Non-Emulsified Vegetable Oil Blend for Enhanced Anaerobic Bioremediation

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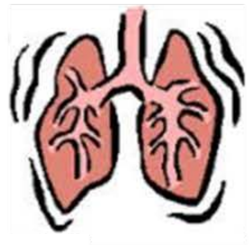
RemTech 2013

Agenda

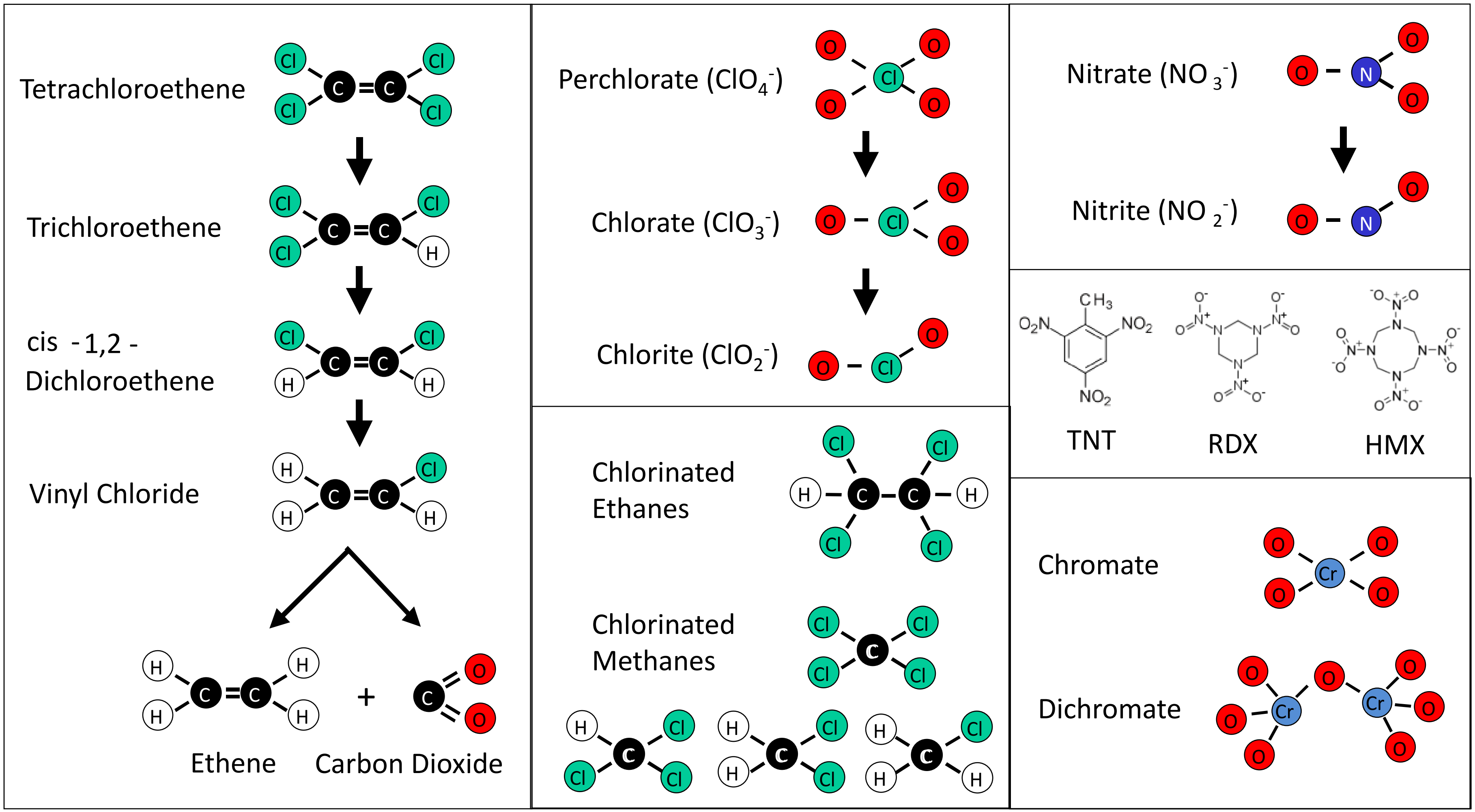
- Overview Anaerobic Bioremediation
  - ➢ CAP 18® and CAP 18 ® ME Anaerobic Bioremediation Products
    - Hydrogen Yield/Hydrogen Efficiency
  - ➢ Design Software
    - Conceptual Approaches/Examples
  - ➢ CAP 18 Case Study
    - Conceptual Approaches
  - ➢ Concluding Remarks/Questions

