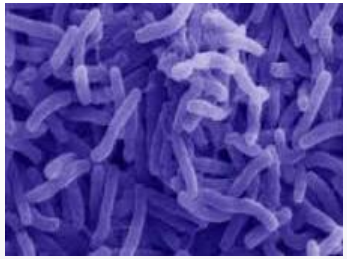
In Situ Bioremediation of the Source Zone for Chlorinated Solvents in Groundwater – Successes and Challenges





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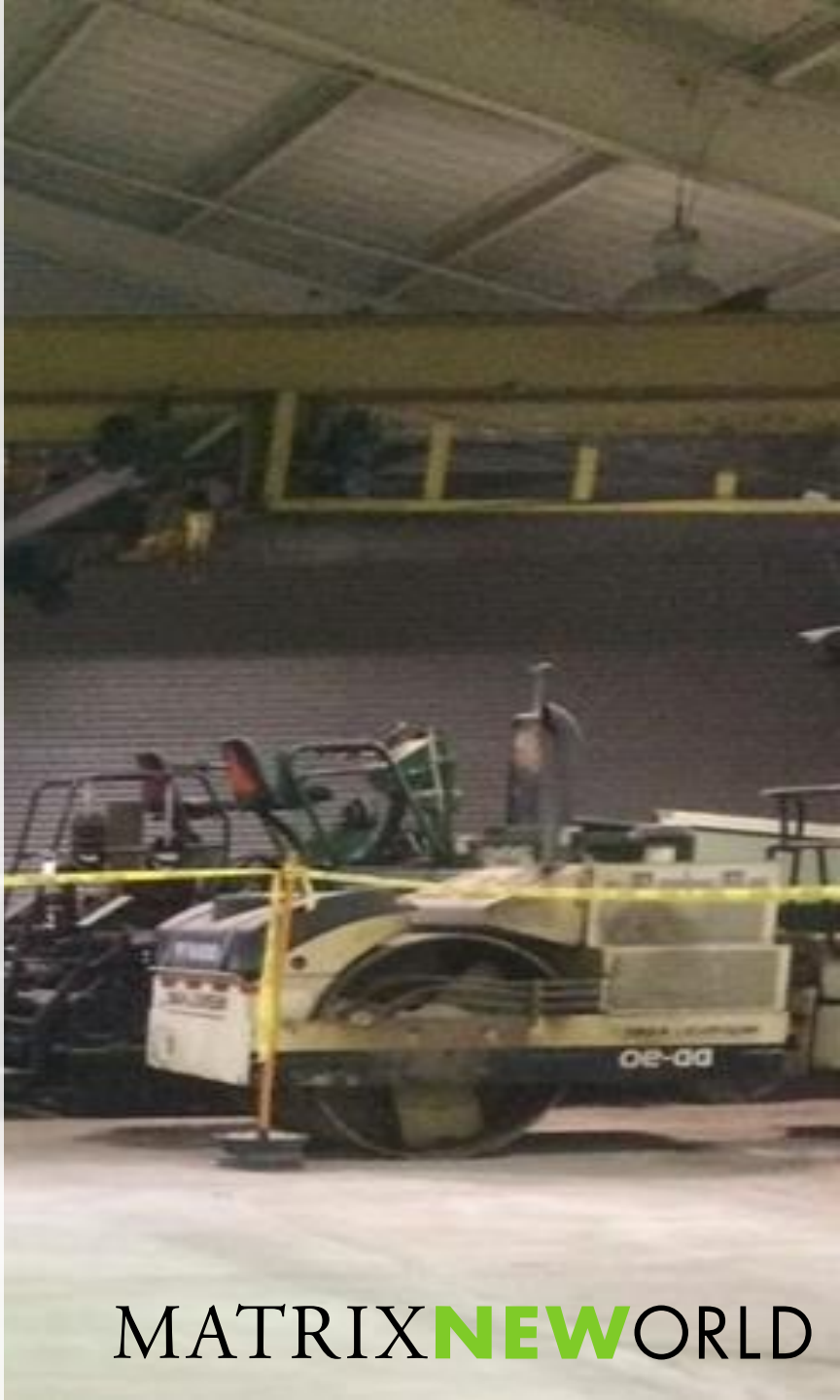
Site History

Aluminum pipe manufacturing co. in Pennsylvania ⇒ 50 years ago.

- Several processing areas - Used chlorinated solvents as degreasers
- Plume in shallow, unconfined aquifer discovered 35 years ago
- Two separate plumes: east and west
  - Eastern plume: high levels of chlorinated VOCs and low 1,4-dioxane
  - Western plume: high levels of chlorinated VOCS and high 1,4-dioxane
- Pump & Treat system operated for several decades with little change in cVOCs in source area or downgradient
- 1,4-dioxane difficult to remediate: not readily volatilized, highly soluble in water, poor adsorption

Current Site Status

- Currently used as an equipment holding facility by municipality
- Numerous cars and trucks in and out of the facility at various times
- Important not to disrupt current operations



