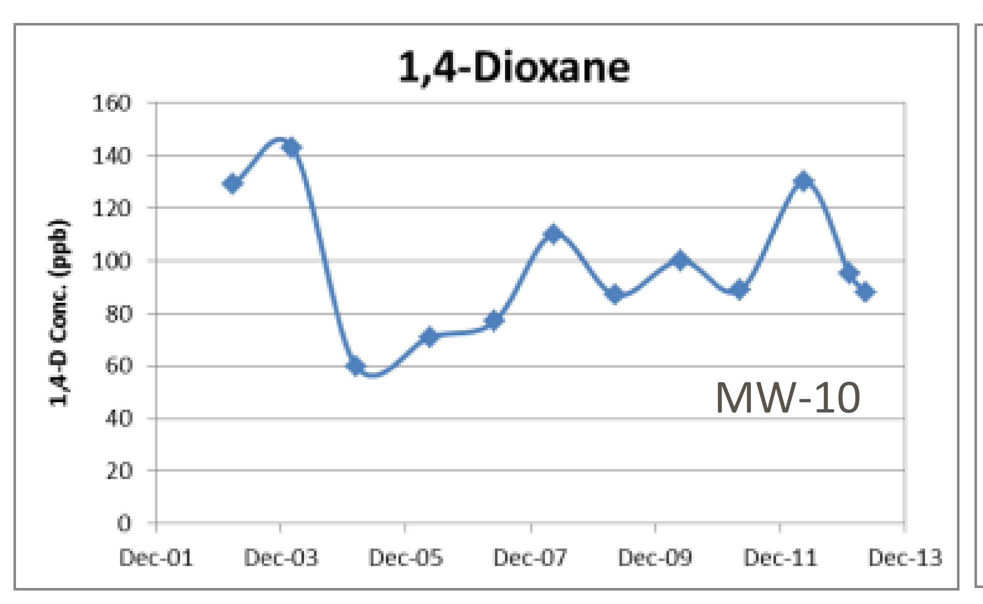
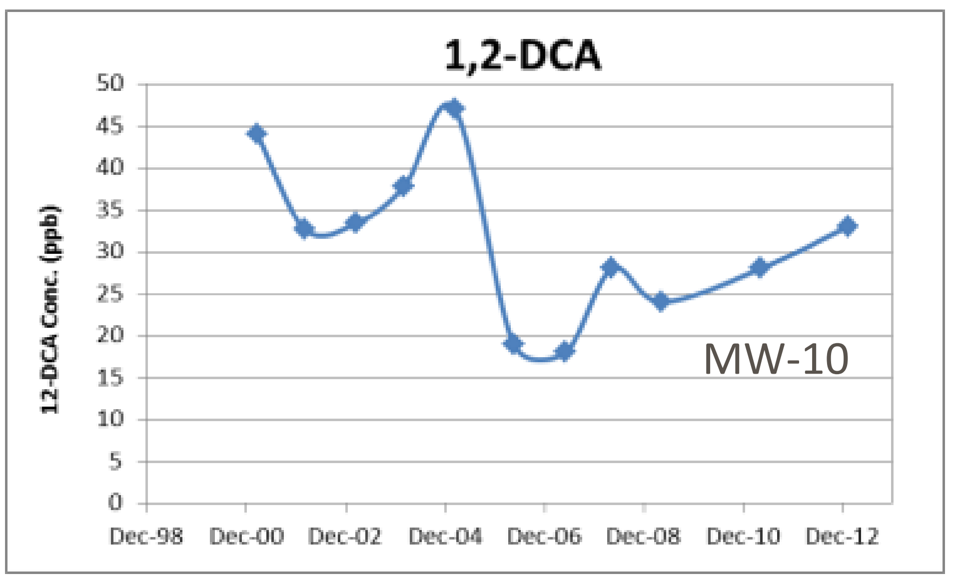
Key Contaminants and Their Concentrations in the Pilot Test Area (Before Recirculation)





