XDD ENVIRONMENTAL

Do it Right, Do it once

Remediation of 1, 4-Dioxane

Presented by
Mike Marley

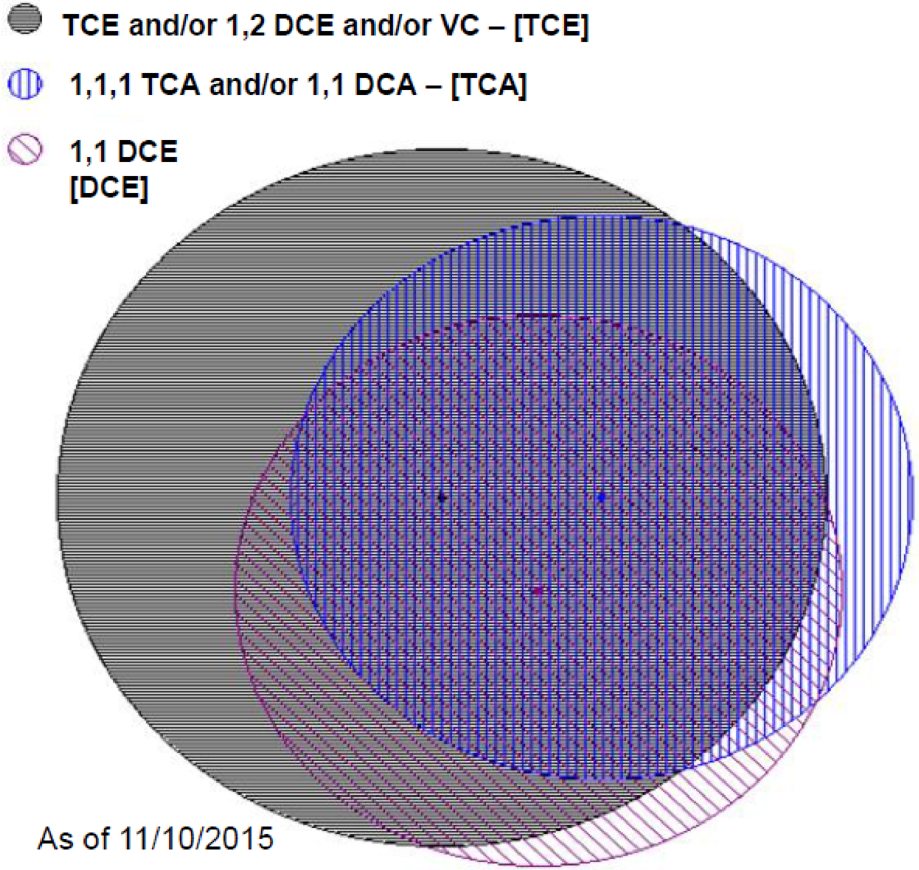
April 26th, 2016

Agenda

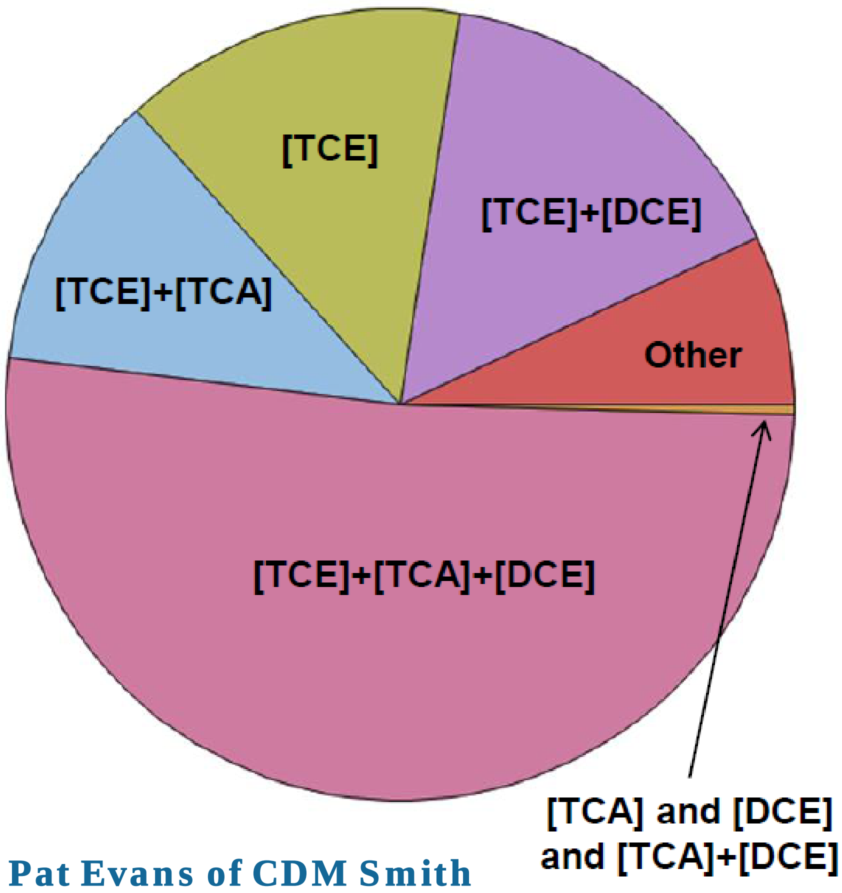
- Basic properties of 1,4-dioxane with respect to remediation
- A discussion of applicable reliable remedial technologies with case studies
  - Ex situ
    - Advanced oxidation
    - Sorption
  - In situ
    - In situ chemical oxidation
- Promising remedial in situ technologies
  - Phytoremediation
  - Air Stripping
  - Thermally enhanced soil vapor extraction
  - Bioremediation
    - 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)