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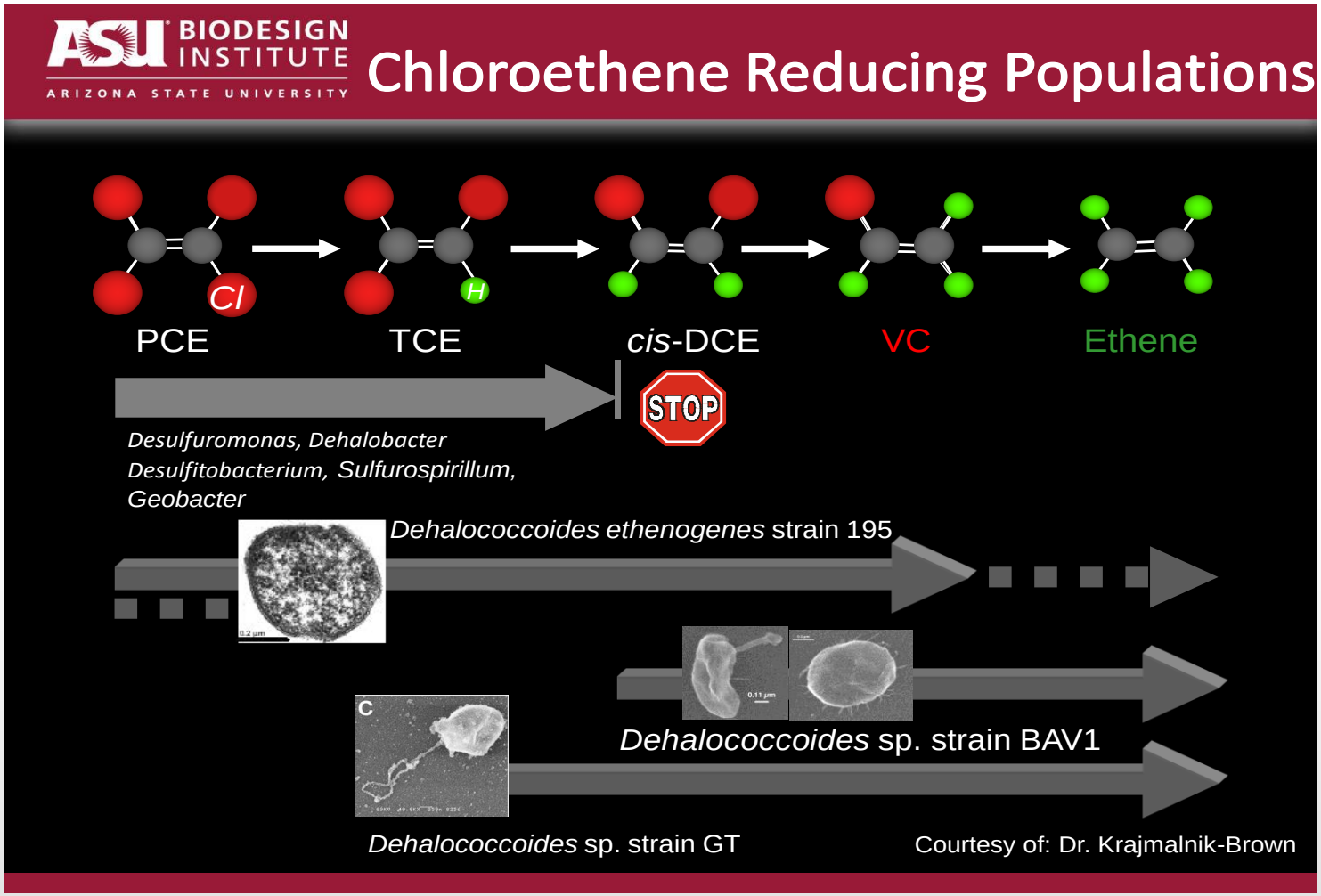
Reductive Dechlorination Pathway



Site Information

- High levels (>20 mg/L) of chlorinated solvents in groundwater, including:
  - Trichloroethene (TCE) up to 25 mg/L
  - *cis*-1,2-Dichloroethene (*cis-1,2*-DCE) up to 1.6 mg/L
  - Vinyl chloride (VC) low detections
  - 1,1,1-Trichloroethane up to 0.25 mg/L
  - 1,1-Dichloroethene up to 0.27 mg/L
  - 1,1-Dichloroethane
  - 1,4-Dioxane up to 3.5 mg/L
- Groundwater velocity is approximately 1–5 ft/day
- Plume has existed for more than 40 years!

Geochemical Results– Why do we care? Need to know what's inhibiting process

- Dissolved Oxygen (DO): <0.5 – 4.3 milligrams per liter (mg/L)
- Nitrate: 1 – 2 mg/L (low)
- Sulfate: 23-32 mg/L (fair)
- Total Organic Carbon: 0.31 – 0.75 mg/L (low)
- Total Kjeldahl Nitrogen: ≤ 0.1 mg/L (low)
- Phosphorus: 0.10 – 0.16 mg/L (low)
- Native microbes need FOOD!!

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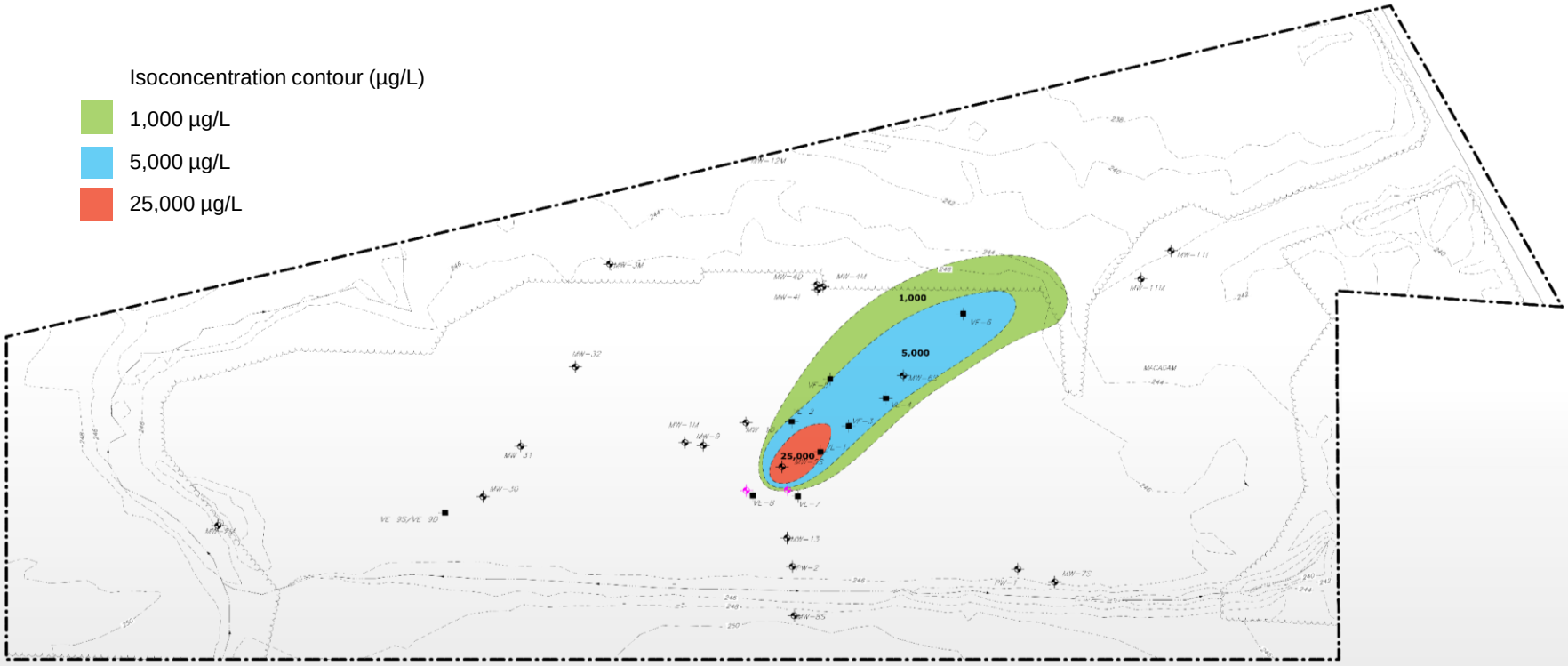
Site Map – Eastern Plume