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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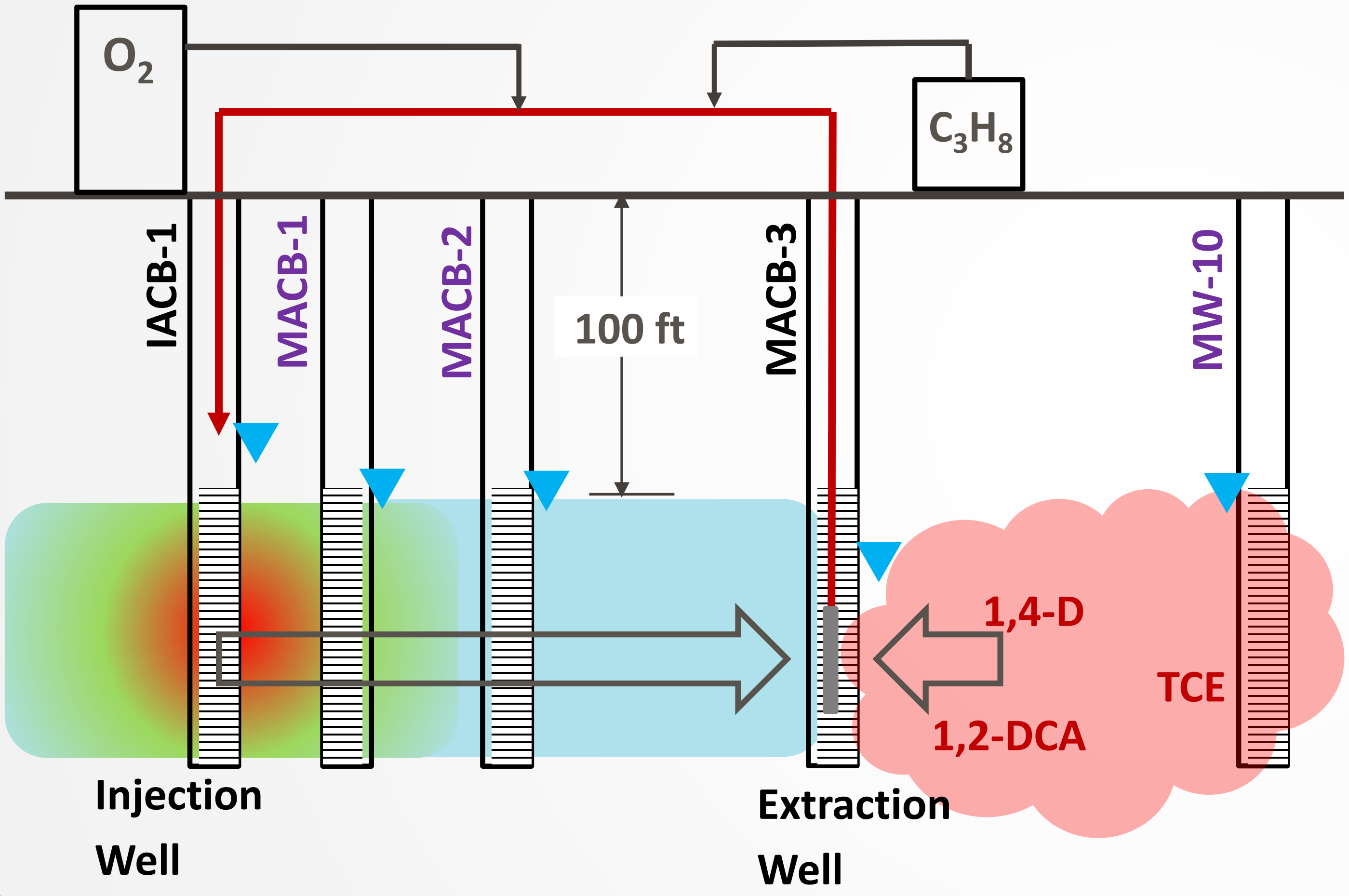
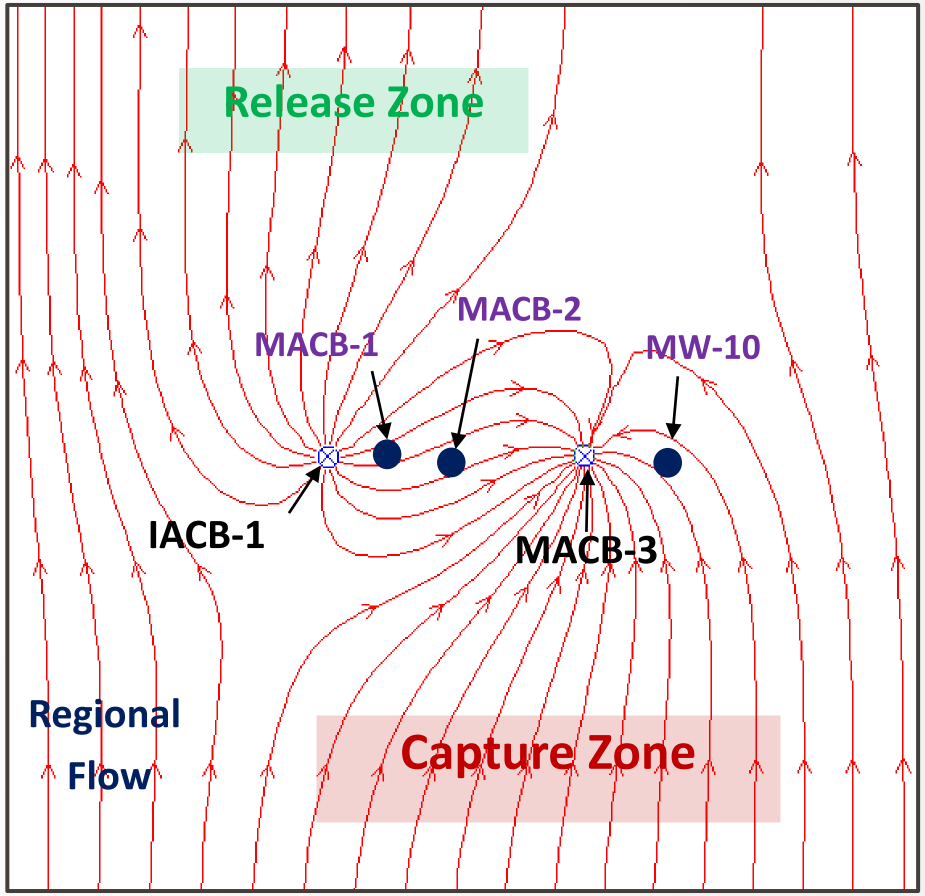
Remediation Approach

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





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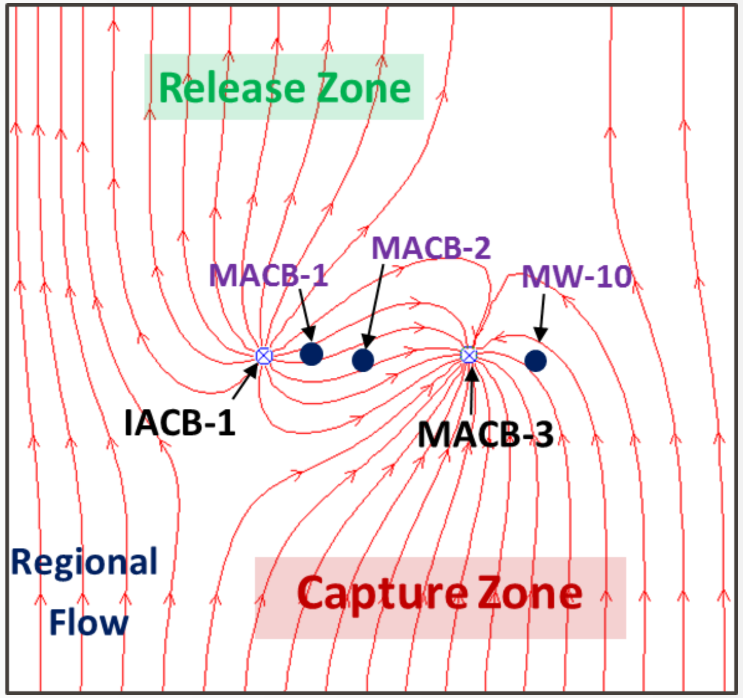
Recirculation Baseline Conditions (8/26/15 - 9/17/15)