From presentation by Pat Evans of CDM Smith

Slide courtesy of Hunter Anderson

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**	**~3***

* = State specific guidelines, levels may be lowered e.g. NJDEP Interim Ground Water Quality Criteria is now **0.4 ug/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

Ex Situ Technologies

- Advanced oxidation
  – key is formation of radical chemistry
- Sorption
  – key is synthetic materials

Advanced Oxidation XDD Case Study

- 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) being added to address 1,4-dioxane that is not treated by PAC / 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 / Balancing Act

- The molar ratio of hydrogen peroxide to ozone ($H_2O_2:O_3$) can be adjusted to minimize the formation of bromate. Typically, by increasing the amount of hydrogen peroxide relative to a fixed dose of ozone (i.e., increasing molar ratio of $H_2O_2:O_3$), the ozone will be more completely reacted with the hydrogen peroxide, and bromate formation will be reduced
- However, the trade-off is that the excess hydrogen peroxide can now react with the hydroxyl radicals (i.e., termed hydroxyl radical “scavenging”), which reduces the treatment efficiency of 1,4-dioxane
- Could use UV instead of ozone to avoid bromate but that has its own issues

1,4-Dioxane Destruction Results

Test Scenario	Impact on 1,4-Dioxane			Impact on Bromate		
High Spike, 240 ug/L 1,4-dioxane **O_3 Dose = 5, 10, 13, 20mg/L** **H_2O_2:O_3 Ratio = 1.0 (all scenarios)** **7 injection nozzles except the 20 mg/L ozone dose which used 9 nozzles.**	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 is more effective as ozone dose is increased.			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).

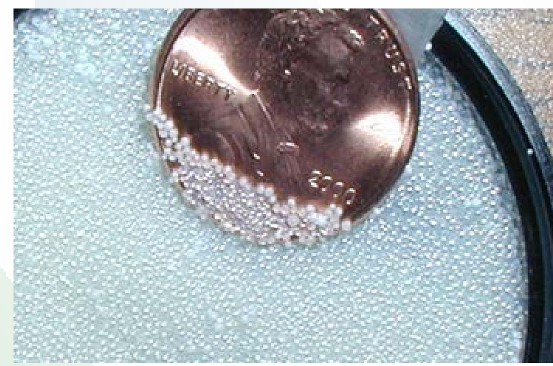
Bromate Formation Control Results

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 Dose = 19.0 and 30.4 mg/L H_2O_2:O_3 Ratio = 2.5 and 4.0 20/30 injection nozzles	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.

