Webinar "Fun Facts"

- The webinar will start promptly at 1:00 EST
- All participants will be on mute
- One day after the webinar has been concluded an email will be sent that will allow you to download a copy of the webinar
- The webinar is being recorded and will also be made available via email
- Please use the "Questions" panel to ask questions for the presenters. Questions will be answered at the end of the webinar. If any questions are missed due to a lack of time, we will follow-up via email after the webinar.

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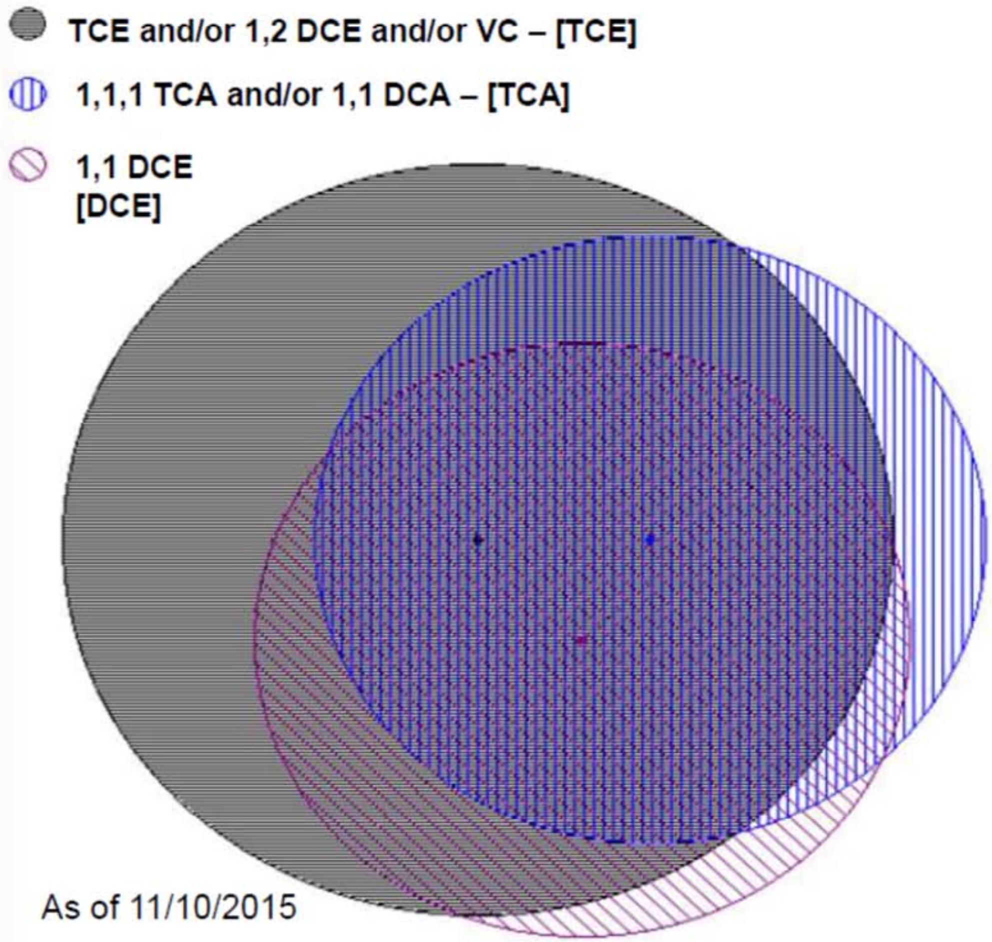
1, 4-Dioxane Remediation

Agenda

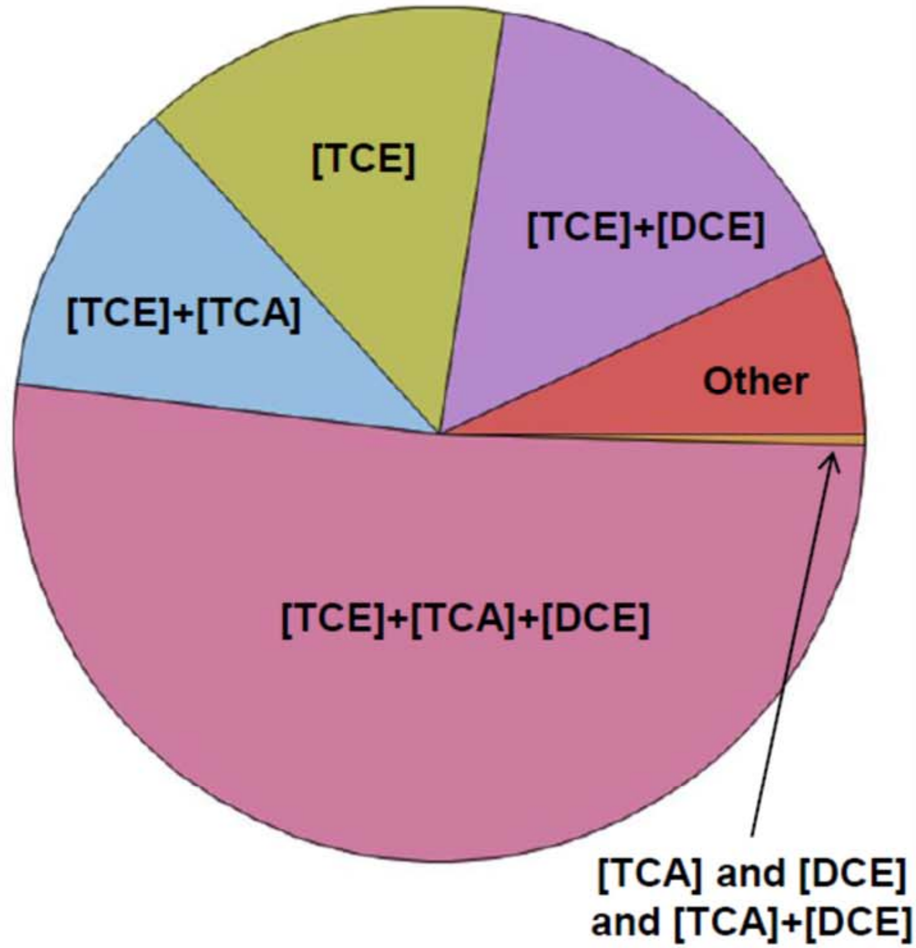
- Basic properties of 1,4-dioxane relative to remediation
- A discussion of applicable reliable remedial technologies with case studies
  - Ex situ
    - Advanced oxidation
    - Adsorption
  - In situ
    - In situ chemical oxidation
- Promising remedial in situ technologies
  - Phytoremediation
  - Air Stripping
  - Thermally enhanced soil vapor extraction
  - Bioremediation / Monitored Natural Attenuation
    - Analytical Methods to demonstrate destruction

Dioxane and Solvents Co-Occur

cVOC co-Occurrence at USAF Sites



Dioxane Detections at USAF Sites (n = 1,663 wells)



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From presentation by Pat Evans of CDM Smith

Basic Properties of 1,4-Dioxane in the Environment

Compound	Solubility (mg/L)	Koc (cm^3/g)	Henry's Law Const. (unitless)	Vapor Pressure (mmHg)	Water Quality Criteria ug/L
MtBE	51,000	7.26	0.025	245	13
PCE	200	155	0.753	24	5
Benzene	179	59	0.227	76	5
1,4-Dioxane	**miscible**	**17**	**0.0002**	**37**	**~0.35•o**

- EPA risk assessment guideline. No federal MCL has been established.
- o The MassDEP's Office of Research and Standards (ORS) drinking water guideline for 1,4-dioxane is 0.3 µg/L

❑ What do these properties mean?