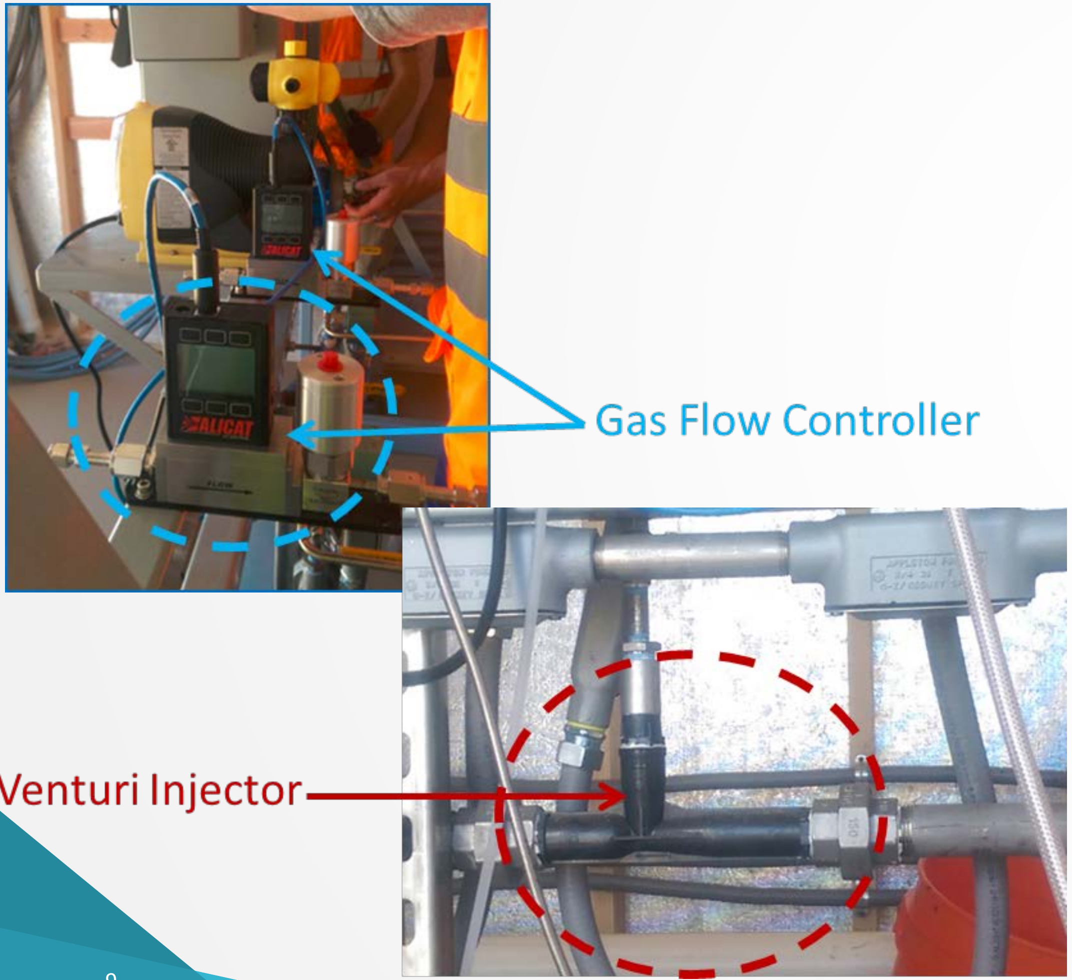
Baseline and Bromide Tracer Testing Phase	1,4-D	µg/L	(EPA 8260B SIM; RL = 3 ppb)			
	Sampling Date	IACB-1	MACB-1	MACB-2	MACB-3	MW-10
No Flow	5/1/2015	62	46	47	45	58
Recirculation Rate 1.75 gpm (Bromide Tracer)	8/26/2015	60	68	61	77	50
	8/28/2015	71	64	60	63	57
	8/31/2015	66	67	66	65	68
Recirculation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



1,4-D concentrations in the recirculation system is stable.

Substrate Addition for Biostimulation

Gas Injection Method



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)