Sorption

- 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



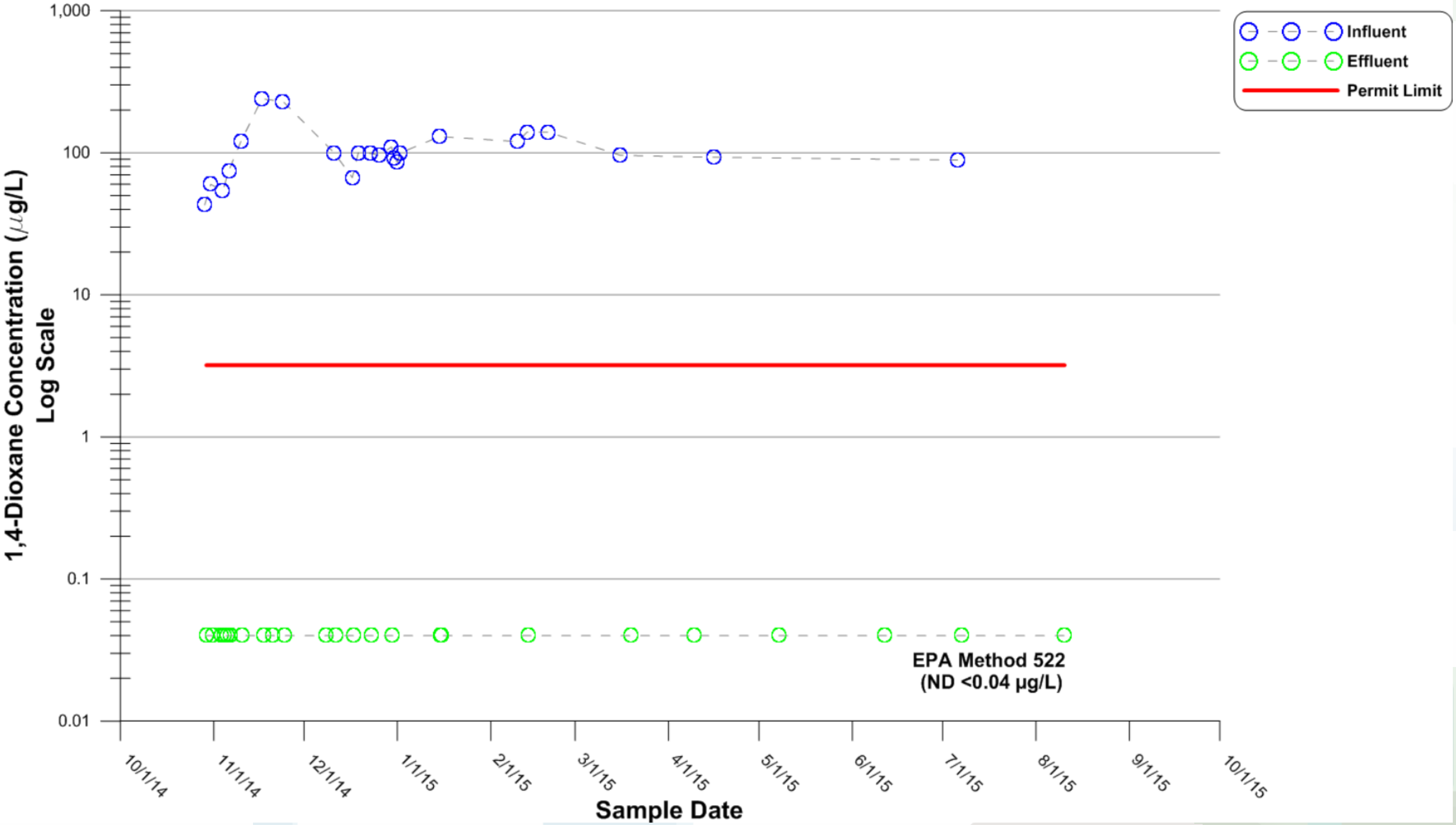
AMBERSORB™ 560

Slides courtesy of Steven Woodard, ect_2

Case Study: 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

- In situ chemical oxidation
  - Generally, key again is radical chemistry

XDD ISCO CASE STUDY

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

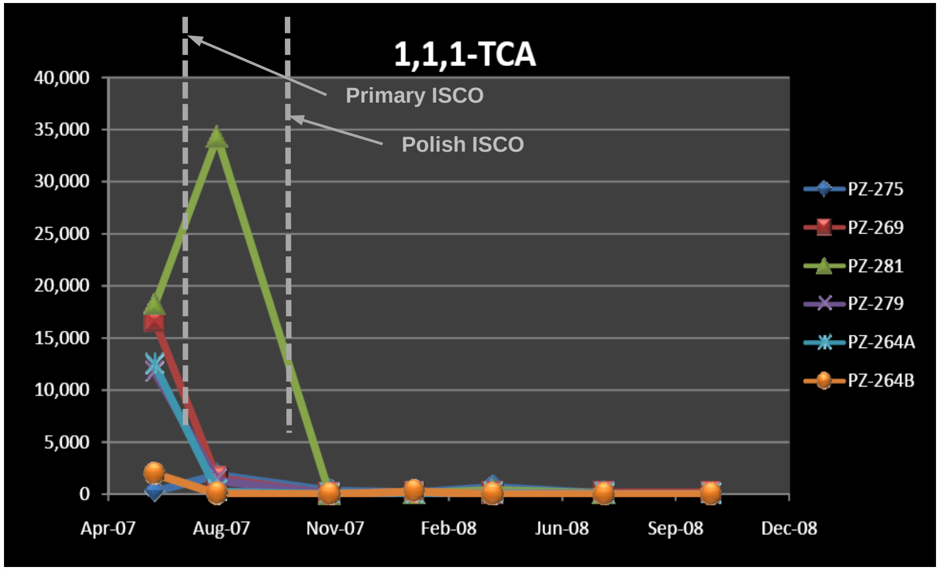
- Treatment Goal:
  - Reduce groundwater to below 1 mg/L in source
  - Goal based on protection of downgradient receptor

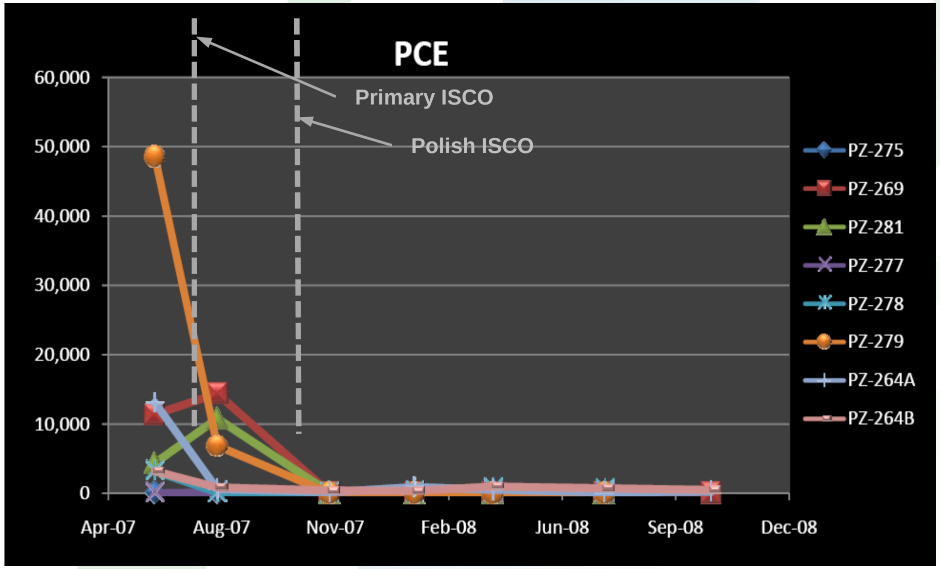
The Solution: ISCO Treatment

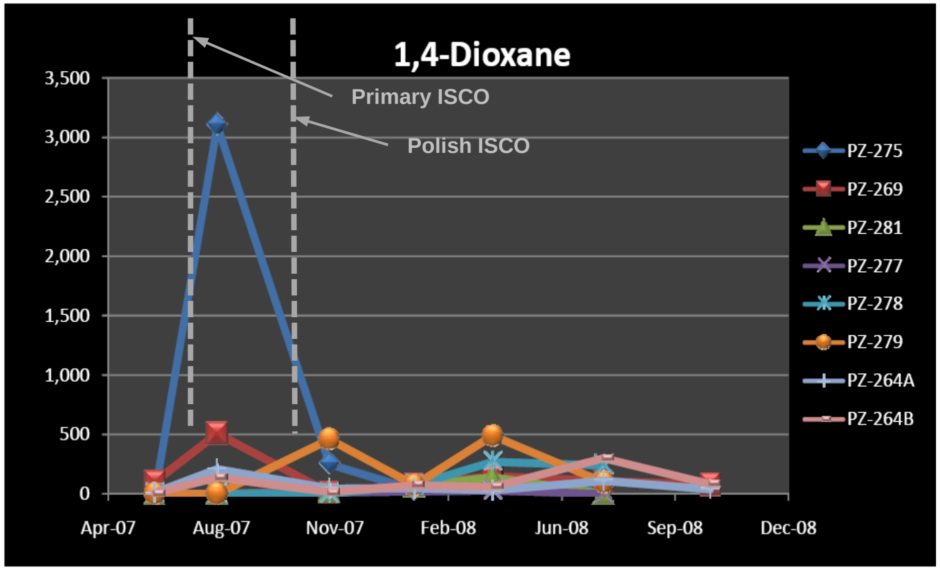
- Selected Alkaline Activated Persulfate (AAP) for safety reasons
  - Greater in-situ stability
  - Reduced potential for gas evolution
- Evaluated AAP on bench scale
  - Soil buffering capacity
  - 2 to 4 g NaOH/Kg Soil
    - **NaOH Mass < Soil Buffering Capacity + acid generated by persulfate reaction**
- 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