- Volatile as a residual product
- Very soluble in groundwater
- When dissolved, not easily adsorbed, therefore is not readily retarded in soils
- When dissolved, prefers to be in aqueous vs. vapor phase i.e. not easily stripped out of groundwater
- TYPICALLY MEASURED ON LEADING EDGE OF PLUME

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Ex Situ Technologies

XDD Case Study: Advanced Oxidation

- Landfill leachate and groundwater extraction system (50-100 gpm)
- 1,4-dioxane up to 322 ug/L (has attenuated over time)
- Water is currently treated using powdered activated carbon/sand filtration
- Advanced Oxidation Process (AOP) was considered to address 1,4-dioxane that is not treated by powdered activated carbon or filtration
- Complication: Bromide up to 1,300 ug/L

AOP Process

- Reaction between H_2O_2 and O_3 produces hydroxyl free radical (•OH) – proven effective on 1, 4-dioxane
- Bromate (BrO_3^-) is a common disinfection by-product
  - Formed during common water treatment process (e.g., chlorination, direct ozonation, AOP, etc.)
  - Naturally occurring bromide ions (Br^-) in the raw ground water/surface water source is the pre-curser to bromate formation.
  - MCL for bromate is 10 ug/L in drinking water

Oxidant Dosing and Impact on Bromate Control a Balancing Act

- The molar ratio of hydrogen peroxide to ozone can be adjusted to minimize bromate formation. Typically, increasing the amount of hydrogen peroxide relative to ozone, the ozone will be more completely reacted, reducing bromate formation
- Trade-off: excess hydrogen peroxide can now react with the hydroxyl radicals (i.e., termed hydroxyl radical "scavenging"), which reduces the treatment efficiency
- Could use UV instead of ozone to avoid bromate, but:
  - High electricity requirements
  - Significant operation and maintenance (O&M)
  - Efficiency dictated by ultraviolet contact time
  - Requires clear water (acidification or pre-treatment).
  - Acidification may require post-treatment pH adjustment

1,4-Dioxane Destruction Results

Test Scenario	1,4-Dioxane			Bromate		
High Spike, 240 ug/L 1,4-dioxane **H_2O_2:O_3 Ratio = 1.0 (all scenarios)**	O_3 (mg/L)	H_2O_2 (mg/L)	Final 1,4-dioxane (ug/L)	O_3 (mg/L)	H_2O_2 (mg/L)	Final Bromate (ug/L)
	5	3.6	48	5	3.6	64
	10	7.1	6.6	10	7.1	190
	13	9.2	1	13	9.2	290
	20	14.2	1	20	14.2	430
	Result: 1,4-dioxane destruction more effective with increased ozone			Result: Bromate conc. increased significantly as ozone dose increased.		

Conclusions: Hydrogen peroxide/ozone molar ratio requires optimization to reduce bromate formation. Also, likely to require more nozzle injection points to reduce bromate while achieving desired 1,4-dioxane destruction (7 to 9 nozzles used in Round 1, increased to 20 and 30 in Round 2).

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Bromate Formation Control Results

Test Scenario	Impact on 1,4-Dioxane			Impact on Bromate		
High Spike, 240 ug/L 1,4-dioxane **O_3 Dose = 10.7 mg/L** **H_2O_2:O_3 Ratio = 2.5 and 4.0**	Molar Ratio	2.5	4.0	Molar Ratio	2.5	4.0
	No. Inj. Noz.	Final 1,4-dioxane (ug/L)		No. Inj. Noz.	Final Bromate (ug/L)	
	20	3.4	10.0	20	12	3
	30	7.2	21.0	30	4.9	2.2
	Result: 1,4-dioxane destruction is less effective as MR increases and as no. of injection nozzles increase.			Result: Bromate concentration decreases as MR increases and as no. of injection nozzles increase.		

Conclusions: Increasing the molar ratio of hydrogen peroxide to ozone reduces the bromate formation and bromate was reduced to below 10 ug/L in some scenarios. However, 1,4-dioxane destruction becomes less efficient. In addition, increasing the number of injection nozzles also reduces bromate, but reduces the 1,4-dioxane destruction.

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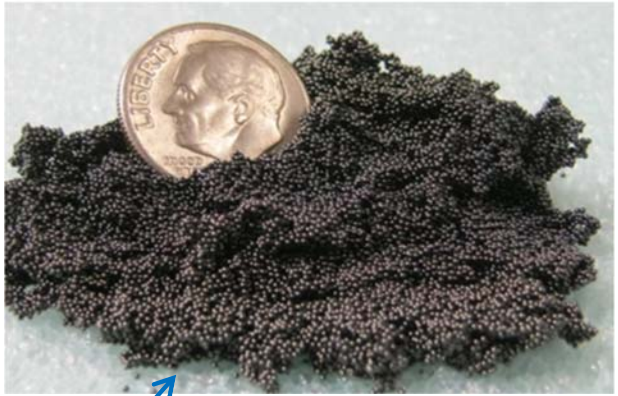
Case Study ect_2:Adsorption

- Granudal activated carbon (GAC) limited effectiveness on 1,4-dioxane – cost effective?
- Synthetic Media can be used to collect various contaminants from liquids, vapor or atmospheric streams and be reused indefinitely



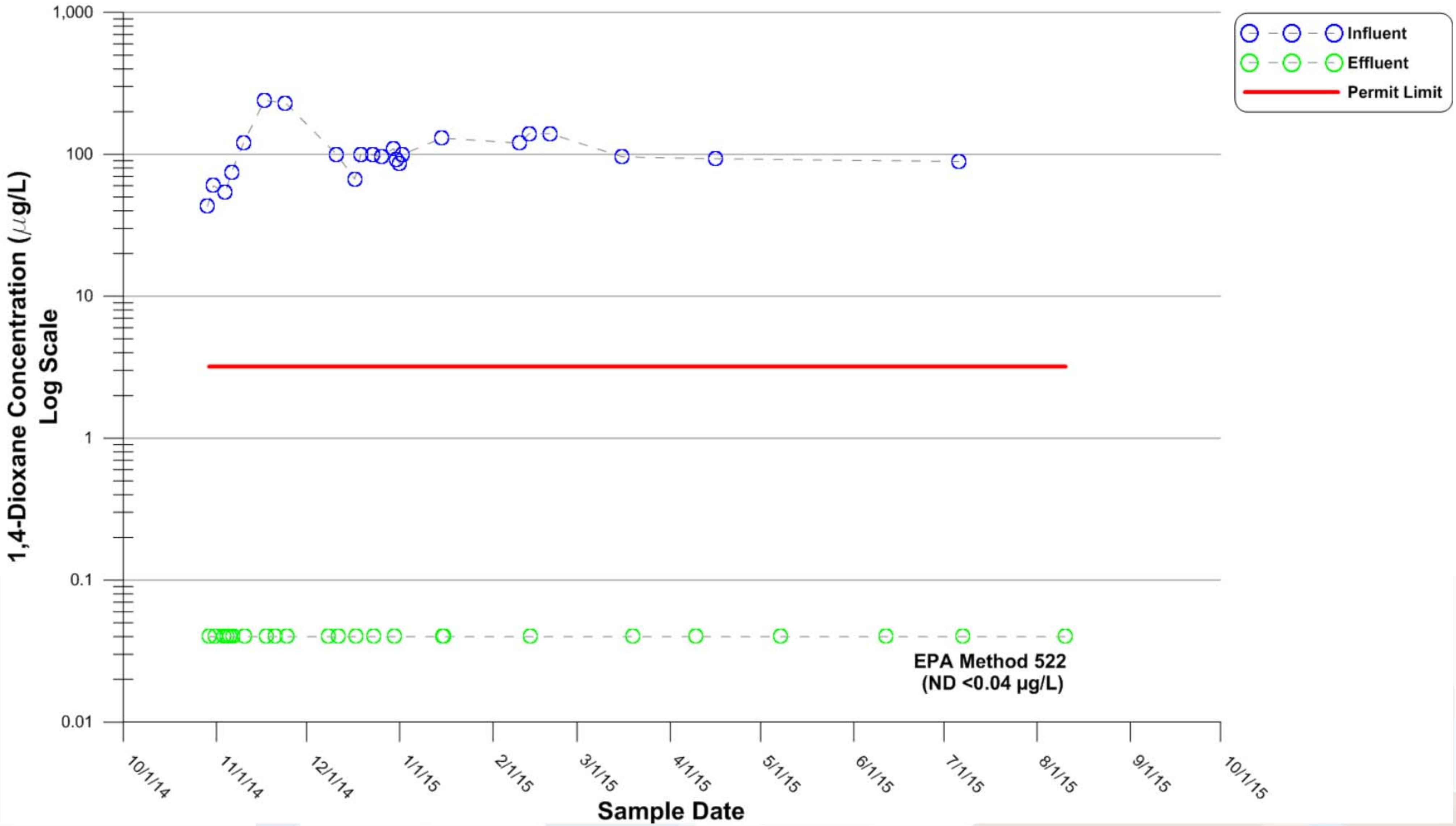
AMBERSORB™ 560

St. Petersburg, FL 140-gpm System

Design Basis:

- Flow = 100-175 gpm
- 1,4-dioxane = 2,535 ug/L MAX more typically 100's ug/L
- Total Organics = 17,450 ug/L
- Iron = 6-30 mg/l

Influent and Effluent 1,4-Dioxane



In Situ Technologies

XDD CASE STUDY: ISCO

The Problem: Solvent Contamination

- **Source Area:**
  - 30 x 60 feet area
  - 15 feet thick
  - Silty sands – dual level system

Compound	Historical Max. Conc. (ug/L)
1,1,1-TCA	101,000
PCE	20,000
1,4-Dioxane	3,000

- Located beneath active manufacturing plant
- **Treatment Goal:**
  - Reduce groundwater to below 1 mg/L in source
  - Goal based on protection of downgradient receptor

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The Solution: ISCO Treatment

- Selected Alkaline Activated Persulfate (AAP) for safety reasons
  - Greater stability
  - Reduced potential for gas evolution
- Evaluated AAP on bench scale
  - Soil buffering capacity
  - 2 to 4 g NaOH/Kg Soil

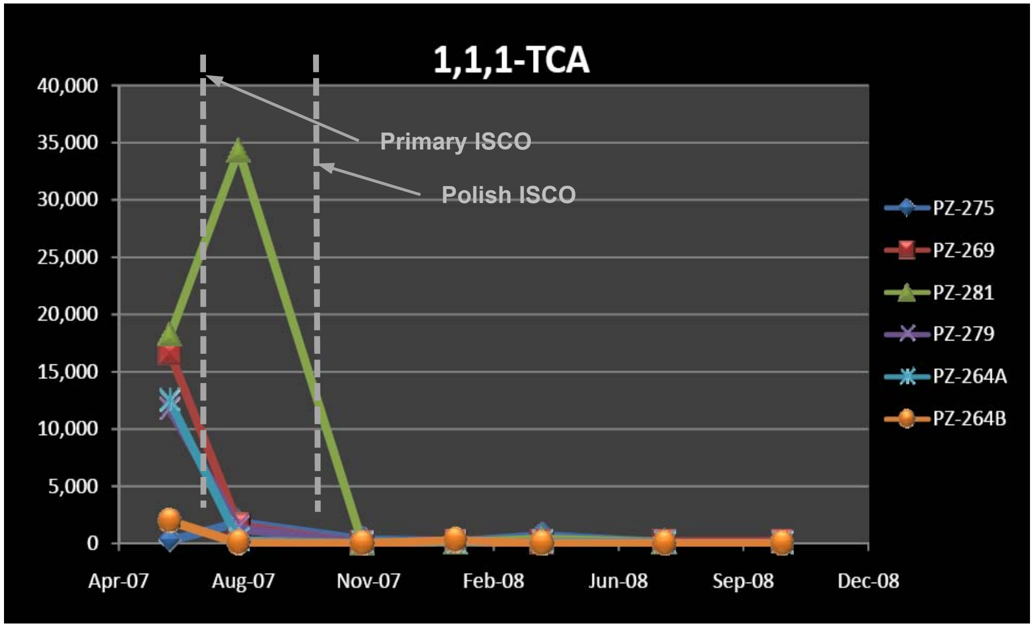
> **NaOH Mass < Soil Buffering Capacity + acid generated by persulfate reaction**

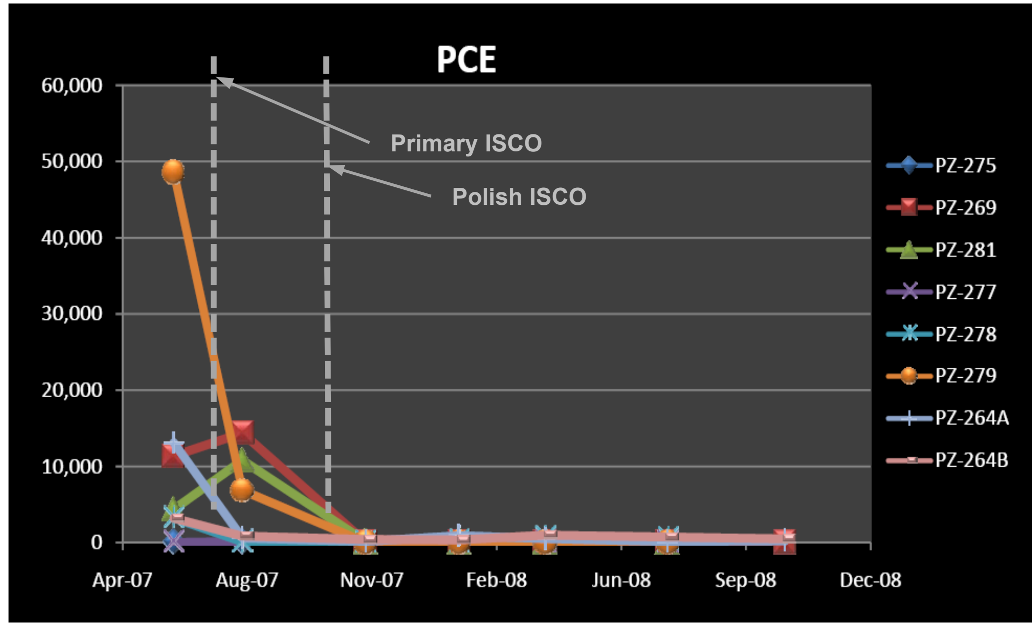
- Two injection events

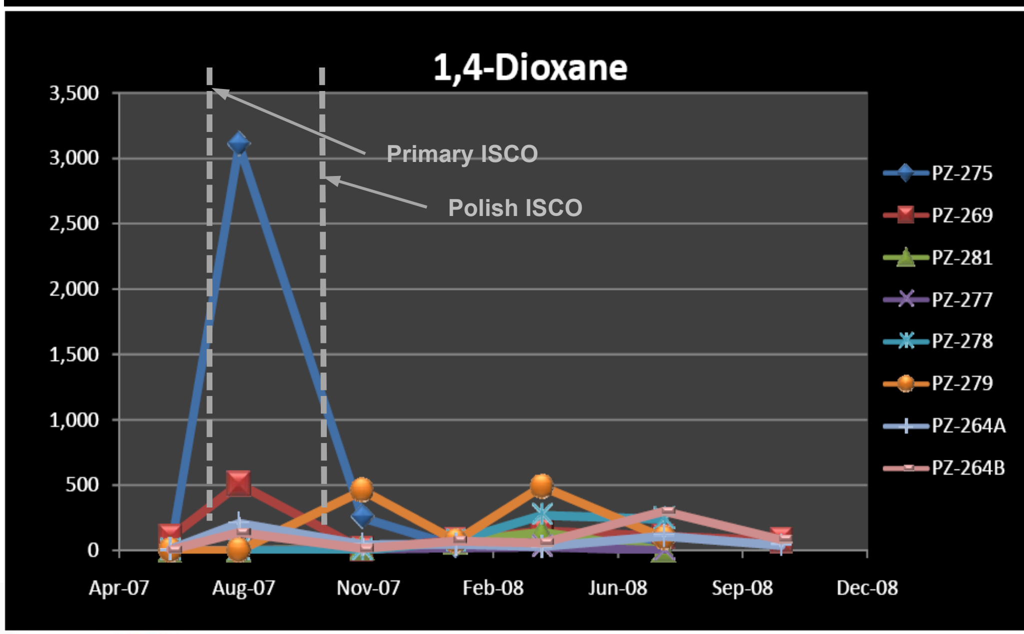
31,000 Kg Klozur (sodium persulfate)