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

System Operation and Optimization for Biostimulation

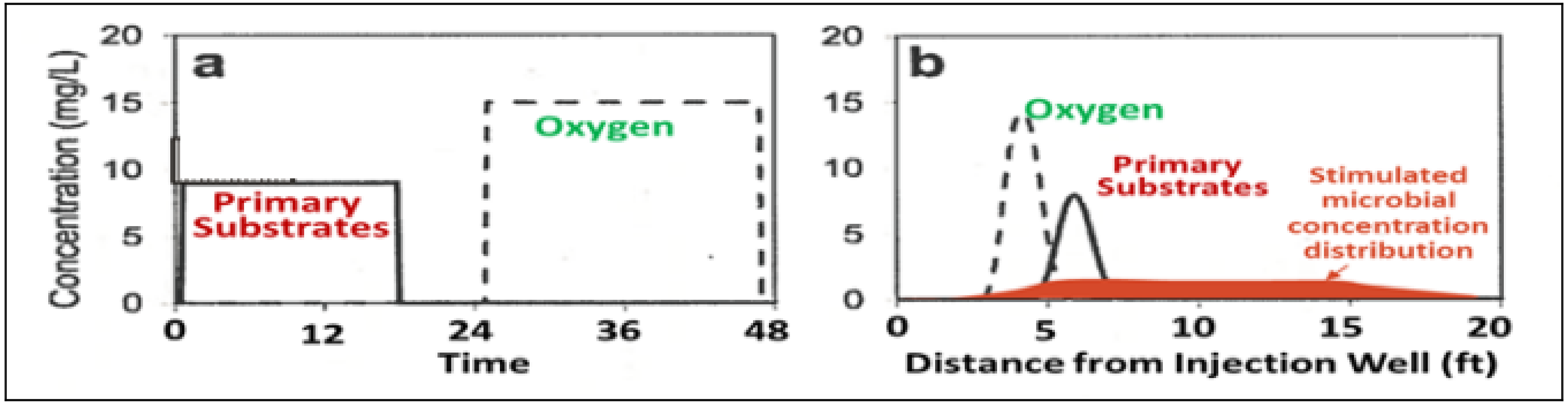
Pulsed Injection

*propane=

Primary substrate

Propane = 5 – 20 mg/L

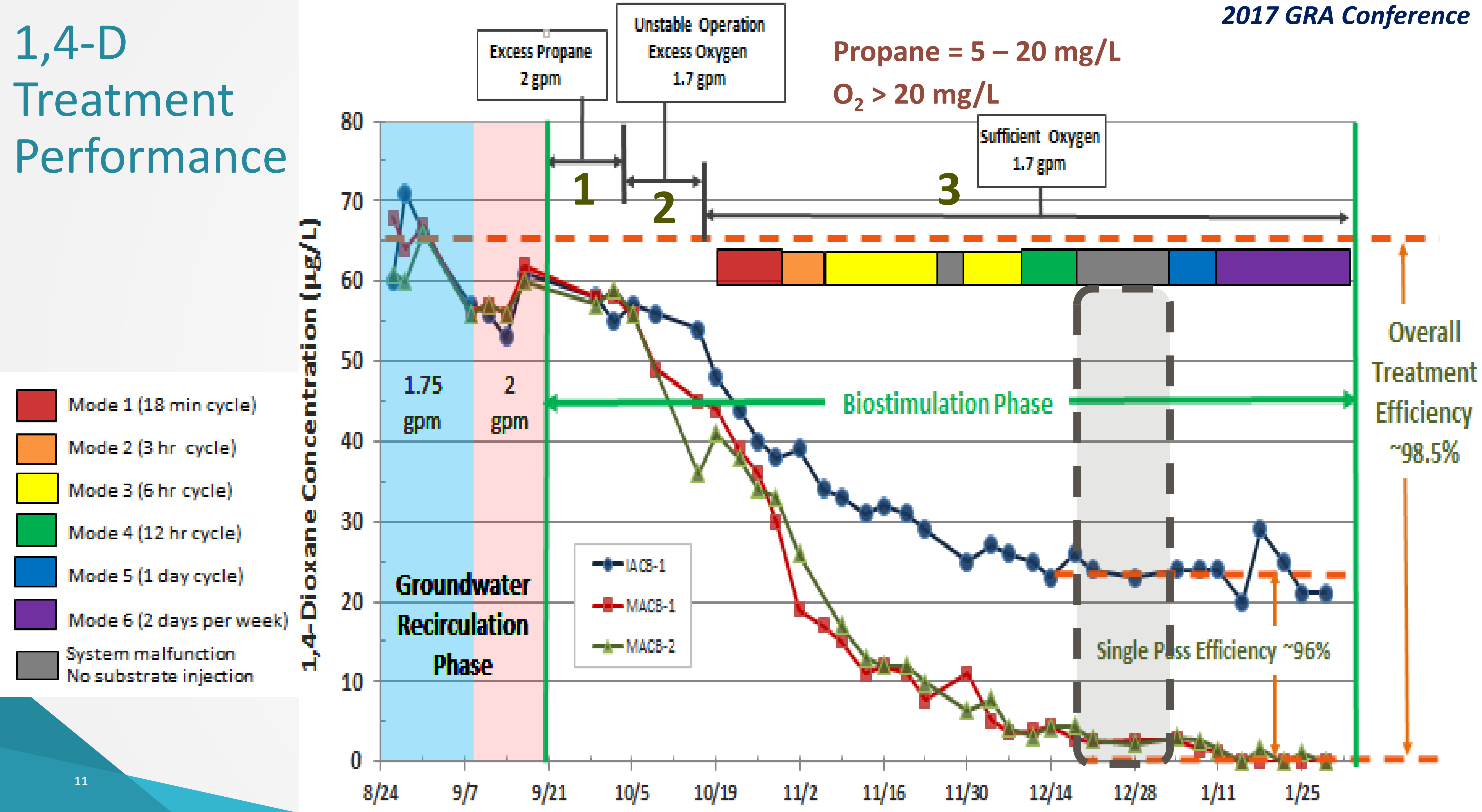
O_2 > 20 mg/L



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

1,4-D Treatment Performance



1,4-D Treatment Efficiency

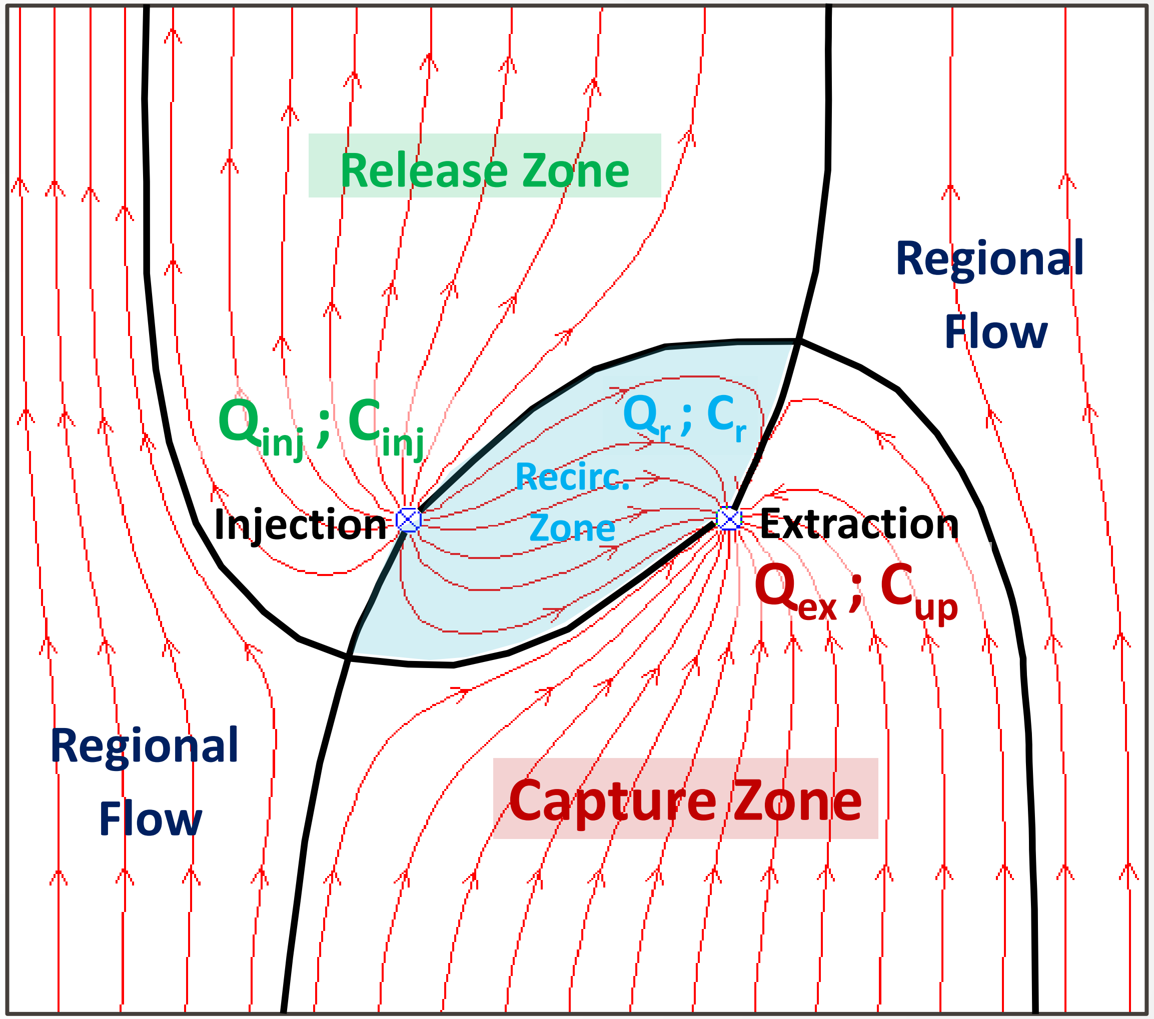
Single pass efficiency (η) = $1 - C_r / C_{inj}$

Overall efficiency ($\eta_{overall}$) = $1 - C_r/C_{up}$

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

Recirculation Ratio (Q_r / Q_{inj})

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).



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