In Situ Chemical Oxidation

Other:

- Carus - Persulfate / Permanganate Slow Release Cylinders – ESTCP- ER- 201324: funded Laboratory Study
- Other hydroxyl radical chemistry
  - Peroxide / ozone systems
  - Ozone only systems?
  - Other catalyzed peroxide / Fenton's type systems

Promising Remedial Technologies

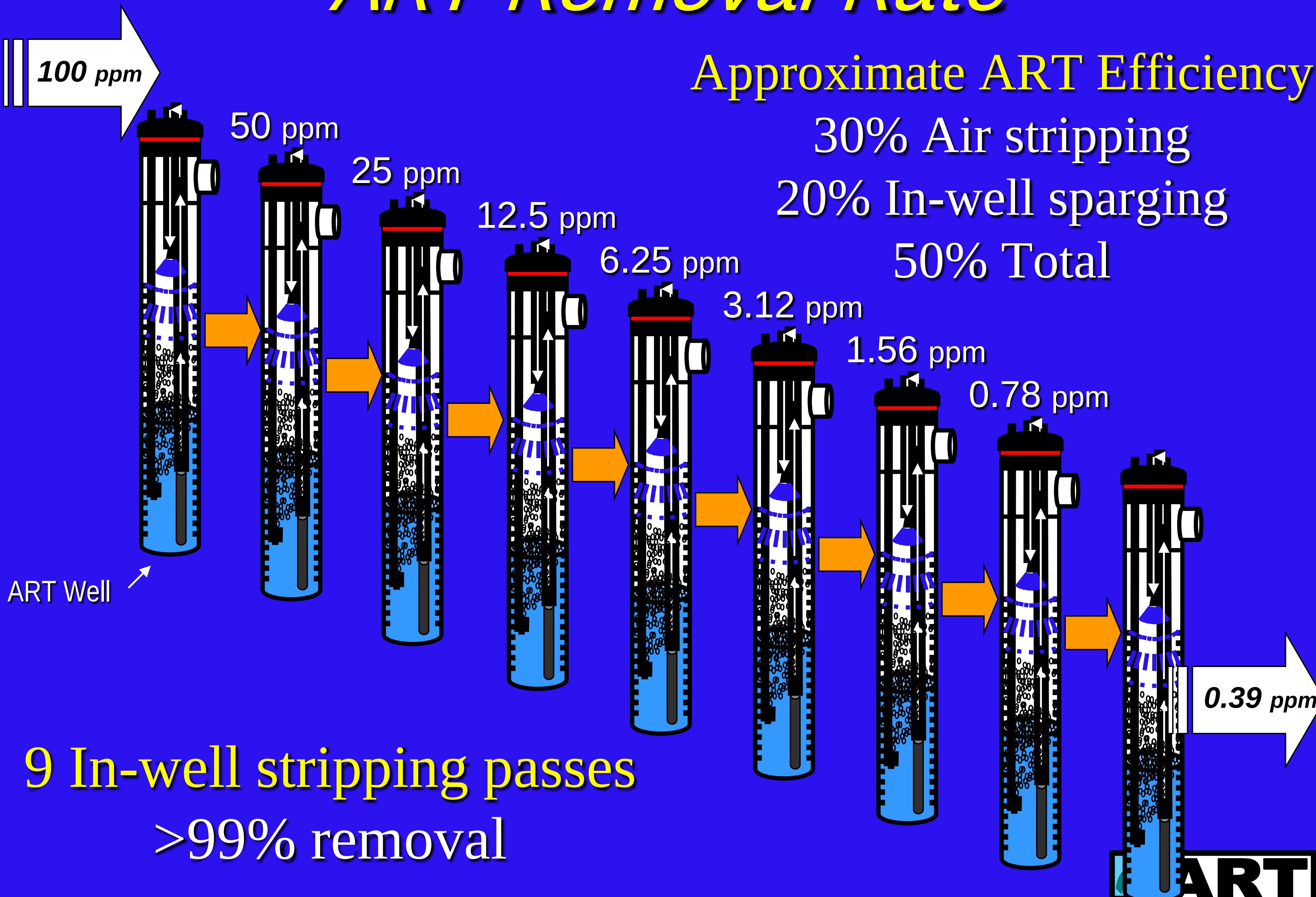
- Phytoremediation
  - primarily removal by transpiration
- Air Stripping
- Thermally enhanced SVE
- Bioremediation - both ex- and in situ

Air Stripping

Slides courtesy of Mohamed Odah, ART

ART Removal Rate

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



9 In-well stripping passes
>99% removal

1,4 Dioxane Case History

- 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

ART
Accelerated Remediation Technologies, LLC

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

ART Accelerated Remediation Technologies, LLC

Thermally Enhanced SVE

Slides courtesy of Rob Hinchee, IS&T

1,4-Dioxane Remediation by Extreme Soil Vapor Extraction (XSVE)