Basics of Bioremediation

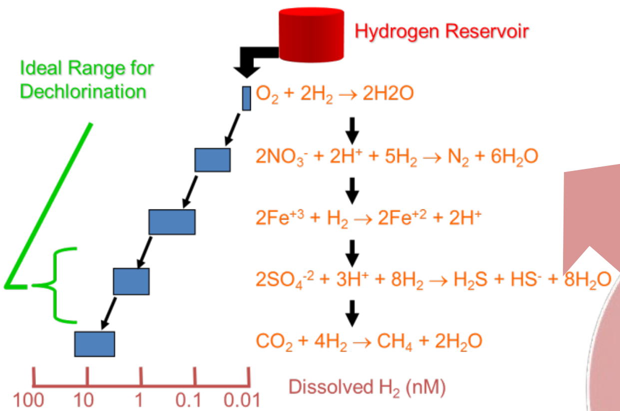
	Electron Donor		Electron Acceptor		Waste		Energy
		+		→		+	
Aerobic	Contaminant (e.g. BTEX, Benzene)		Oxygen IXPER		Waste Products (CO_2 and H_2O)		Energy
Anaerobic	Organic Substrate (e.g. molasses, vegetable oil, **H_2**) CAP18 CAP18 ME		Contaminant (e.g. PCE, TCE)		Waste Products (ethene, ethane, CO_2 and H_2O)		Energy

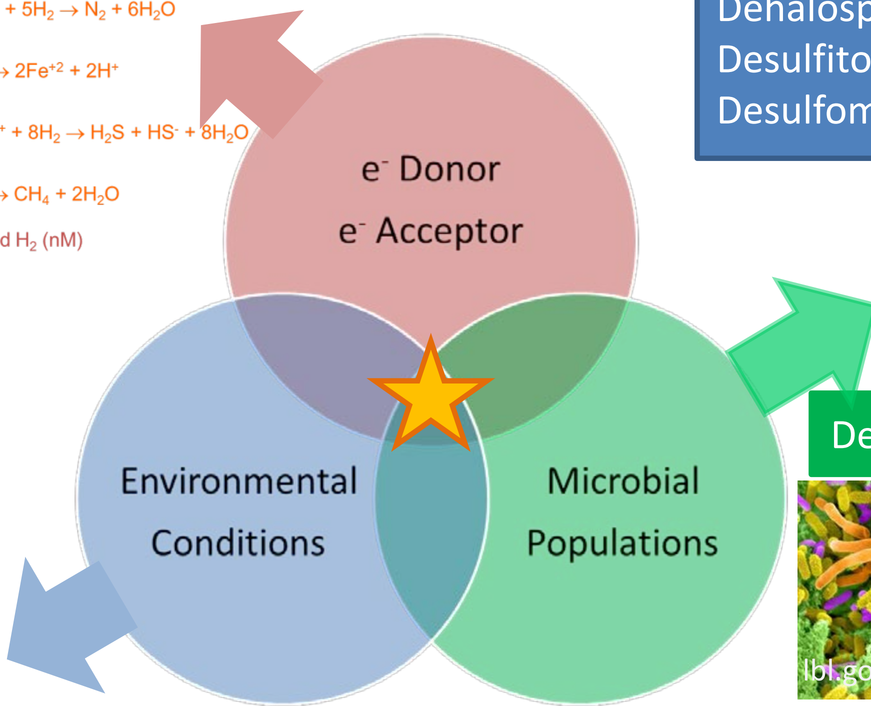
Adapted from Todd Wiedemeier

Potential Contaminants Anaerobic



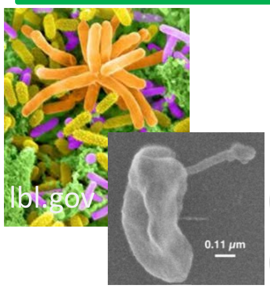
When does Bioremediation Work?