15,300 Kg Sodium Hydroxide (NaOH)

Long Term Monitoring Results-VOCs







- 2-3 Orders Magnitude Reduction from baseline
- Target compounds remain below 1 mg/L objective
- Target compounds dropped to low ug/L level and remained over number years post treatment

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Other Oxidation Chemistries

- Carus - Persulfate / Permanganate Slow Release (wax) Cylinders – ESTCP- ER- 201324: funded Study
- Persulfate slow release cylinders
- Potassium persulfate – slow release systems
- Persulfate / zero valent iron slow release cylinders
  - Too much Fe^{2+} formation inhibits reaction
- Other hydroxyl radical chemistry
  - Peroxide / ozone / persulfate systems
  - Ozone only systems?
  - Other catalyzed peroxide / Fenton's type systems
  - Heat activated persulfate

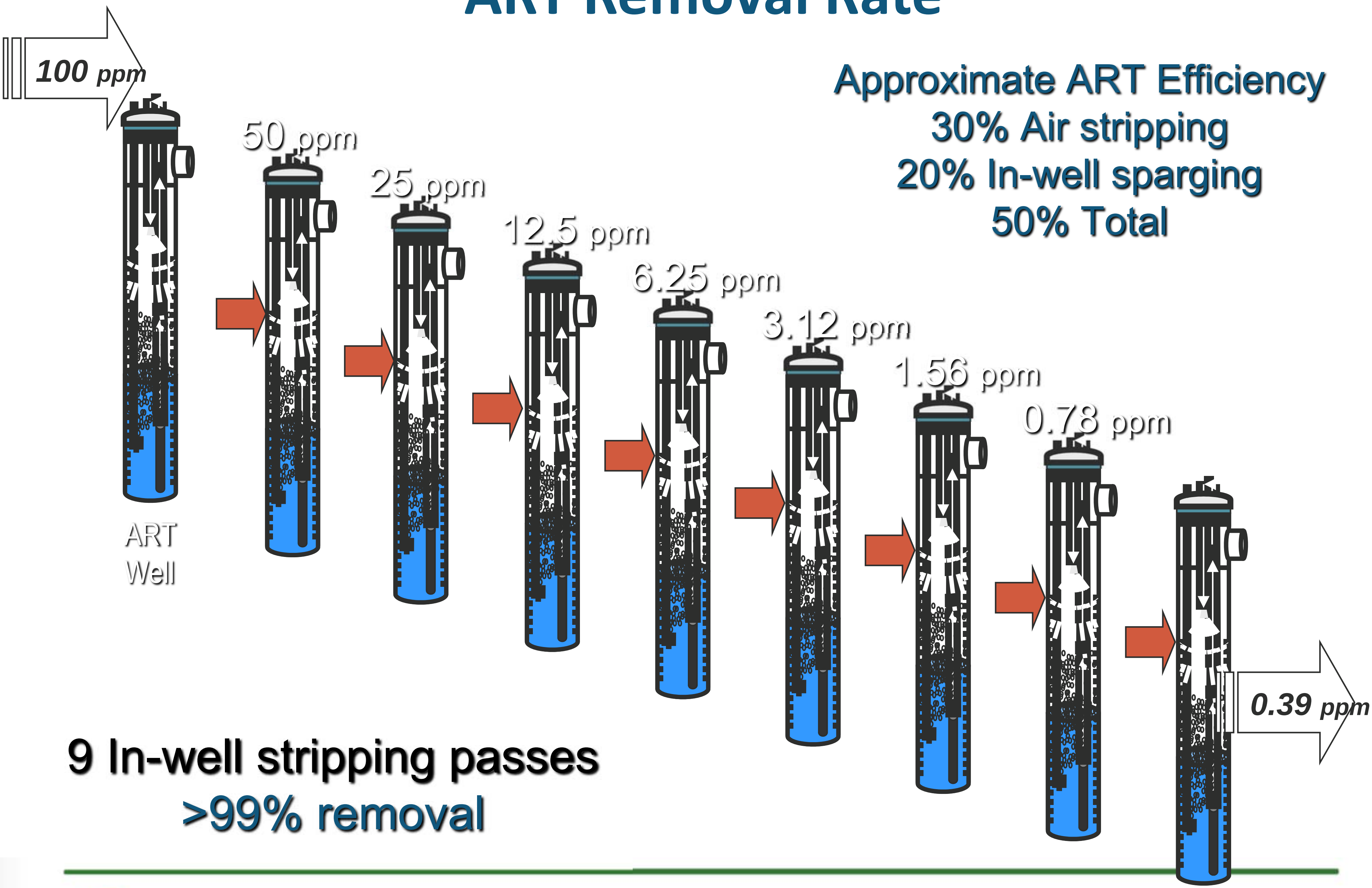
Promising In Situ Remedial Technologies

- Phytoremediation
  - Primarily removed by transpiration, which is then degraded quickly in the atmosphere (photolysis)
- Air Stripping
- Thermally enhanced SVE
- Bioremediation - both ex- and in situ

Air Stripping

ART Removal Rate

Approximate ART Efficiency
30% Air stripping
20% In-well sparging
50% Total



9 In-well stripping passes
>99% removal

ART Case Study: 1,4-dioxane

- 1,4-dioxane and VOC impacted site
- Bedrock overlain by saprolitic soils
- Levels reached asymptote
- Numerous technologies screened
- ART demonstration project
- Selection based on past recalcitrant/VOC performance history