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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

- 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

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

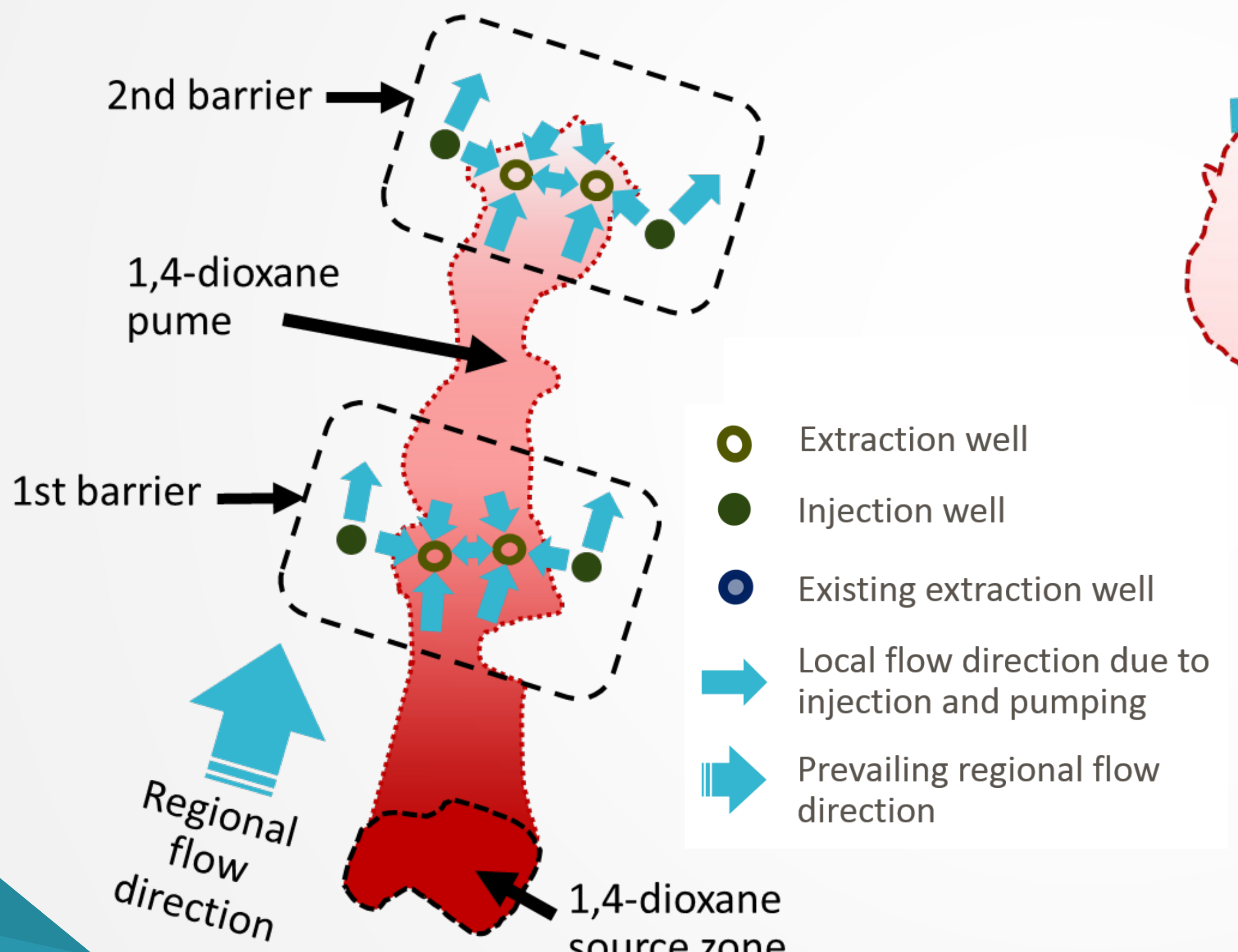
Literature Cited:
McCarty et al. 1998. Full-scale evaluation of in situ cometabolic degradation of trichloroethylene in groundwater through toluene injection. ES&T. Kuo et al. 2004. Pilot studies for in-situ aerobic cometabolism of trichloroethylene using toluene-vapor as the primary substrate. Water Research. Hopkins et al. 1993. Trichloroethylene concentration effects on pilot field-scale in-situ groundwater bioremediation by phenol-oxidizing microorganisms. ES&T.