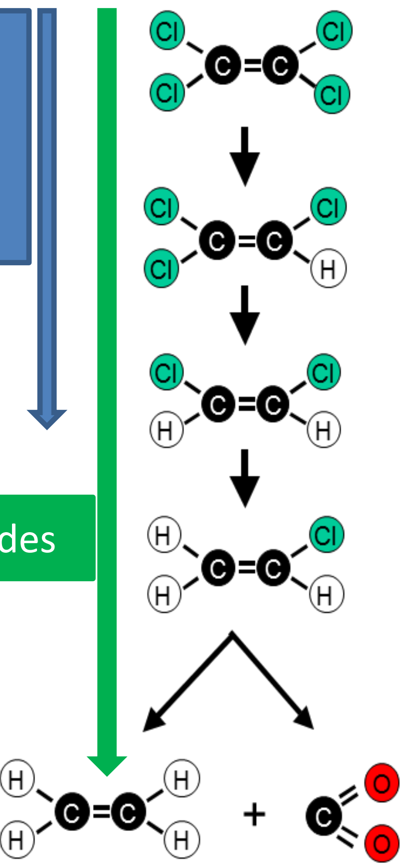


Dehalobacter
Dehalospirillum
Desulfitobacterium
Desulfomonile

Dehalococcoides



SEM image by Dr. Robert P Apkarian & Jeanette Taylor, Emory University



Ethene

Ideal Conditions:

Neutral pH (5.5-7)

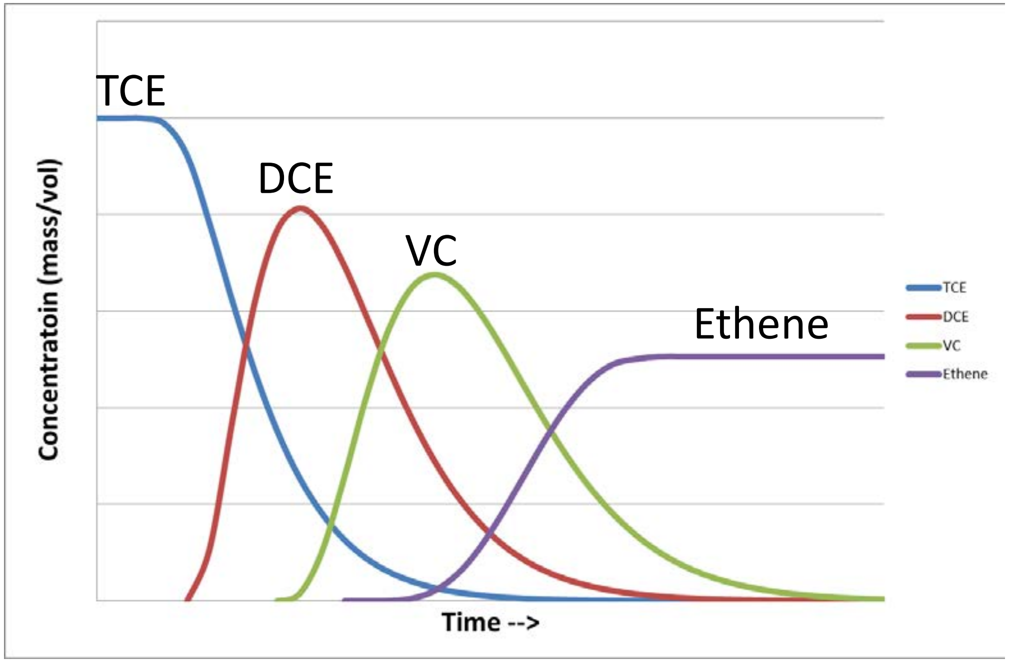
Water

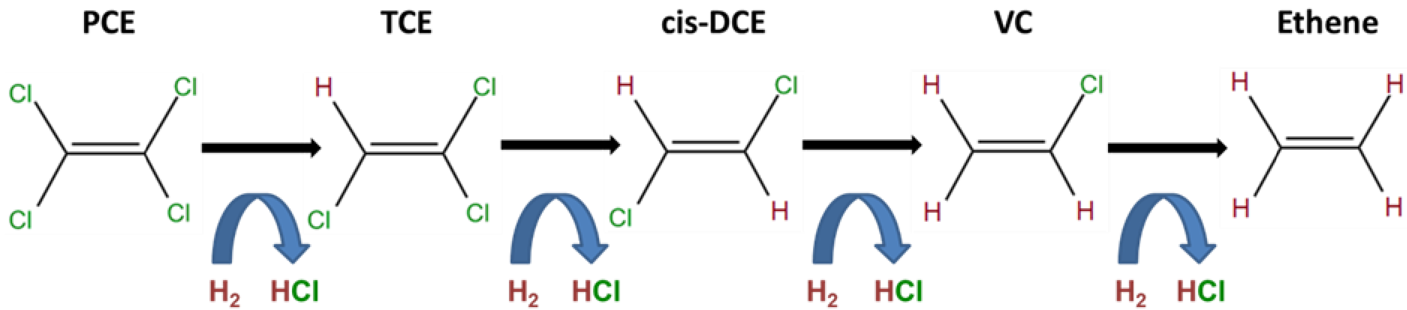
Low oxygen

Highly reducing (Low ORP)