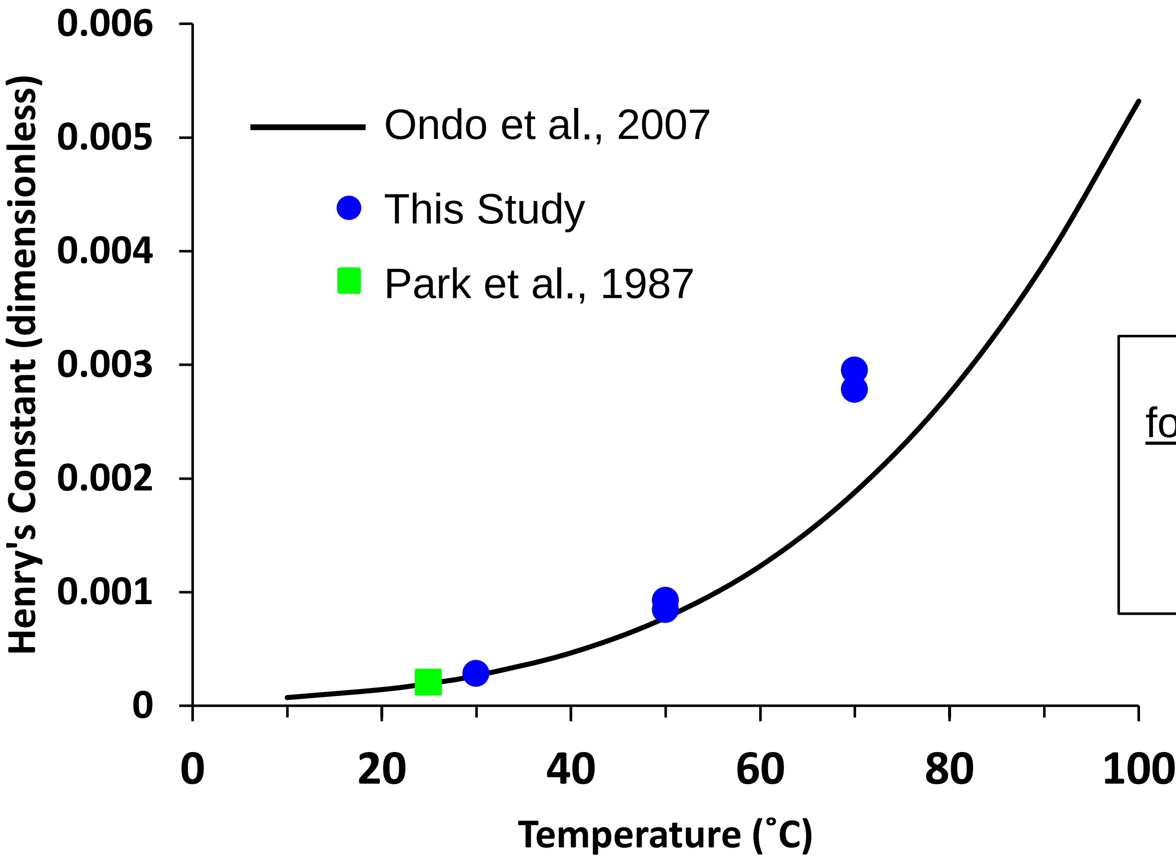
ER 201326

Rob Hinchee

Integrated Science & Technology, Inc.; Arizona State University; CO School of Mines; AECOM