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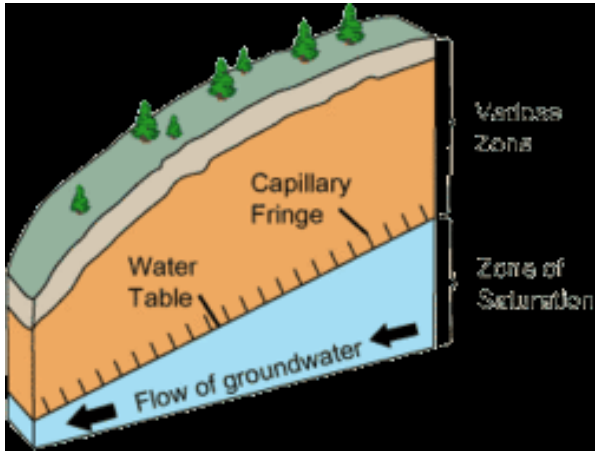
Site Hydrogeology

- Two distinct water-bearing zones, separated by siltstone and shale layers
- Groundwater in the shallow, unconfined aquifer occurs from 4 to 9 feet below ground surface (bgs)



- Second water-bearing zone at depth of approximately 118 to 152 feet bgs
- Contaminants identified in shallow groundwater aquifer are NOT observed in deep aquifer monitoring wells

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Groundwater Data: Competing Electron Acceptors

Well	Target Range	MW-5S (source area)	MW-10	MW-12M
Units	**mg/L**	**mg/L**	**mg/L**	**mg/L**
Electron Acceptors				
Dissolved Oxygen	<0.5	<1	1.95	3.58
Nitrate as N	<0.5	0.67	2	1.9
Manganese	Already low	0.82	0.016	0.025
Iron	Low in source area, higher downgradient	0.038	0.590	2.5
Sulfate	Already low	23	32	29

Water Quality Data

Field Parameters	pH	Dissolved Oxygen (mg/L)	Spec. Conductivity (mS/cm)	Oxidation/ Reduction Potential (ORP) (mV)	Groundwater Depth (ft below ground surface [ft bgs])
MW-3M	7.1	0.8	0.52	176	7.2
MW-4I	7.3	1.5	0.43	61	3.8
MW-4D	7.7	<0.5	0.55	-63	4.2
MW-5S	6.1	<0.5	0.44	155	4.1
MW-7S	6.0	1.4	0.52	100	5.6
MW-8S	6.2	2.4	0.34	201	8.7
MW-10	7.2	1.9	0.36	84	3.7

Groundwater Data: Nutrients

Units	Comments	MW-5S mg/L	MW-10 mg/L	MW-12M mg/L
Nutrient Information:				
Dissolved Organic Carbon	Very low	0.9	0.5	0.3
Ammonia* (distilled)	Limiting	0.08	0.1	0.08
Nitrogen, Total Kjeldahl (TKN)	Non-detect	<1.7	<1.7	<1.7
Orthophosphate as P	Low**	0.2	0.07	0.07
Total Phosphorus as P	Low**	0.23	0.11	0.11

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Groundwater Data: VFA and Gases

	MW-5S	
Units	**mg/L**	**Comments**
Volatile Fatty Acids		In order for reductive dechlorination of cVOCs to occur, the microbes need to have hydrogen present in the groundwater. The native groundwater contained non-detectable levels of VFAs. Likewise, there was no ethene production.
Acetic acid	<1.0	
Formic-acid	<0.02	
Lactic acid	<1.0	
n-Butyric acid	<1.0	
Propionic acid	<1.0	
Pyruvic Acid	<1.0	
Gases	**ug/L**	
Ethane	<5.0	
Ethene	<5.0	
Methane	11	

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Soil Microbial Data

Microbial Populations	(cells/g)
Dehalococcoides spp. (DHC)	2.13E+03
tceA Reductase (TCE)	<1.00E+03
bvcA Reductase (BVC)	4.41E+02 (J)
vcrA Reductase (VCR)	<1.00E+03
Dehalobacter spp. (DHBt)	<1.00E+04 (fair amount)
Total Eubacteria (EBAC)	7.61E+05

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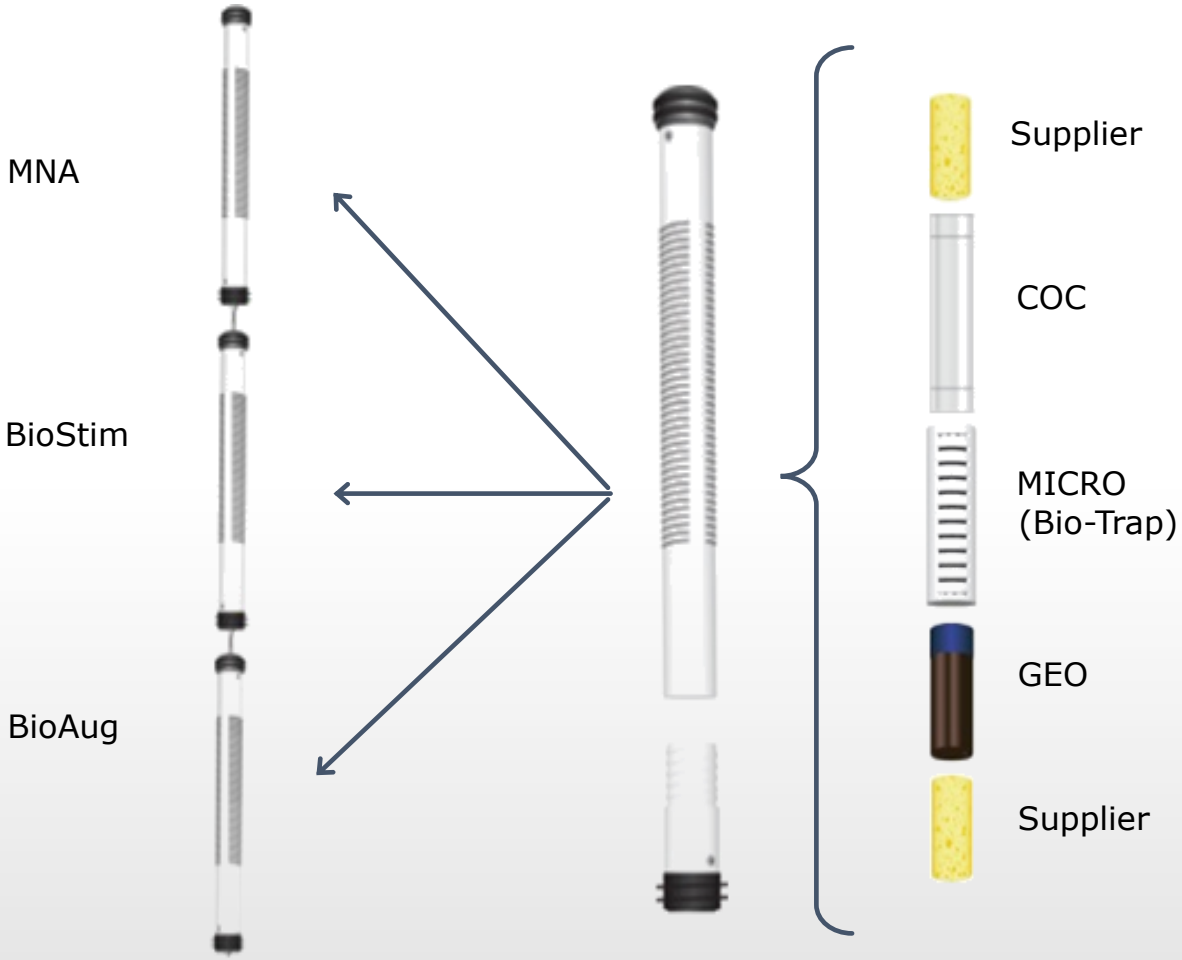
In Situ Evaluation Tools: *In Situ* Microcosm Study