Moderate-to-Low Contaminant Concentrations

Reductive Dechlorination



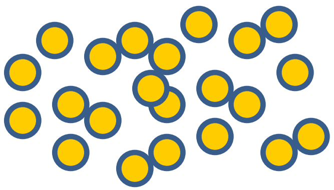


What are CAP 18 and CAP 18 ME?

CAP 18 and CAP 18 ME

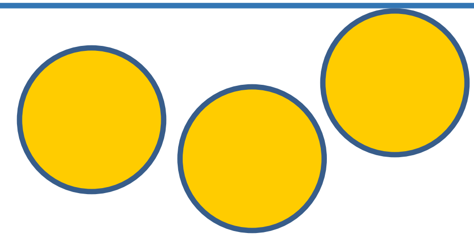
- Unemulsified oil products
- Refined from natural vegetable oils
  - Blend of triglycerides
- Much longer lifetime
- Lower cost
  - Product – cost per unit of hydrogen production
  - Injection/remobilization – single injection lasts years
- CAP 18 ME formulated for accelerated onset of dechlorination

Comparison to Emulsified Products



Vegetable Oil Emulsions

- 40-60% vegetable oil
- Tiny droplets
- Higher surface area
  - Consumed faster
- Shorter lifetime (months to 1-2 years)
- Higher cost per pound of active ingredient
- Lower hydrogen yield per Kg