March 23, 2016

1,4-Dioxane Henry's Constant

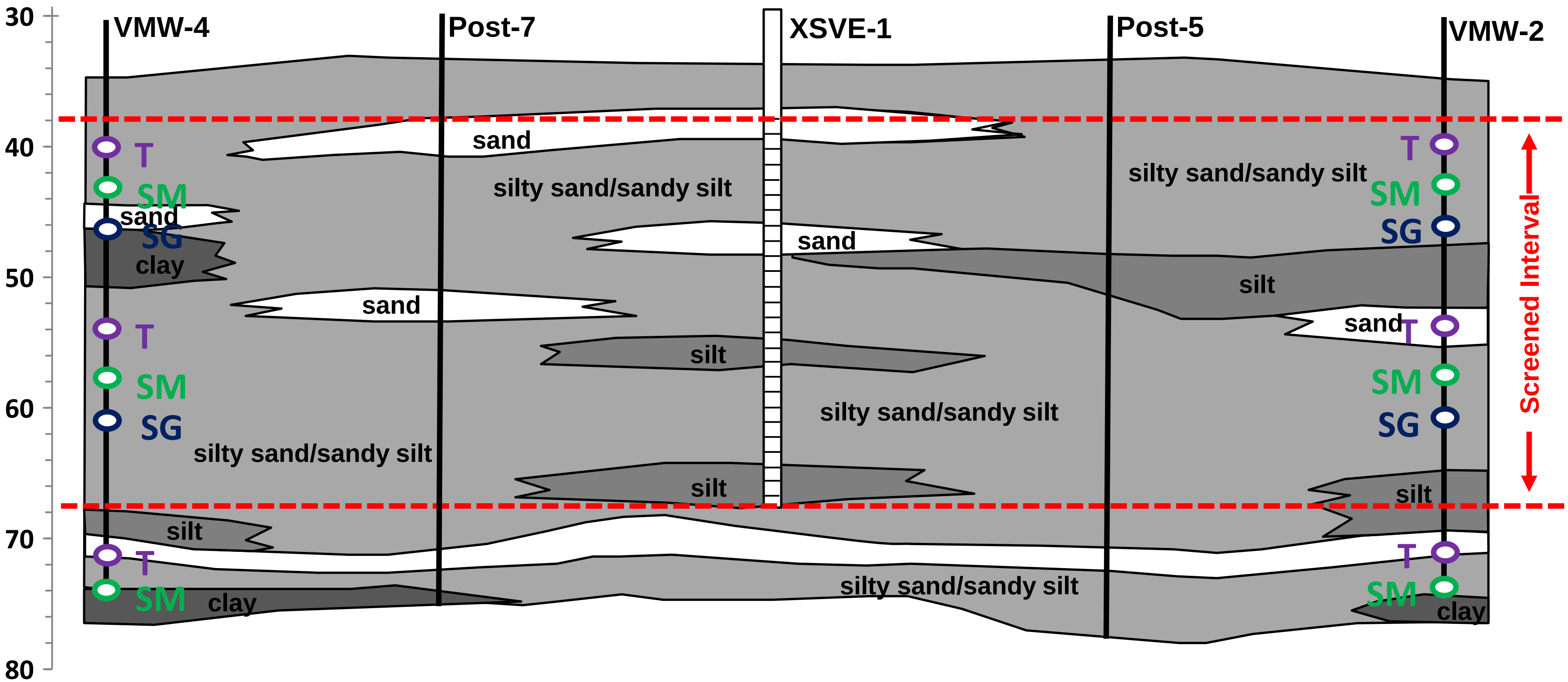


Henry's Constants
<u>for Comparison (25˚C):</u>
TCE – 0.40
1,1,1-TCA – 0.70
1,1-DCE – 1.1