Insights from the Field Test

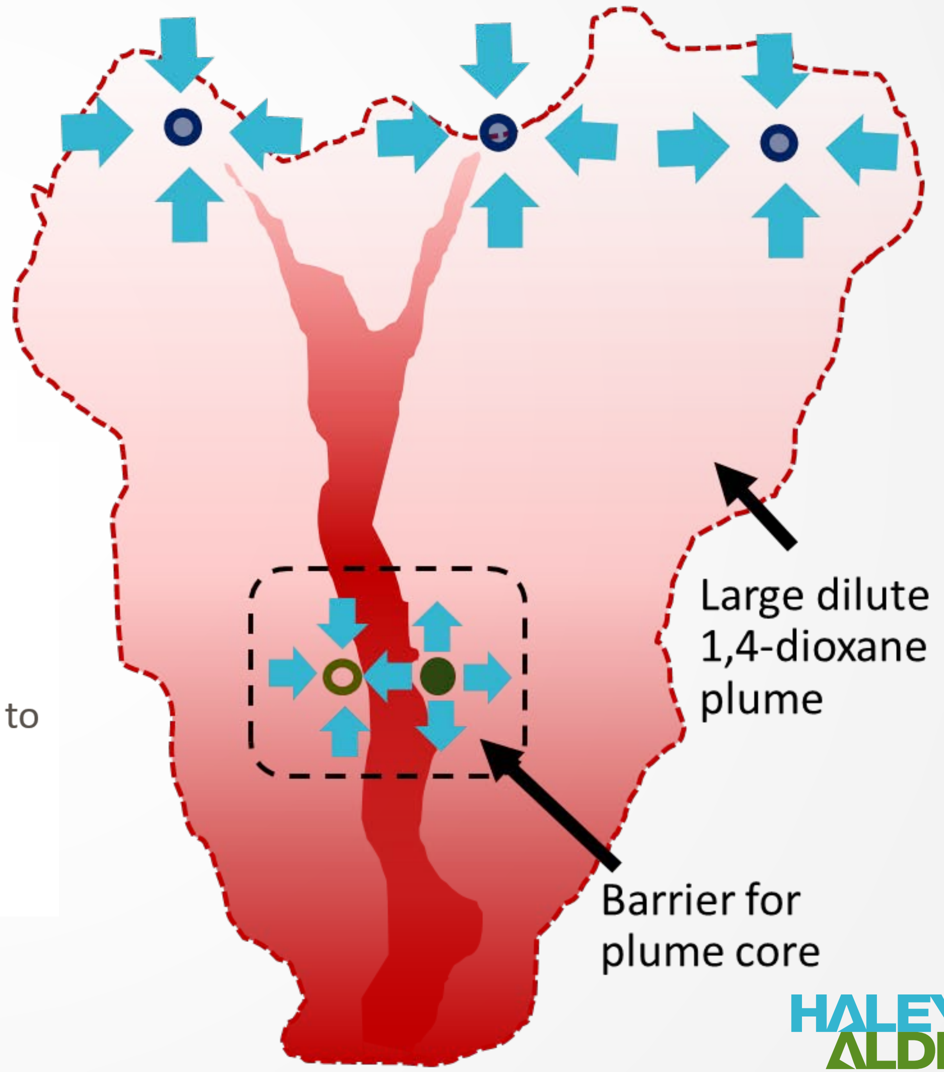
- Concurrent treatment of multiple contaminants by ACB is feasible.
- While the treatment efficiency is contaminant-specific, it can reach over 90% for 1,1-DCE and TCE and more than 95% for 1,4-dioxane and 1,2-DCA.
- ACB may achieve all site-specific cleanup goals simultaneously.
- A much lower substrate loading rate is needed in comparison with anaerobic bioremediation.