1,4-Dioxane Demo Results

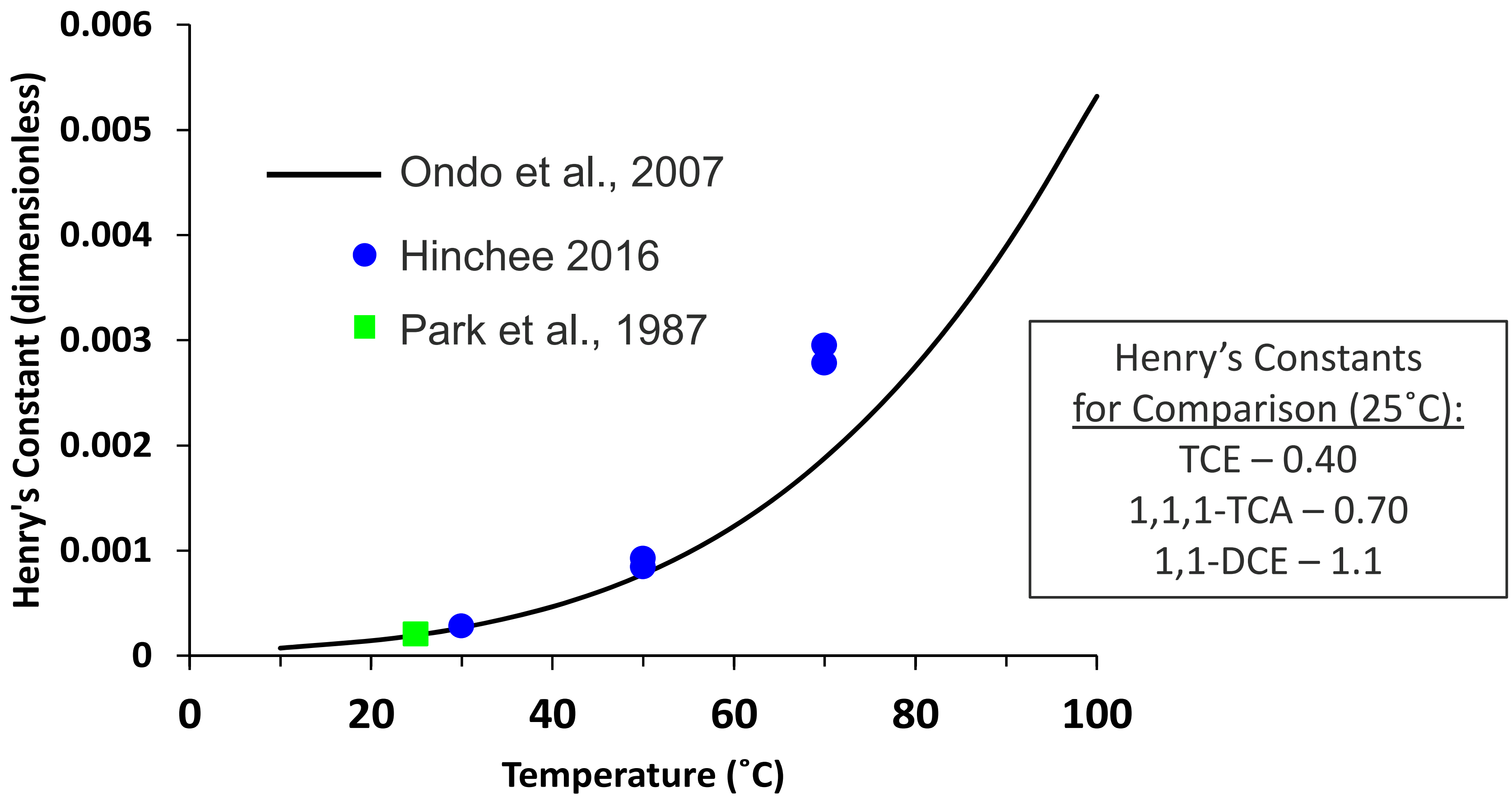
	MW-1	MW-2
Initial concentrations (µg/L)	25,000	28,000
90 days later (µg/L)	7,400	2,400
Percent reduction	76%	91%

- *1,4-dioxane vapor concentrations exceeded 1.1 PPMV*
- *2.25 pounds removed*

Mass balance suggests partial biodegradation, partial stripping

Thermally Enhanced Soil Vapor Extraction (Case Study)

1,4-Dioxane Henry's Constant



- Henry's Constant increases ~13-fold from 20 to 70˚C
- SVE removal efficiency for 1,4-dioxane should increase at elevated temperatures

XDD Case Study: Thermal Enhanced Pilot Test

- Provided modeling and design support for Kennedy Jenks Consultants Inc.
- Pilot test thermally enhanced SVE for 1,4-dioxane removal
- Project consisted of:
  - Numerical modeling for SVE design parameters (Baehr, A. and C. Joss. 1995)
    - Flowrates
    - Vacuum/pressure distribution
    - Pore volume exchanges/soil gas velocities
    - Well head vacuum/pressure
  - Modeling via HypeVent XSVE^{tm}
    - Heat distribution
    - Soil moisture changes
    - 1,4-dioxane mass removal rates
    - Heat input estimates

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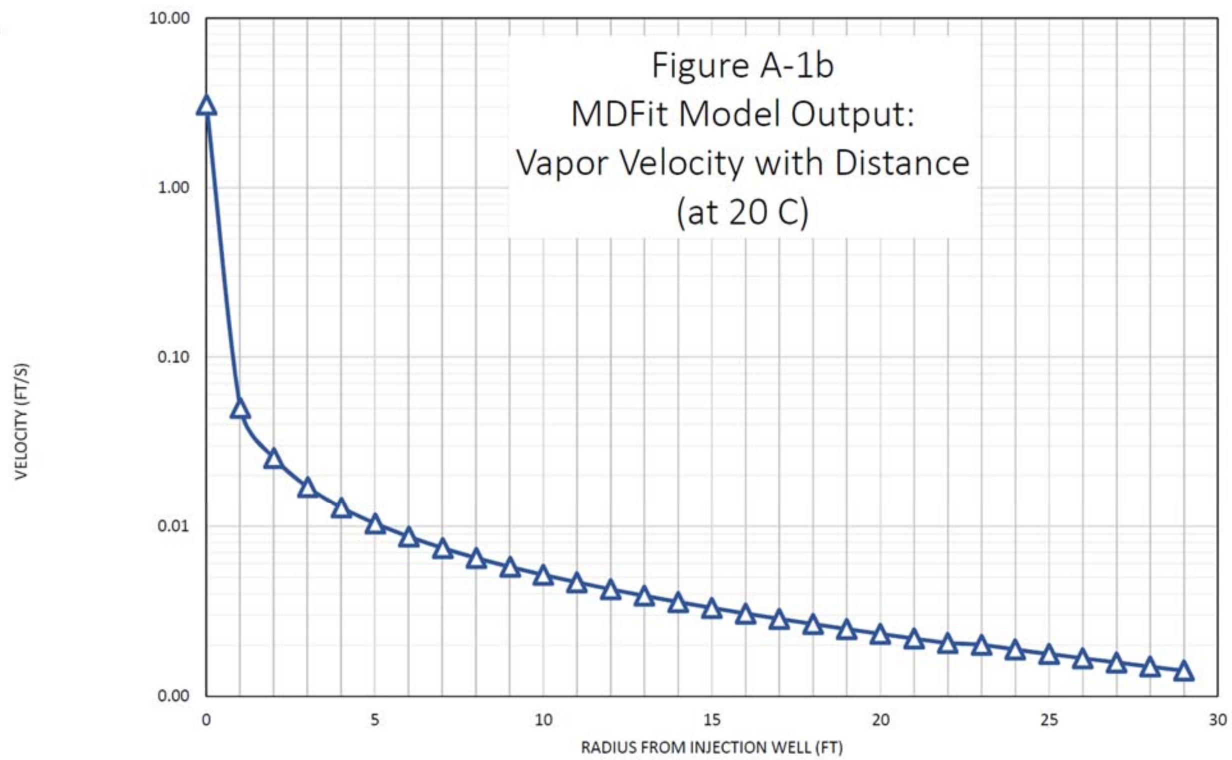
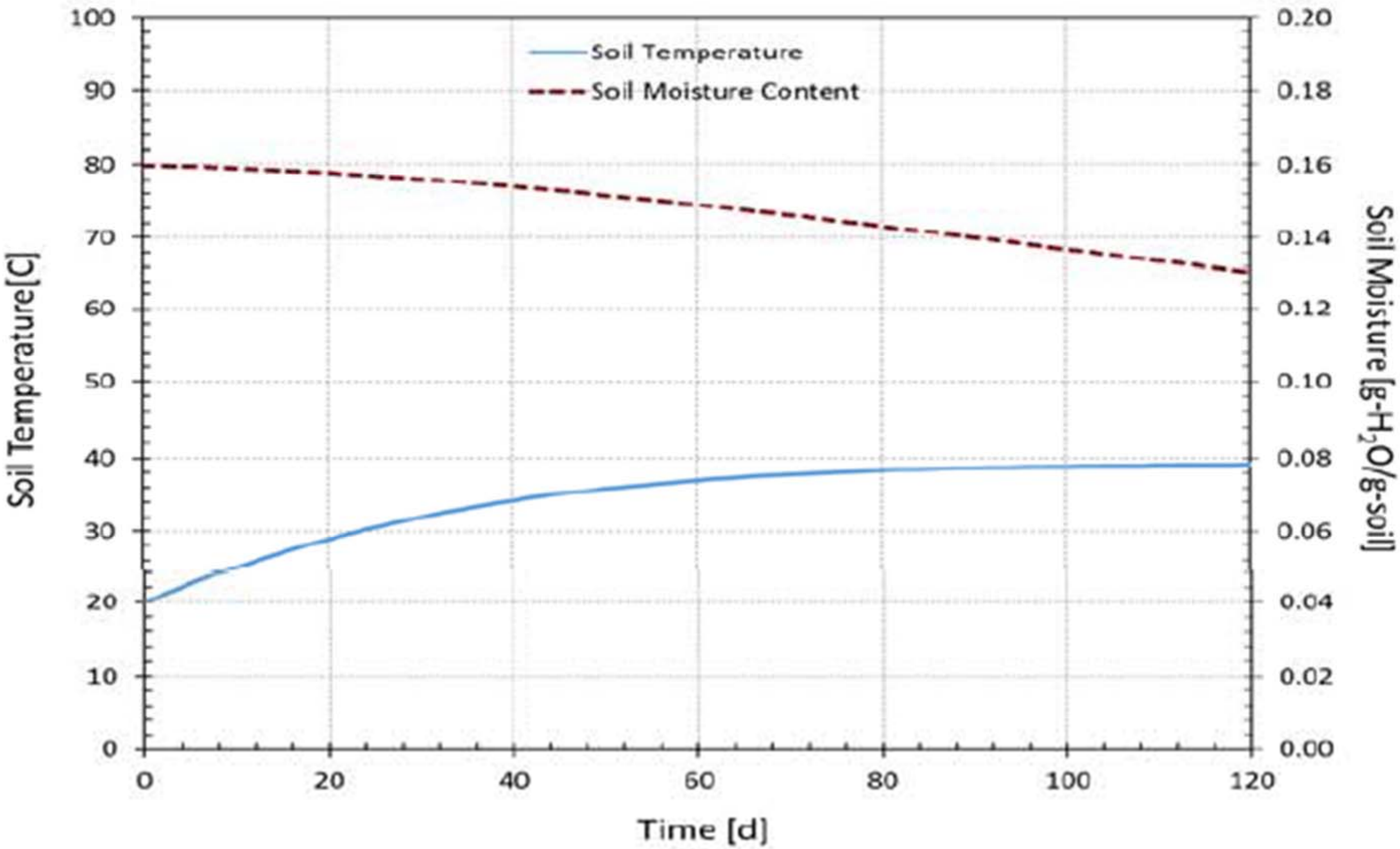
Pilot Design Specifications