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Bio-Trap Installation – Air Force Plant 4, Texas

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Bio-Trap Study: cVOC Results

	MW-5S	MW-5S	MW-5S	MW-5S
	Biostimulation		Biostimulation+Bioaugmentation	
Carbon Substrate & Other Treatments:	ABC	EHC	EHC, **SDC-9**	EOS AquabupH, **SDC-9**
Contaminant of Concern (µg/L)				
Tetrachloroethene	<10	25.9	<10	30.9
Trichloroethene	110	859	573	1250
cis-1,2-Dichloroethene	3900	4030	6770	5780
trans-1,2-Dichloroethene	22.1	25.9	52.3	39.3
1,1-Dichloroethene	50.7	66.9	86	79.8
Vinyl chloride*	10.1	<10	**93.3**	**322**

Note: * When *Dehalococcoides* consortium (SDC-9) was added, we started to see significant production of VC, especially with EOS substrate

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Source Zone *In Situ* Bioremediation Design

- Establish an *in situ* bioremediation treatment zone using a **temporary recirculation system:** two injection wells upgradient of source area
- Inject **quick-release carbon substrate (QRCS)** to begin **biostimulation phase**
- Followed with injection of **slow-release carbon substrate (SRCS)** to support extended bioremediation of cVOCs
- Monitor groundwater parameters
- Inject microbial consortium SDC-9 for **bioaugmentation phase**
- Evaluate biodegradation over time, modify the injection program as needed over time

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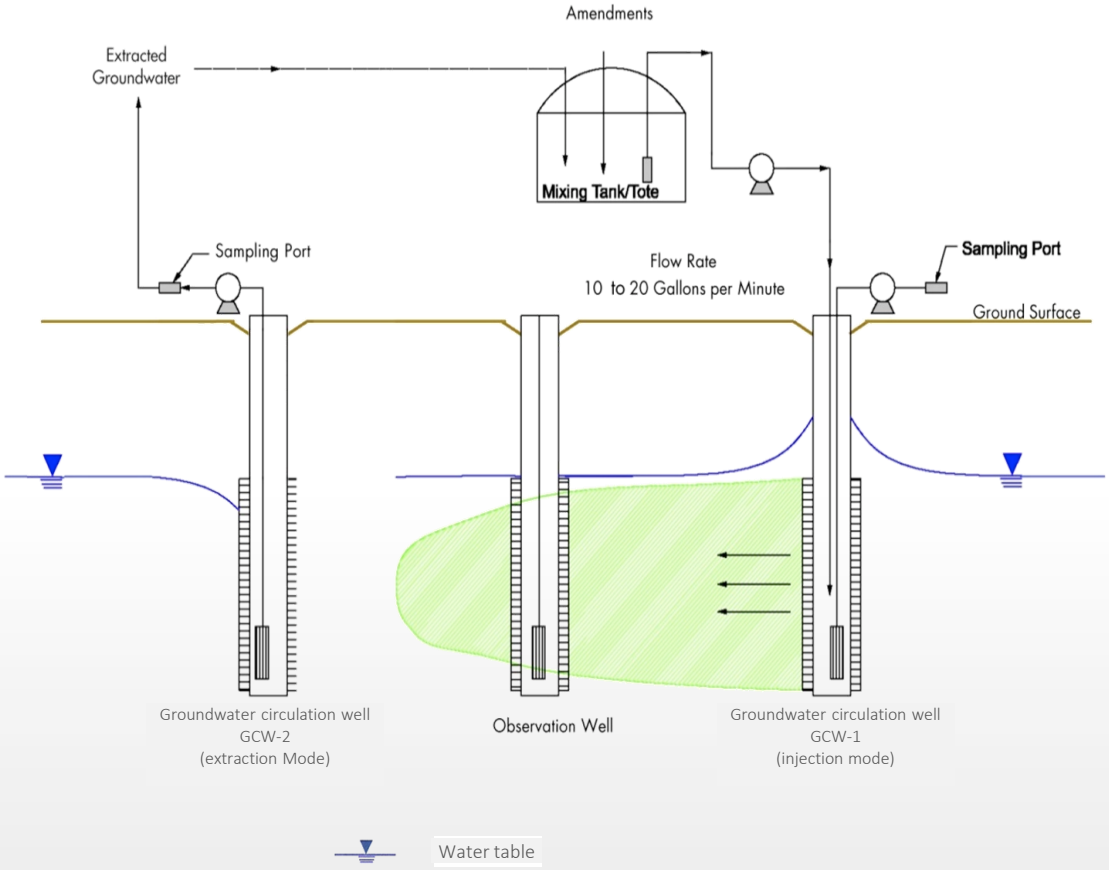
Injection Schematics