Using ACB to Manage a Large Dilute Plume (1)

(a) Biobarriers for the entire plume



(b) Biobarrier for Focused Mass Flux Reduction



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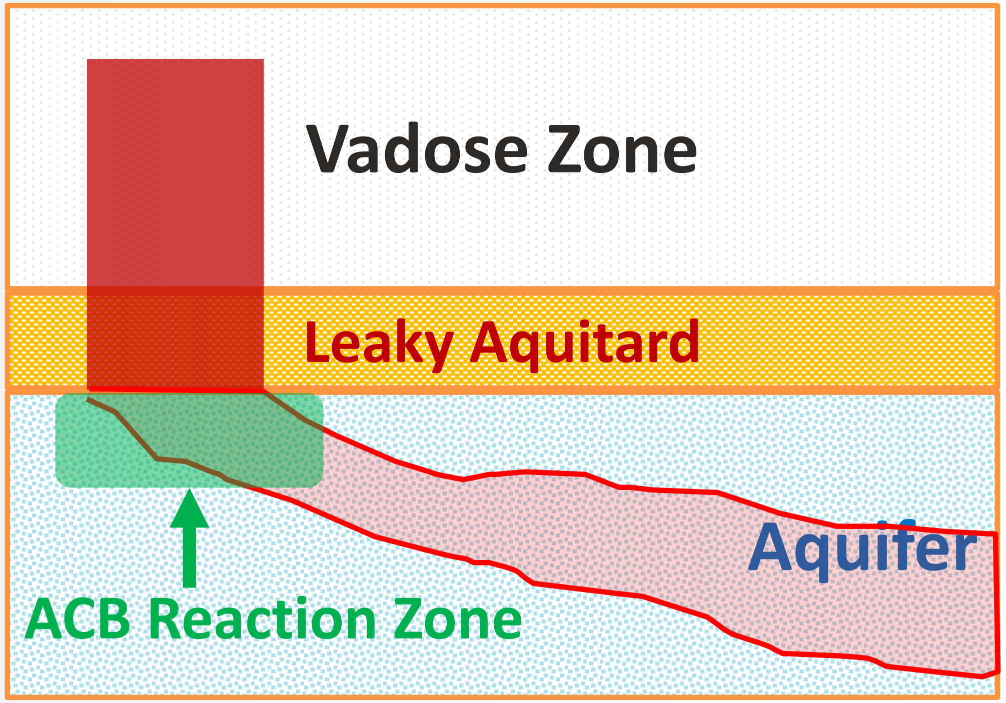
Using ACB to Manage a Large Dilute Plume (2)

(c) Slow Releasing Source Zone Management

- Mass Flux Control



Future Research on ACB

- Potential treatment of Cr(VI) and effective treatment of more recalcitrant cVOCs (e.g., 1,1-DCE and 1,1,1-TCA)
- More knowledge regarding effective substrate combination to stimulate desired ACB activity
- More research on innovative substrate delivery methods to reduce access constraints and promote system reliability
- Better microbiological assessment tools for ACB performance monitoring
- A useful ACB culture for bioaugmentation

Thank you!

Questions?