- To achieve 95% reduction of 1,4-dioxane mass:
  - Air injection of 100 stand. cubic feet per minute @ 120°C
  - Target pore volume exchange at radius of influence less than 15 feet
  - Duration of 60 – 90 days



HypeVent XSVE Modeling Results - Temperature



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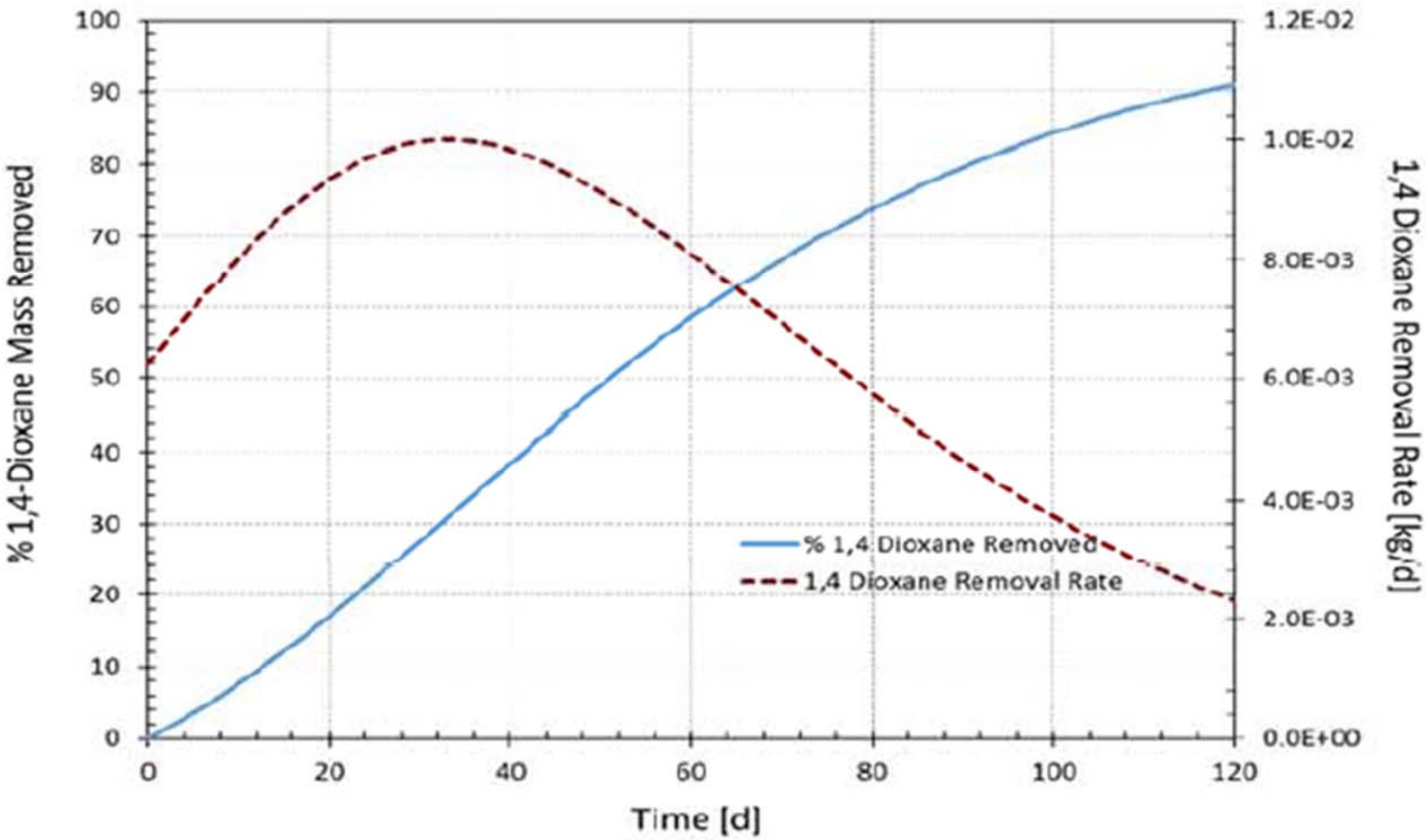
HypeVent XSVE Modeling Results - Mass