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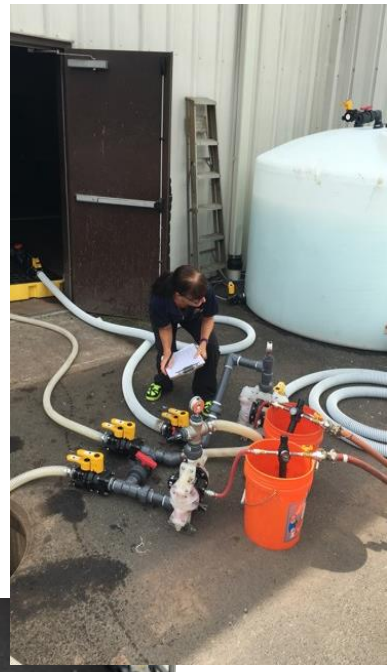
Source Zone Injection Set-Up

- Injection set-up included site groundwater amended with:
  - Quick release carbon substrate (ABC)
  - Slow release carbon substrate (EOS)
  - pH adjustment compound
  - SDC-9 (*Dehalococcoides*) microbial consortium



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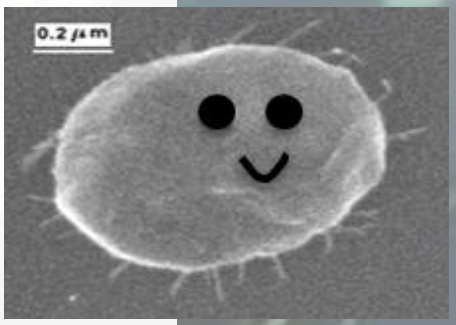
Monitoring Program

- Monitor field parameters: pH, DO, ORP, conductivity, temperature
- Monitor analytical parameters:
  - cVOCs
  - TOC
  - Terminal electron acceptors (O_2, nitrate, Fe, Mn, sulfate)
  - Volatile fatty acids (acetate, propionate, etc.)
  - Total Kjeldahl nitrogen, ammonia, nitrate, nitrite
  - Total P and ortho-phosphate
  - Dissolved metals
  - Dissolved gases: methane, ethane, ethene, carbon dioxide
  - Microbial biomass: key microbes - *Dehalococcoides*
  - Phospholipid fatty acid (PLFA)



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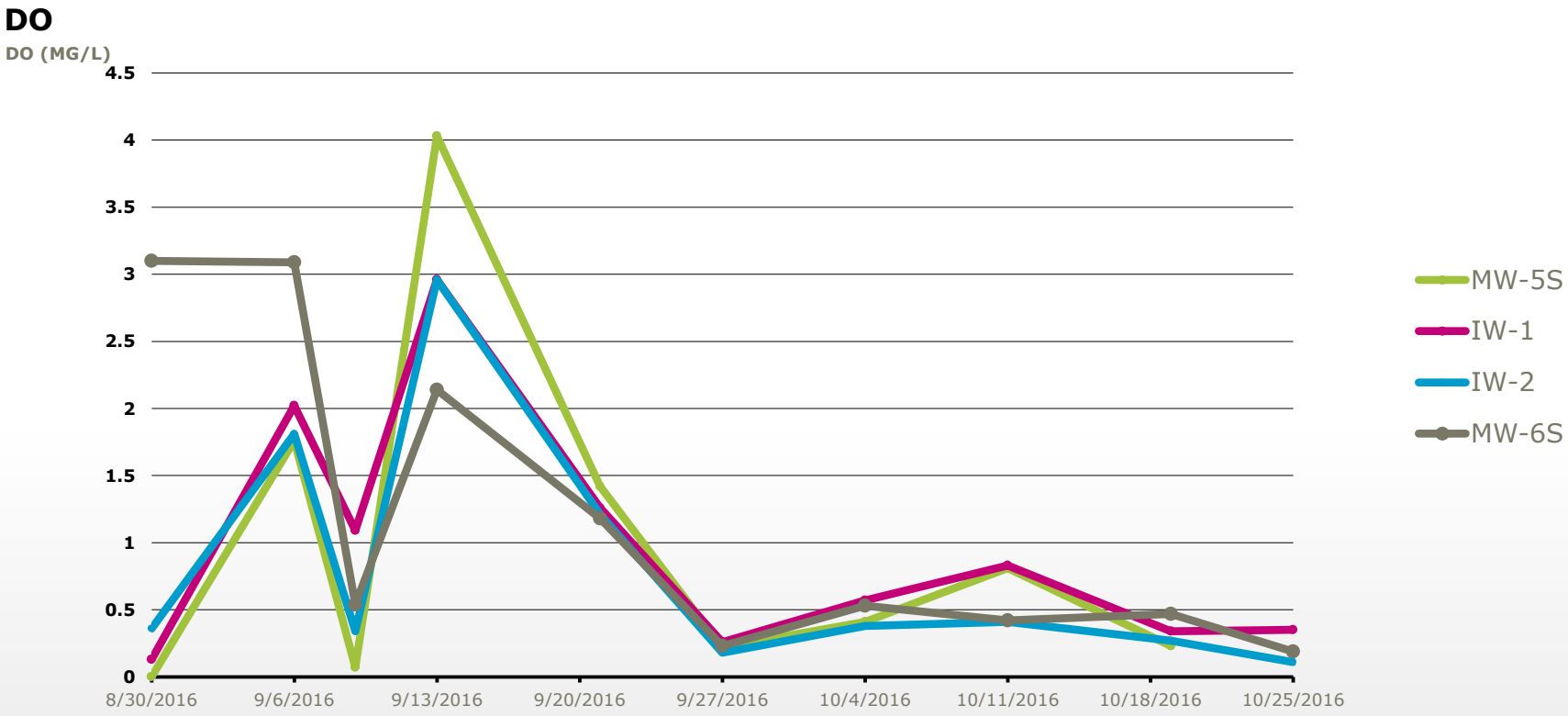
Dissolved Oxygen Data



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TOC, Sulfate, and Volatile Fatty Acid Results

Well #	Back-ground TOC	Recent TOC	Back-ground Sulfate	Recent Sulfate	Recent Acetate	Recent Propionate	Recent Butyrate	Recent Pentanoic acid
Units (mg/L)								
MW-5S	< 1	1,330	23	1.6	1,400	640	250	180
IW-2	< 1	2,310	20-30	1.2	2,100	890	240	5