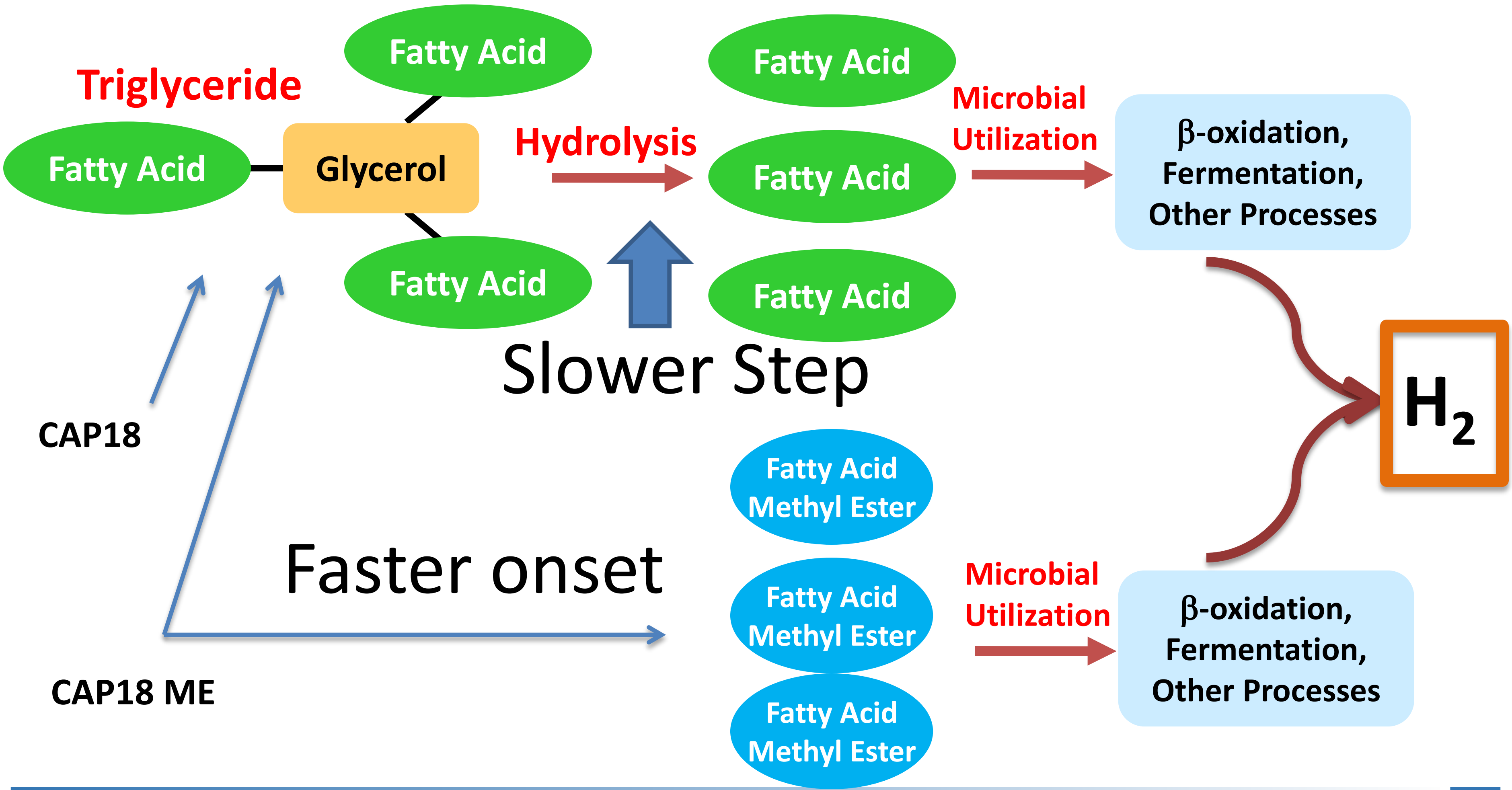


CAP 18/ CAP 18 ME

- 100% vegetable oil blend
- Large droplets
- Lower surface area
  - Consumed slower
- Longer lifetime (3-5 years or longer)
- Lower cost per pound of active ingredient
- Higher hydrogen yield per Kg

Vegetable Oils Hydrolyze to Release Fatty Acids

Hydrolysis of volatile fatty acids (VFA) occurs slowly, CAP18 provides long-term VFA release



Quantify Substrate Longevity – H_2 Release Potential

Substrate + Water → H_2 + Bicarbonate$^{(-)}$ + Hydrogen ion$^{(+)}$

Ethyl Lactate:

$$C_5H_{10}O_3 + 12H_2O \rightarrow 12H_2 + 5HCO_3^- + 5H^+$$

Sodium Lactate:

$$NaC_3H_5O_3 + 6H_2O \rightarrow 6H_2 + 3HCO_3^- + Na^+ + 2H^+$$

Ethanol:

$$C_2H_6O + 5H_2O \rightarrow 6H_2 + 2HCO_3^- + 2H^+$$

Molasses:

$$C_{12}H_{22}O_{11} + 25H_2O \rightarrow 24H_2 + 12HCO_3^- + 12H^+$$

Glycerol:

$$C_3H_8O_3 + 6H_2O \rightarrow 7H_2 + 3HCO_3^- + 3H^+$$

Soybean Oil (Linoleic Acid):

$$C_{18}H_{32}O_2 + 52H_2O \rightarrow 50H_2 + 18HCO_3^- + 18H^+$$

For each mole of ethyl lactate fermented, produce 12 moles of hydrogen

For every mole of soybean oil, we produce 50 moles of hydrogen

Hydrogen Release Potential

Using complete conversion to hydrogen cation, bicarbonate, and dihydrogen gas									
Bioremediation Product	**Chemical Formula**	**MW**	**Percent Composition (% by weight)[1]**			**H_2 (mol) per substrate (mol)[2]**	**H_2 (g) per substrate (mol)**	**H_2 (g) per product (kg)[3]**	**H_2 (g) per product (lb)[3]**
	--	grams/mol	Substrate	Emulsifier	Water	--	--		
Ethyl Lactate	$C_5H_{10}O_3$	118.2	98	--	2	12	24.24	201.06	91.22
Sodium Lactate	$NaC_3H_5O_3$	112.1	60	--	40	6	12.12	64.89	29.44
Ethanol	C_2H_6O	46.1	80	--	20	6	12.12	210.42	95.47
Molasses	$C_{12}H_{22}O_{11}$	342.3	60	--	40	24	48.48	84.97	38.55
Glycerol	$C_3H_8O_3$	92.1	75	--	--	7	14.14	115.13	52.24
CAP 18® Anaerobic Bioremediation Product	**Proprietary blend**	**~280**	**100**	**--**	**0**	**50**	**101**	**360.07**	**163.37**
Emulsified Vegetable Oil (60%)	$C_{18}H_{32}O_2$	280.5	60	10	30	50	101	216.04	98.02
Emulsified Vegetable Oil (40%)	$C_{18}H_{32}O_2$	280.5	40	10	50	50	101	144.03	65.35
Emulsified Vegetable Oil (35%) +	$C_{18}H_{32}O_2$	280.5	35	10	20	50	101	197.83	89.76
Ethyl Lactate (35%)	$C_5H_{10}O_3$	118.2	35			12	24.24		