Treatment radius = 15 feet



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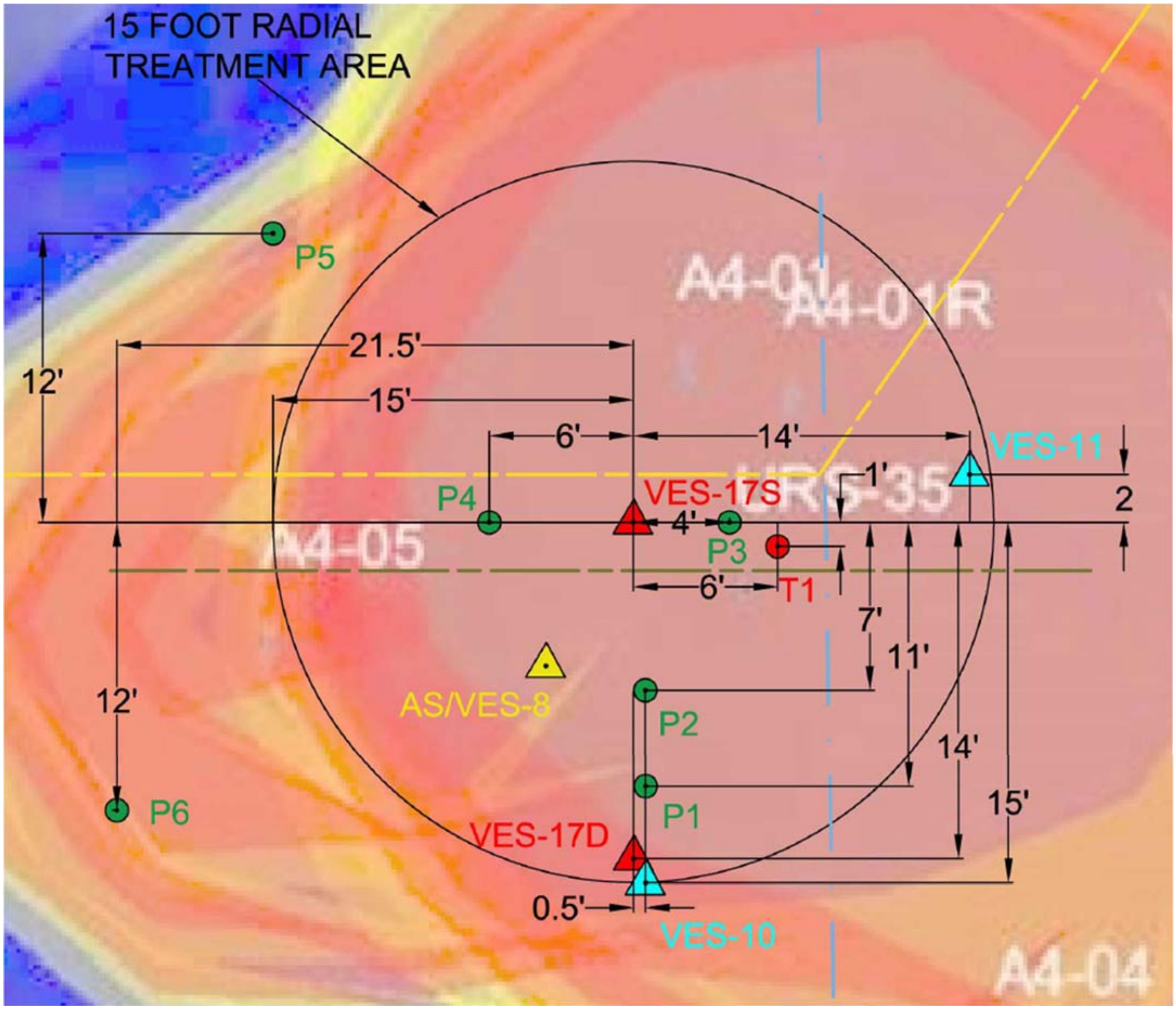
Pilot Testing Setup

- One injection well, with two extraction wells
- Vapor probe measurements at 4-, 8-, and 12-foot spacing from injection well
- Injection at 100 standard cubic feet per minute at 120 ^{o}C using trailer mounted blower with in-line 6,000-watt electric heater
- Testing occurred over 77 days

Pilot Test Layout



LEGEND

- EXISTING AS/VES WELL
- EXISTING VAPOR PROBE
- PROPOSED AIR INJECTION WELL
- PROPOSED SVE WELL
- PROPOSED VAPOR PROBE
- PROPOSED TEMPERATURE MONITORING PROBE

Pilot Testing Results

- Majority of lateral temperature increases:
  - Shallow (15' bgs): 4 – 6 feet
  - Deep (23 ' bgs): 8 feet
- Model provided reasonable prediction of soil drying adjacent, but heterogeneous distribution at greater distances from injection location
- 1,4-Dioxane was reduced by an average of 79% as measured at an 11-foot radius from VES-17S after 77 days
- 1,4-Dioxane concentration reductions ranged between 58% and 97% were measured between 12 and 32 ft bgs

Bioremediation

1,4-Dioxane Bioremediation

- Aerobic
  - Few organisms use 1,4-dioxane as an energy source (CB 1190)
    - More effective at higher 1,4-dioxane concentrations, not as good for low concentrations
  - THF/Propane/Toluene + others as energy source:
    - Cometabolic processes
    - Primary substrate concentration cannot be too high (1,4-dioxane may be ineffectively treated)
    - *May* need bioaugmentation in some cases

1,4-Dioxane Bioremediation

- Aerobic (continued)
  - Chlorinated ethenes (especially 1,1-DCE) can inhibit 1,4-dioxane biodegradation
    - Recent identification of cometabolic bacteria Azoarcus DD4 that can degrade 1,4-dioxane and 1,1-DCE (needs 1,1-DCE to degrade to relatively low concentration first)
  - Metals can also inhibit biodegradation e.g. copper, cadmium
  - Activity commonly associated with monooxygenase enzymes

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1,4-Dioxane Bioremediation

- Anaerobic (Nitrate, Iron, Sulfate, and Methanogenic)
  - Shown in laboratory experiments (2008) using iron reducing bacterium sludge with humic acid additions – no significant field observations
  - 2015 microcosms of field samples with high acetone, isopropanol, and chlorinated solvents showed no degradation after 4 years incubation

CBI Case Study: Cometabolic Biodegradation

From Lippincott et al., 2015, Ground Water Monitoring & Remediation, 35, no. 2: 81-92

Supported by contract FA8903-11-C-8101 US Air Force Civil Engineer Center

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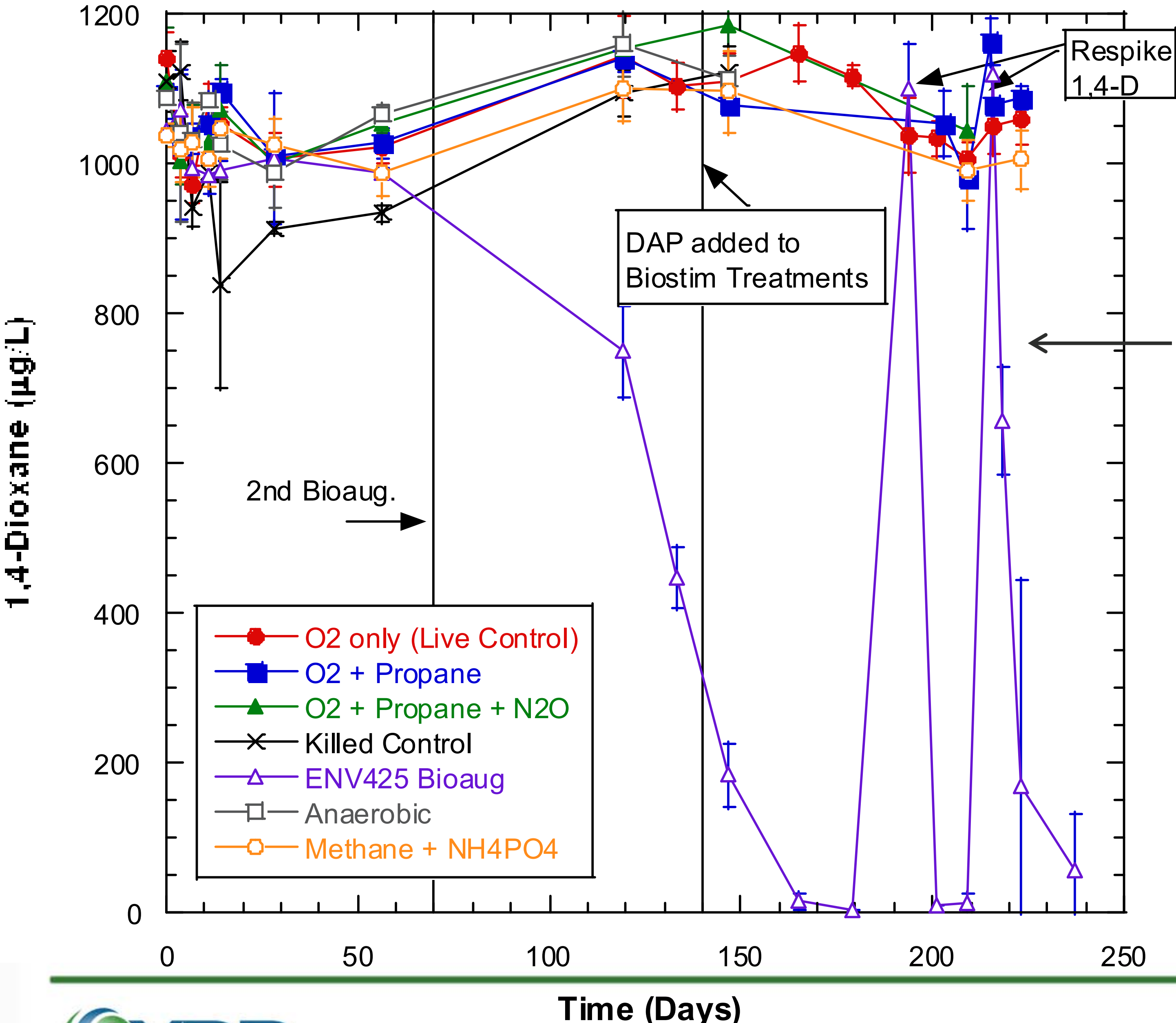
1,4-Dioxane in Vandenberg AFB Microcosms