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Chlorinated VOC Results

Sample Location	Sample Date	1,1,1-TCA	1,1-DCE	PCE	TCE	cis-1,2-DCE	trans-1,2-DCE	Vinyl Chloride
Units (ug/L)								
MW-5S (19-35)	5/7/2015	260	240	340	28,000	1,600	<18	<6
	9/9/2015	140	190	330	24,000	850	29	4.1
	11/19/2015	150	140	290	19,000	1,100	<18	<6
	2/19/2016	120	160	320	19,000	930	<9.0	<3.0
	12/9/2016	<2.8	18	5.1	47	4,000	13	72
	3/13/2017	<2.8	11	1.3	4.6	3,400	8.8	120
	7/26/2017	<2.8	0.71	0.95	11	99	9.5	63
	2/15/2018	**<0.3**	**<0.4**	**<0.2**	**<1**	**4**	**2.4**	**14**

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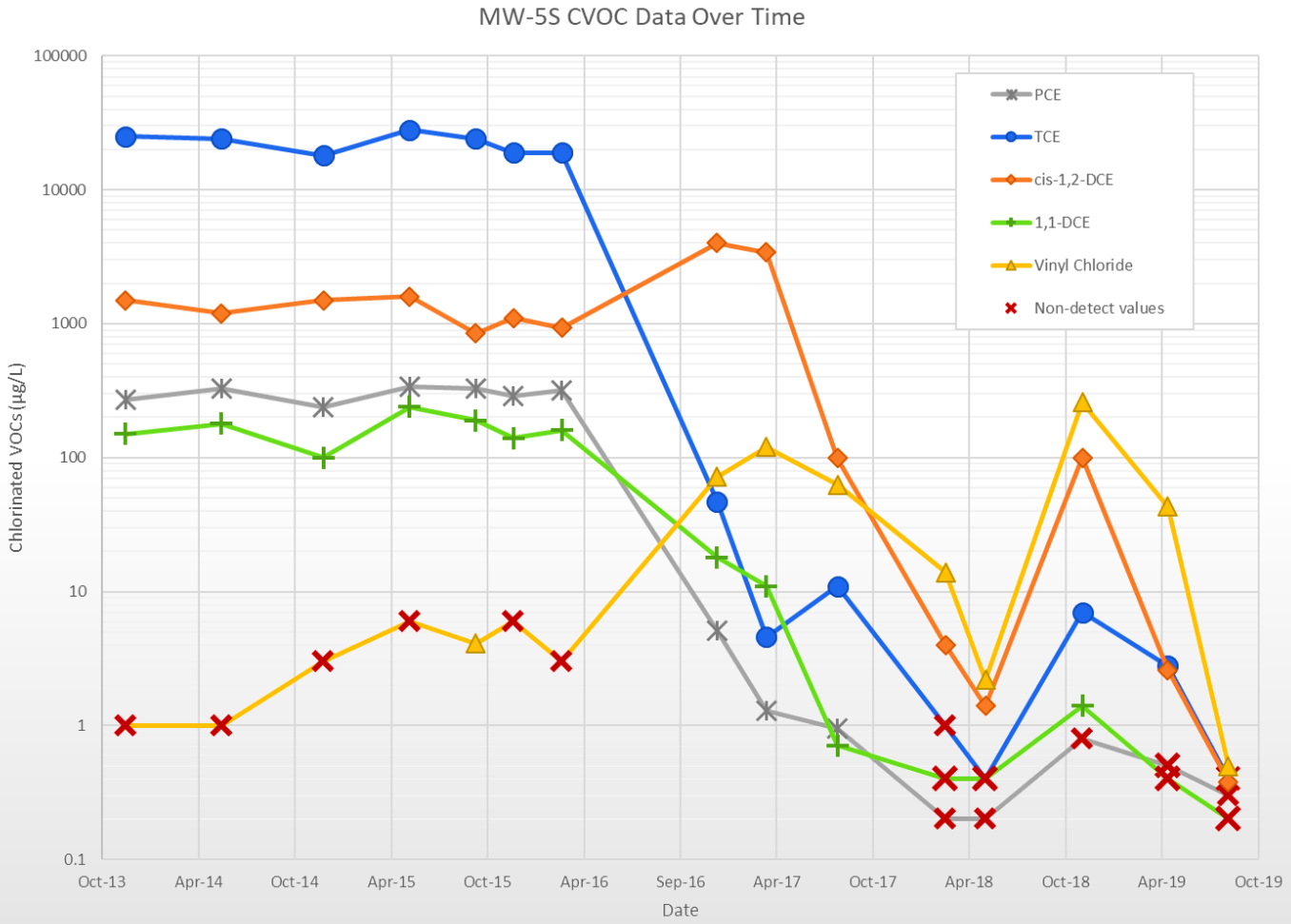
Chlorinated VOC Results



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Summary of Eastern Plume

- Bio-Trap testing provided key information for field-scale design.
- Performed biostimulation first, followed by bioaugmentation
- Increase in TOC led to a significant increase in microbial populations and reduction in cVOCs
- Major increase in VFAs
- **The combination of biostimulation and bioaugmentation resulted in a 2–4 order of magnitude reduction in chlorinated ethene concentrations**
- Elevated levels of *Dehalococcoides* and ethene observed in source area wells.

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Western Plume: Groundwater Chlorinated VOC and 1,4-Dioxane Results

Sample Location (Screen)	Sample Date	1,1,1-TCA	1,1-DCE	cis-1,2-DCE	PCE	trans-1,2-DCE	TCE	Vinyl Chloride	1,4-Dioxane	TOTALS
Act 2 NRUA MSC[(1)]		200	7	70	5	100	5	2	32	
MW-30 (15-40)	6/10/2016	430	1000	510	2300	2.5	2300	18	3700	10,260
MW-31 (15-40)	6/10/2016	190	1700	860	2100	4.3	3300	20	4300	12864
MW-32 (15-40)	6/10/2016	600	1400	2100	2000	9.1	2400	55	1900	10174

Notes: 1 – Pennsylvania Dept of Environmental Protection Act 2 Non-Residential Used Aquifer (NRUA) Medium Specific Concentrations (MSC)