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

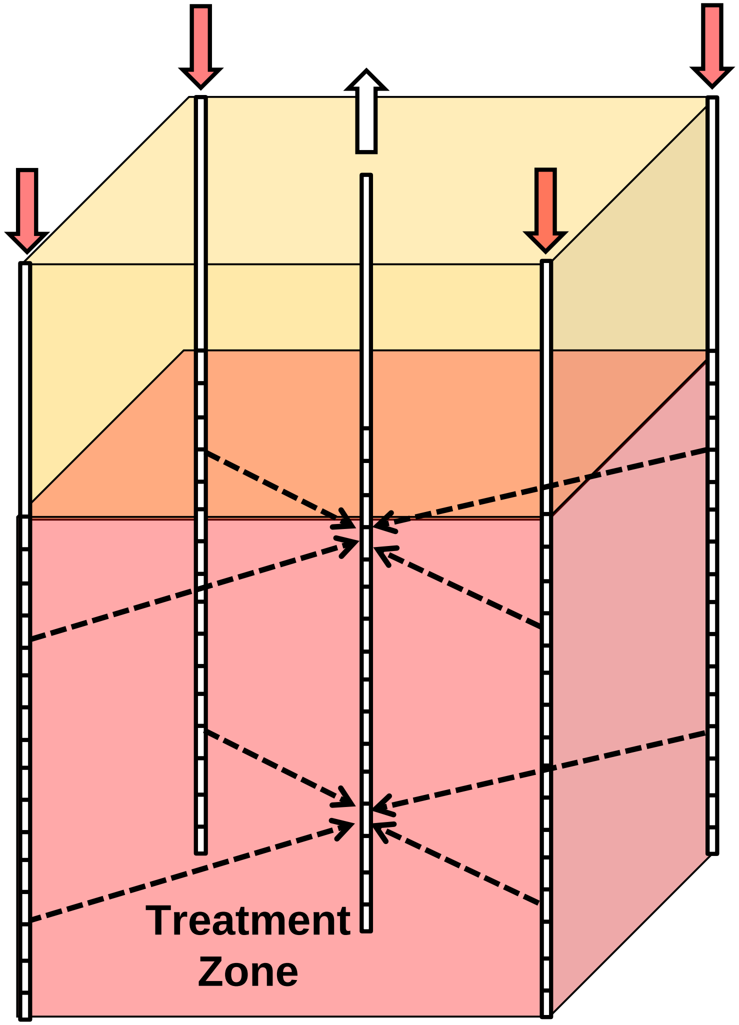
Cross-Section

Former McClellan AFB, CA

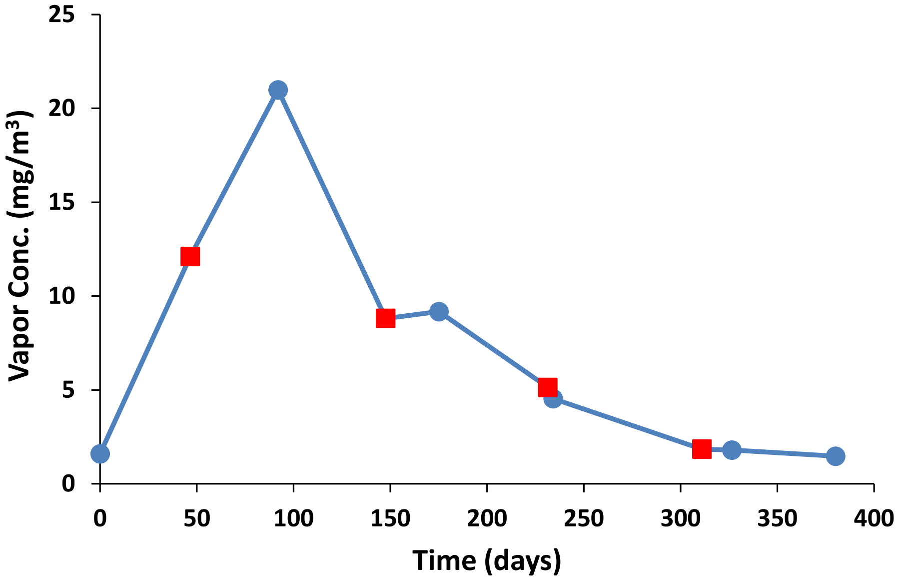


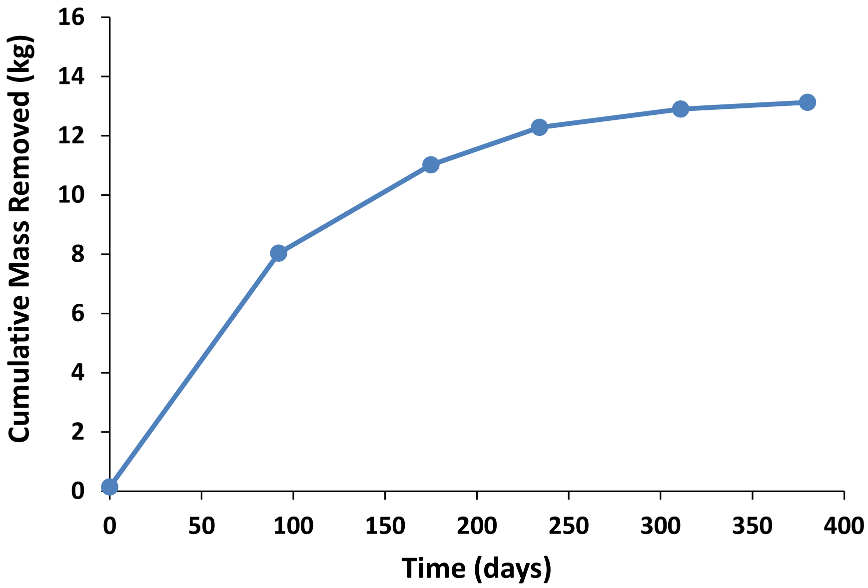
Test Design

- 4 injection wells - 20 ft corners
  - ~100 cfm; ~90 ºC
- 1 extraction well – center
  - ~100 cfm
- low carbon steel well casing
- concrete grout
- screened interval 38 – 68 ft
- existing vapor treatment system
- condensate collection



Operation (1,4-Dioxane Mass Removal)





Demonstration Objectives

- *Reduce 1,4-dioxane in treatment zone by >90%*
- *Minimize potential downward migration of 1,4-dioxane*

Project Progress and Results

- *1,4-dioxane was reduced > 90% in treatment zone*
  - ✓ Mass removal estimates (~13 kg 1,4-dioxane at shutdown) consistent with before and after soil concentrations
- *No apparent downward migration of 1,4-dioxane*