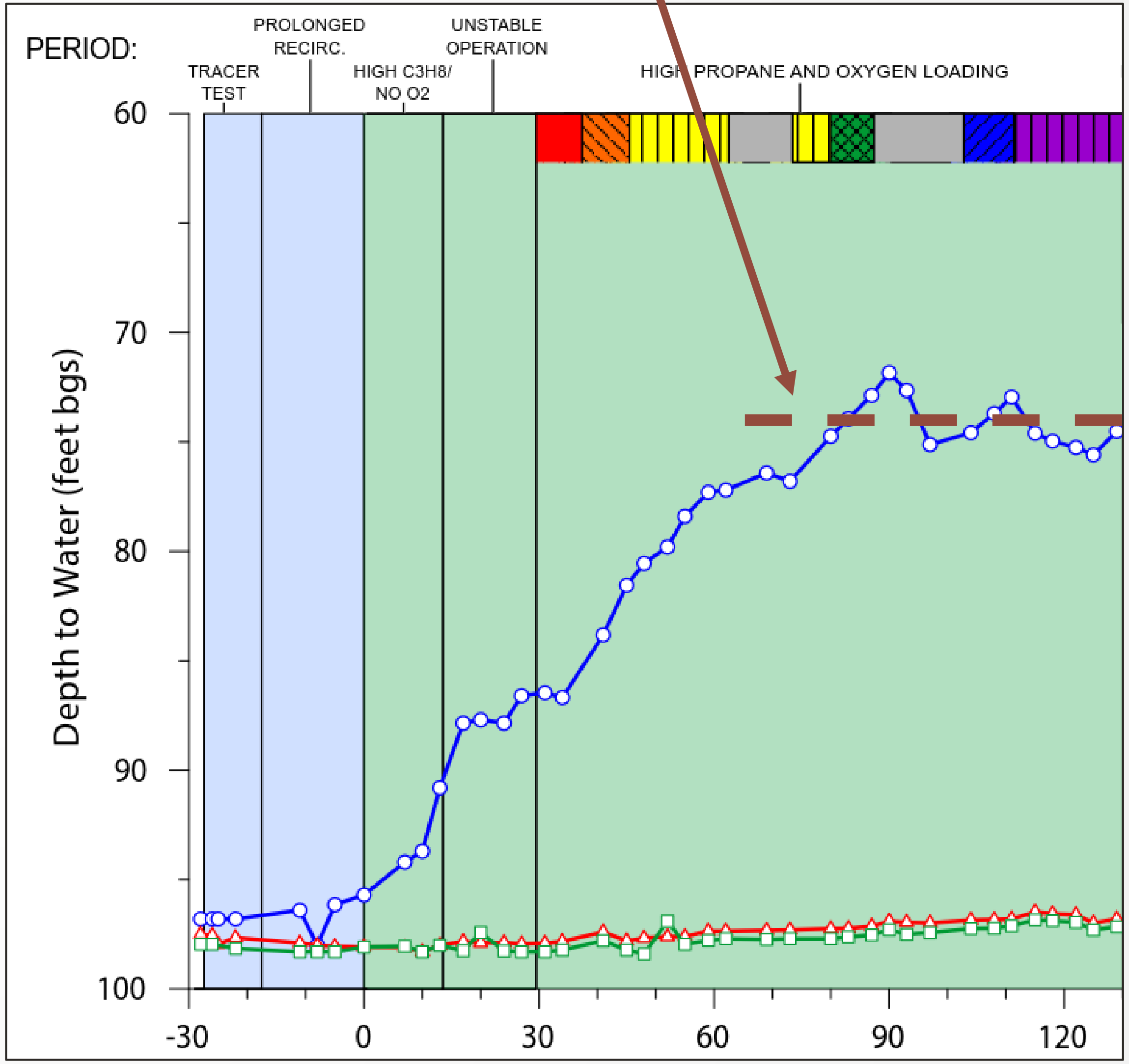
Acknowledgements

Funding support for the field test study from the Air Force Civil Engineer Center (AFCEC)

Is Biofouling Manageable?

- The ACB field test results at the Edwards AFB (McCarty et al., 1988) indicated that the major O&M cost resulted from biofouling of injection wells.
- Our field test shows that biofouling is likely very manageable because a **low substrate loading rate** is needed to sustain ACB activity.

Relative stable water levels at injection well during the period of lower substrate loading rates



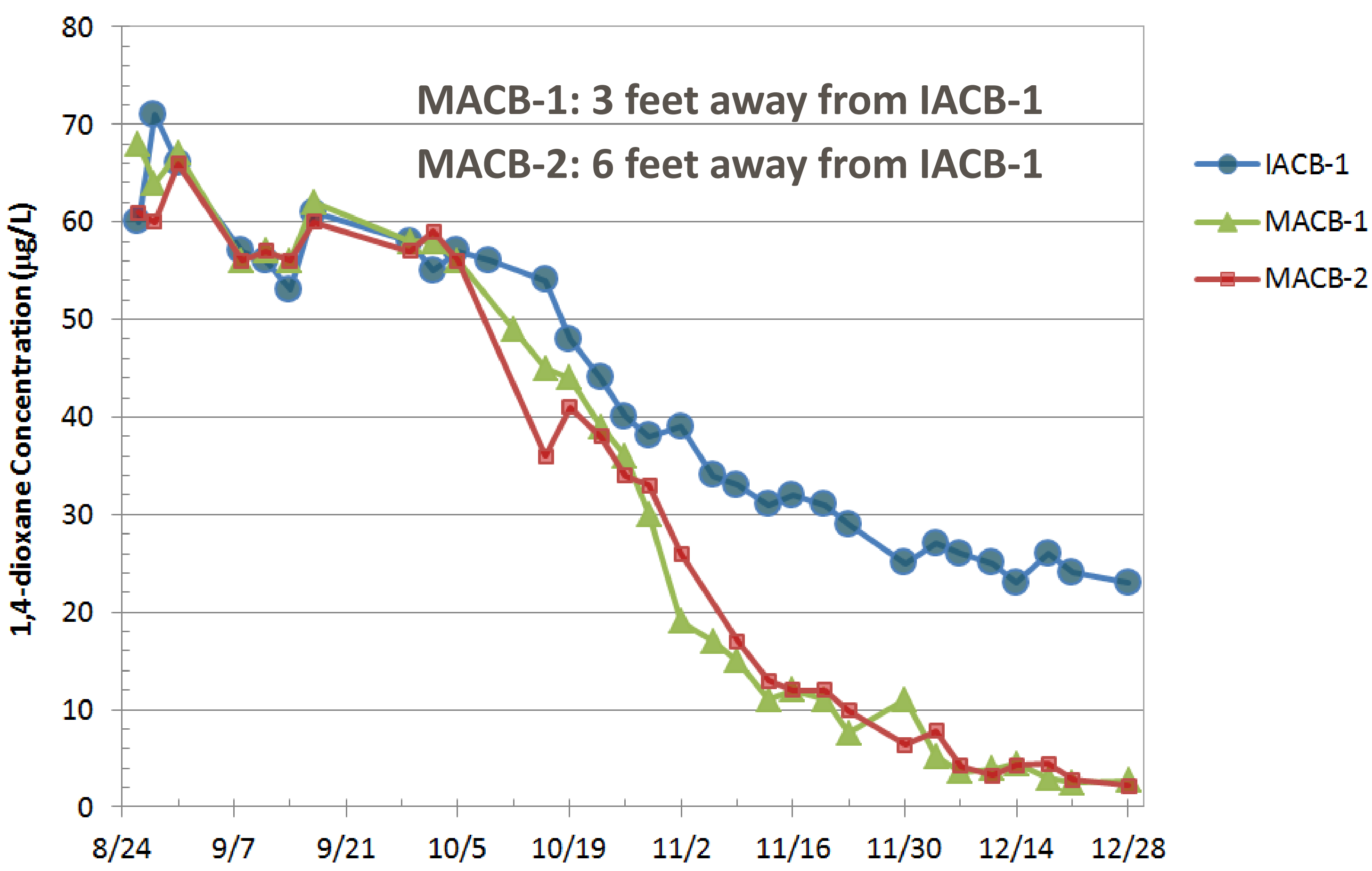
The Size of the Reaction Zone

- 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 site showed that most degradation occurs within 15 feet from the injection well (McCarty et al., 1998).

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



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