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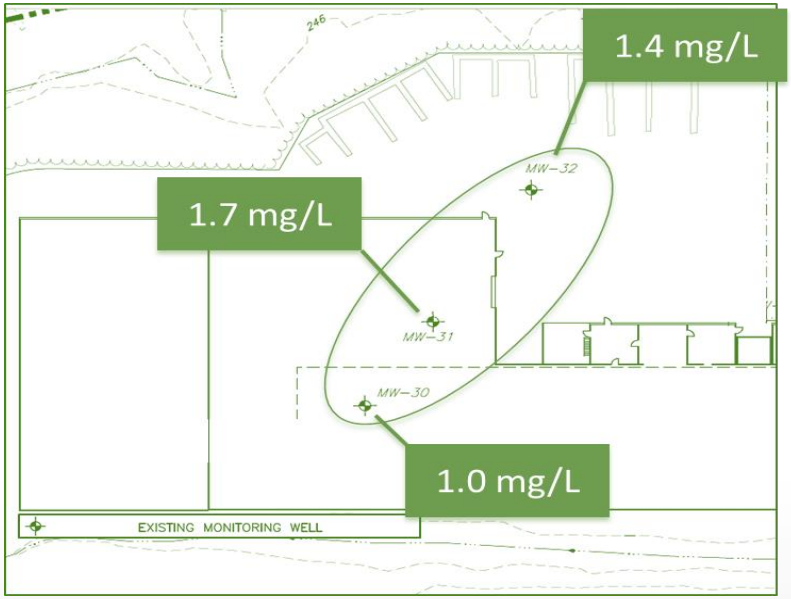
Previous Studies

- Showed inhibition by 1,1-DCE and by *cis*-1,2-DCE (0.5 to 2.1 mg/L)
- DXMO and ALDH enzymes are suppressed when exposed to > 5 mg/L (Zhang et al.)



S. Zhang et al., Environ. Sci. Technol. 2016, 50, 9599−9607

- Question - Are concentrations of 1,1-DCE and cis-1,2-DCE too high to allow effective biodegradation of 1,4-dioxane to occur?

Remediation Challenges

- Mildly anaerobic conditions in some areas (need aerobic conditions)
- 1,1-DCE present (suppresses DXMO and ALDH enzymes)
- Multiple source areas
- Low levels of nutrients

Parameter	Concentration (µg/ L)
NO_3^-	600 - 1100
Organic Nitrogen	<100
Phosphorus	90 - 200
1,1-DCE	1000 - 1700
cis-1,2-DCE	500 - 2100

Bio-Trap Study Background Results

Client Sample ID: (flow path wells)	MW-30	MW-31	MW-32
Dioxane Monooxygenase DXMO	<5.10E+00	1.00E-01 (J)	<5.00E+00
Aldehyde Dehydrogenase ALDH	<5.10E+00	<5.10E+00	<5.00E+00

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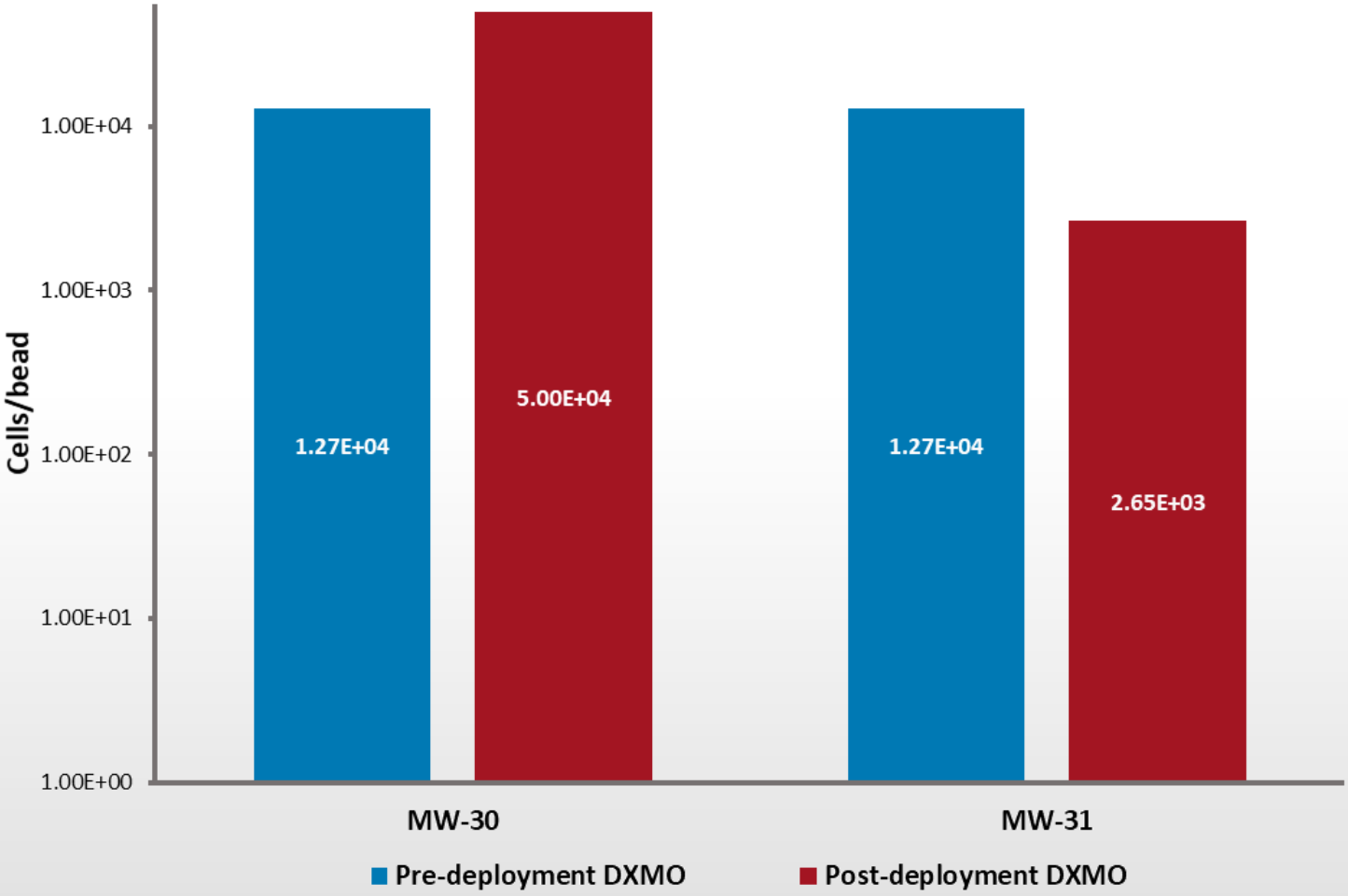
Bio-Trap Study Results with Bioaugmentation



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ISM Study with Biostimulation & Bioaugmentation

- *In Situ* Microcosm Study
  - Analysis of robustness of CB1190
  - Will bioaugmentation work at this site?
  - Is biostimulation via O_2 required?
  - Are nutrients needed at this site?
- How they work
  - Each unit represent a treatment option
  - Each unit contains passive samplers
  - Deployed for 60 days, recovered, and analyzed

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In Situ Microcosm Study Results