Bioremediation

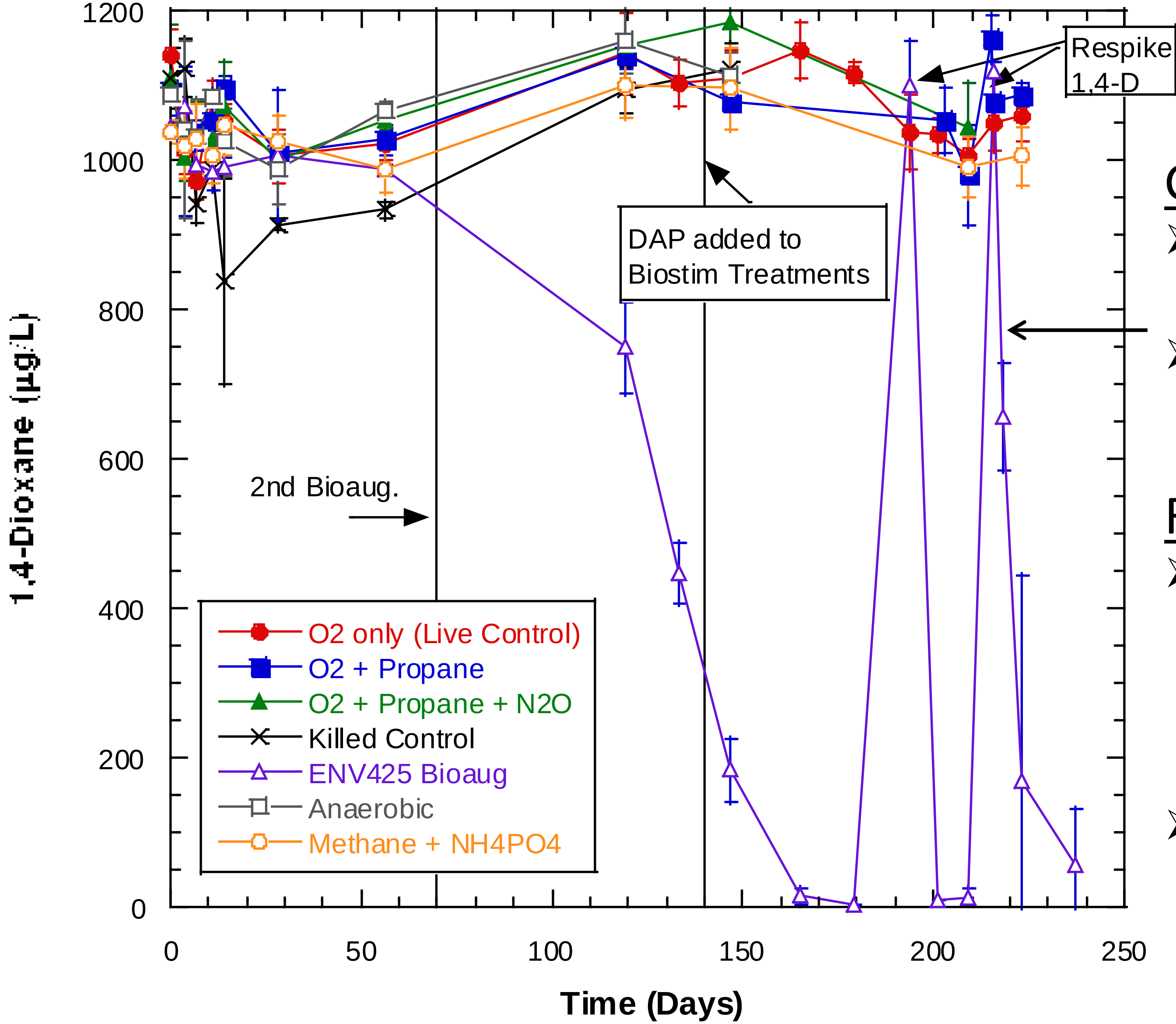
1,4-Dioxane Bioremediation

- Aerobic
  - –Few organisms use 1,4 dioxane as an energy source (CB 1190)- appears more difficult for remediation
  - –THF/Propane/Toluene + others as energy source: co-metabolic processes – more reliable in remediation, but *may* need bioaugmentation
  - –Activity common with monooxygenase enzymes
- Anaerobic (Nitrate, Iron, Sulfate, and Methanogenic)
  - –SERDP ER-1422 Study in 2007 [Rob Steffan, CB&I]: no degradation - ?

Co-metabolic Bioremediation

Slides courtesy of David Lippincott, CB&I

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

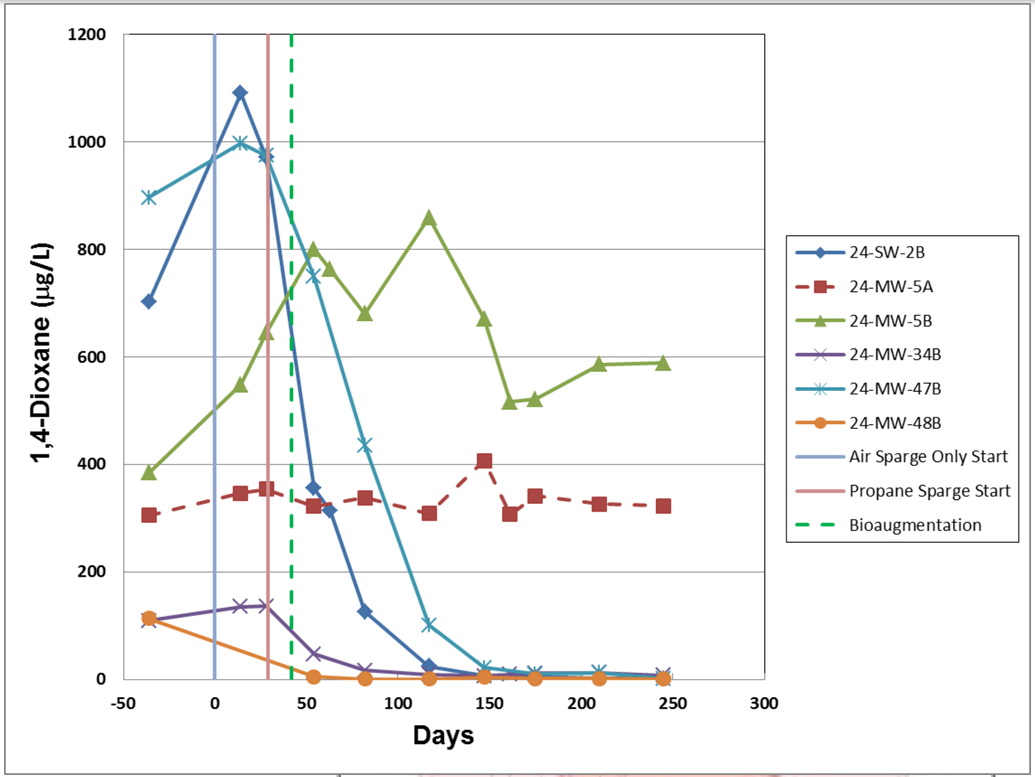
Results

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

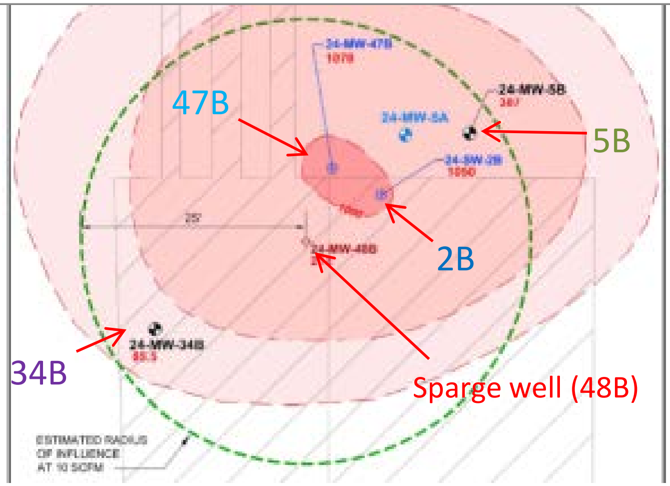
Startup and System Operation

- Startup → 10 SCFM
  - Monitoring for water level mounding, bubbling, and DO
- 1 month air sparge only (control phase)
  - One 45 minute pulse per day
- Optimization Period
  - Up to 40% of the LEL (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)

1,4-Dioxane Treatment 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 - CA GeoTracker + Air Force 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 OoM 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 and metals
  - Median half-Life 20-48 months for statistically significant attenuating sites / wells

Diagnostics for Degradation

- CSIA on 1,4-dioxane
  - unequivocal 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

- qPCR
  - Dioxane monooxygenase (DXMO) and ALDH to assess aerobic metabolism by *P. dioxanivorans* CB1190
  - Soluble methane monooxygenase (sMMO) and ring hydroxylating toluene monoxygenases (RMO, RDEG, PHE) to assess aerobic cometabolism
- Stable Isotope Probing (SIP)
  - ^{13}C "label" serves as a tracer
  - Quantification of ^{13}C in biomass and CO_2 demonstrates dioxane biodegradation

DISCUSSION

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