Deep Zone

Goals

- Demonstrate *in situ* biodegradation of 1,4-D
- Achieve regulatory limits (1 ppb) within deep zone

Results

- 1,4-D degraded only in microcosms bioaugmented with strain ENV425
- Propane enrichment culture eventually grown from site samples

Bioremediation Field Pilot Test

- 1-month air sparge only (control phase)
  - One 45-minute pulse per day
- Optimization Period – propane addition
  - Up to 40% of the lower explosive limit (0.83 lbs./day)
  - 6 cycles per day (36-minute pulses)
- Bioaugmentation with ENV425 on day 42 (36 liters)
- Nutrient Injections (DAP)
- Performance Monitoring
  - GW Sampling
  - Well headspace (LEL)
  - Biotraps (3 deployments)

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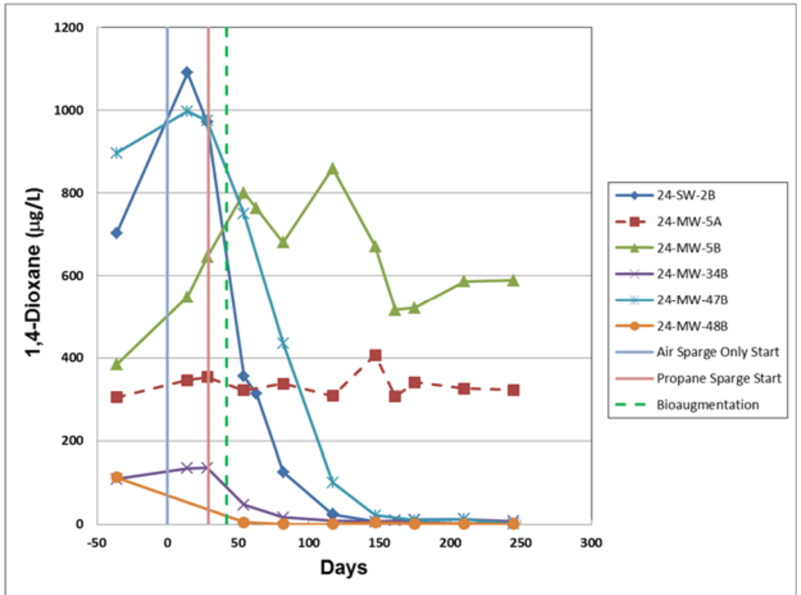
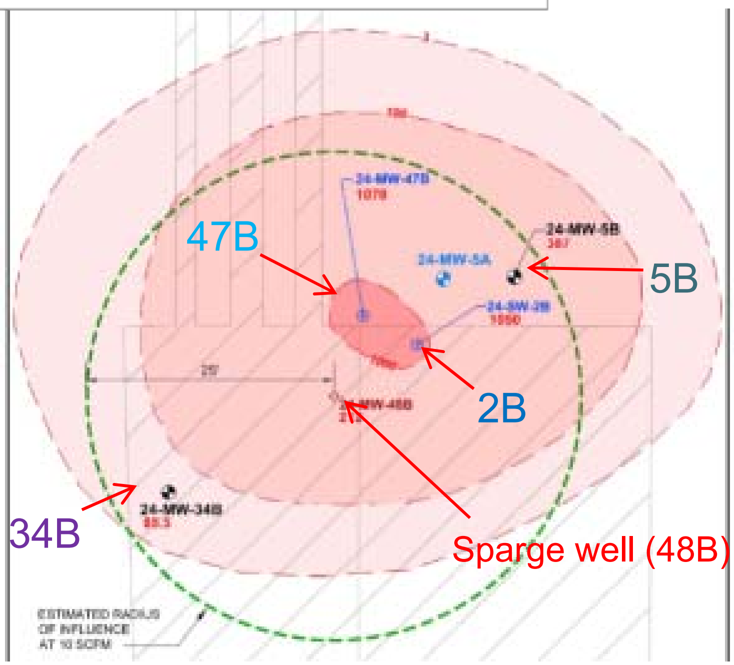
Field Pilot Test Results





Well	Day 14	Day 245	% Degraded
48B (sparge)	113 ppb	<1.0 ppb	>99 %
47B	997 ppb	1.2 ppb	>99%
2B	1090 ppb	1.1 ppb	>99%
34B	135 ppb	7.3 ppb	95%
5B*	548 ppb	588 ppb	<1%
5A (control)	346 ppb	323 ppb	<1%

From Lippincott et al., 2015, Ground Water Monitoring & Remediation, 35, no. 2: 81-92

Supported by contract FA8903-11-C-8101 US Air Force Civil Engineer Center

1,4-Dioxane MNA Evaluation

(SERDP ER-2307: David T. Adamson et. al., ES&T, 2015, 49, 6510−6518)

- Data Source - California GeoTracker + Air Force (AF) Sites / Wells
  - Only 30% of 193 CA sites had a statistically significant source decay term
  - About 23% of CA sites had order of magnitude reduction in max. vs. recent 1,4-dioxane levels, very few with higher than 2 or 3 orders of magnitude reduction
  - 30% of 441 AF wells with decreasing trends, 70% with stable, no trend or increasing trend (increasing was 9%)
  - AF wells : attenuation correlated positively with dissolved oxygen, and negatively for CVOCs (1,1-DCE in particular) and metals
  - Median half-Life 20-48 months for statistically significant attenuating sites / wells

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Diagnostics for Degradation / MNA

- Compounds specific isotope analysis (CSIA)
  - proof of degradation
  - rates of degradation
  - potentially prove multiple sources
- CSIA Detection Levels for 1,4-dioxane
  - $\delta^{13}C$ = 1 ug/l
  - $\delta^{2}H$ = 20 ug/l

- Quantitative polymerase chain reaction (qPCR)
  - Dioxane monooxygenase (DXMO) and ALDH to assess aerobic metabolism by *P. dioxanivorans* CB1190
  - Soluble methane monooxygenase (sMMO) and ring hydroxylating toluene monooxygenases (RMO, RDEG, PHE) to assess aerobic cometabolism
  - SCAM (short chain alkane monooxygenase). small chain alkane monooxygenases are induced by a wide variety of gaseous alkanes and are especially effective for 1,4-D cometabolism
- Stable Isotope Probing (SIP)
  - ^{13}C “label” serves as a tracer
  - Quantification of ^{13}C in biomass and CO_2 demonstrates dioxane biodegradation

Q&A

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