Client Sample ID:	Units	MW-32MNA	MW-31 BioAug	MW-30 BioAug+ORC+Osmo	MW-30 BioAug+Osmo
CSIA of 1,4-dioxane Carbon	$\delta^{13}C$ (‰, VPDB)	-27.0	-29.3	-26.4	-23.8
CSIA of 1,4-dioxane Hydrogen	$\delta^{2}H$ (‰, VSMOW)	ND	-79.9	ND	ND

BioAug = Bioaugmentation
ORC = Oxygen releasing compound
Osmo = Osmocote (nutrient source)

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In Situ Microcosm Study Results

Gene Targets	Units	MW-32MNA	MW-31 BioAug	MW-30 BioAug+ORC+Osmo	MW-30 BioAug+Osmo
Dioxane Monooxygenase (DXMO)	Cells/bead	<2.5E+02	1.71E+05	1.53E+04	3.39E+05
Aldehyde Dehydrogenase (ALDH)	Cells/bead	<2.5E+02	1.36E+05	1.14E+04	2.27E+05

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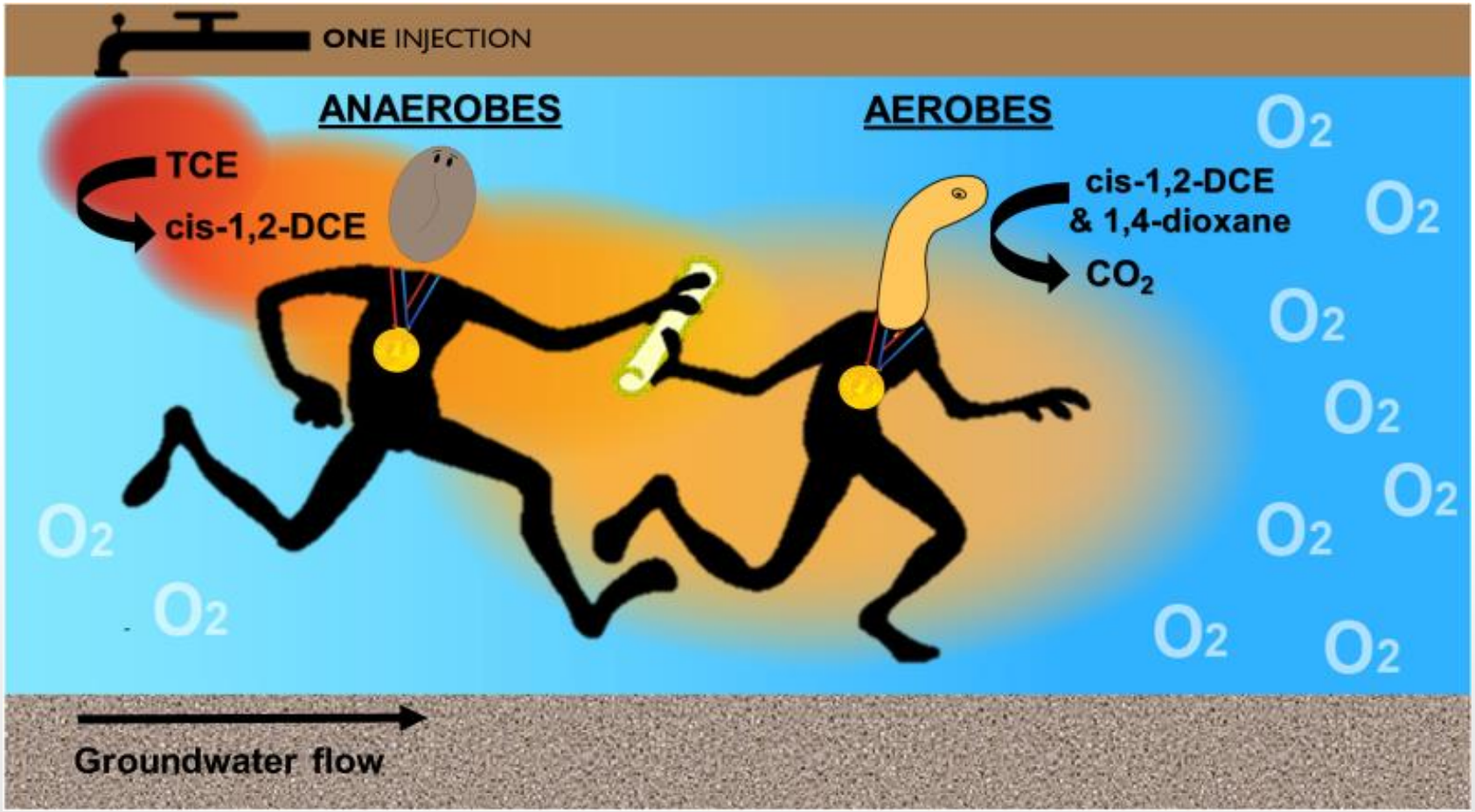
Olympic Microbes at Work!



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Conclusions

- CSIA and Gene Probe results indicate the following:
  - DXMO and ALDH were not detected in **MNA MW-32** Bio-Trap
  - DXMO and ALDH were detected at high levels > 1.3E+05 cells/bead in **BioAug MW-31** Bio-Trap
  - Significant $\delta^{13}C$ increases were observed in 1,4-dioxane in BioAug units amended with nutrients only and nutrients and oxygen in **MW-30** Bio-Trap
  - Elevated levels of DXMO and ALDH observed in the **MW-30 BioAug** Bio-Traps compared to the prior MNA Bio-Trap
  - Increasing $\delta^{13}C$ of 1,4 Dioxane was observed in the **MW-30 BioAug** Bio-Trap with CB1190 and nutrients (-23.8‰, VPDB) compared to the Bio-Trap amended with CB1190, nutrients and ORC (-26.4‰, VPDB)
  - Nutrients may play a larger role than previously expected

Conclusions

- CSIA and Gene Probe results indicate the following:
  - These results demonstrate that bioaugmentation using ***Pseudonocardia dioxanivorans CB1190*** may be appropriate for *in situ* biodegradation of dioxane at this site
  - Preparing for field implementation; plan to monitor for DXMO, ALDH, $\delta^{13}C$ 1,4 Dioxane, dissolved oxygen, TOC and nutrients

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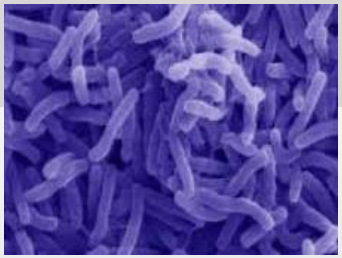

THANK YOU

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