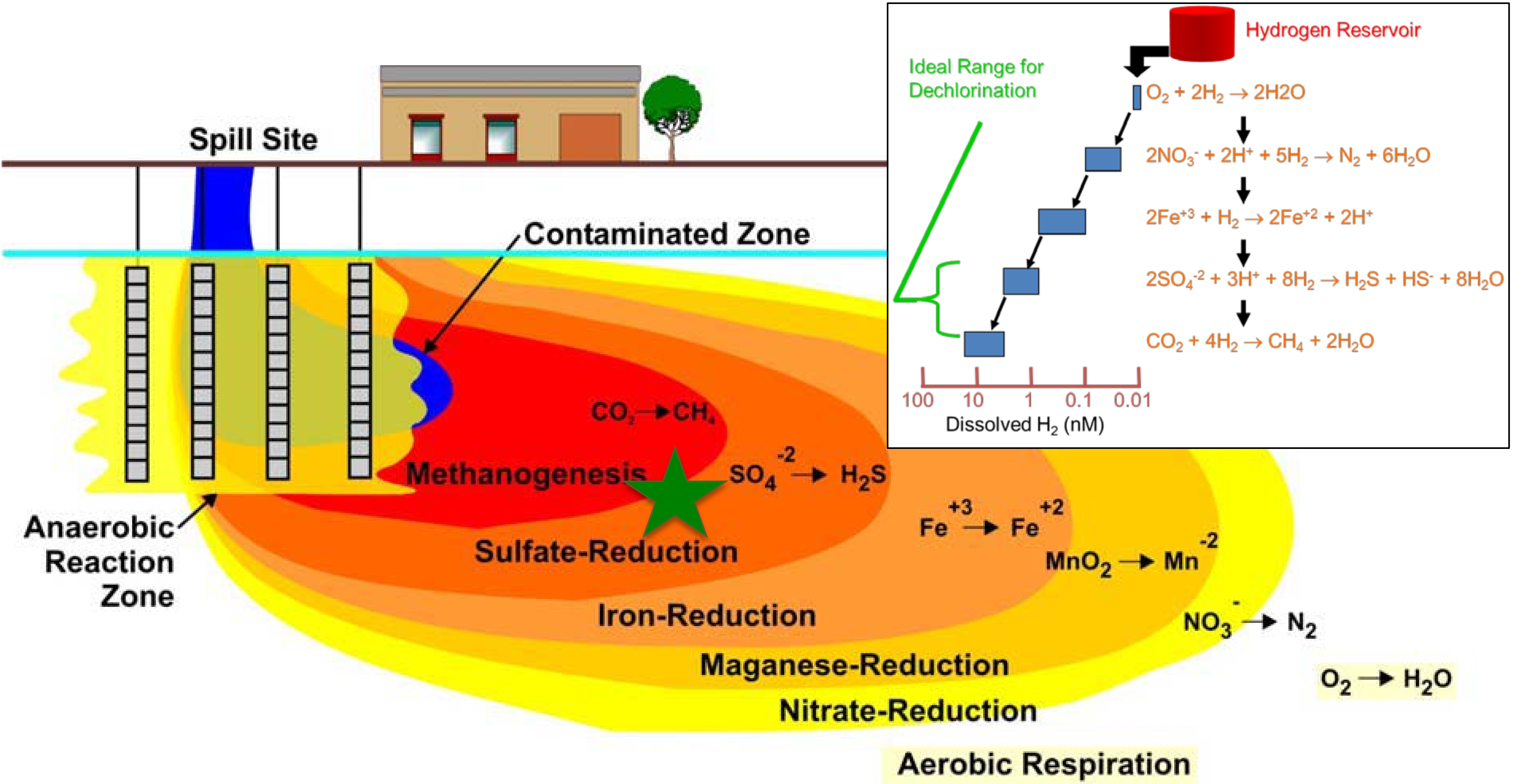
[1] General formulations for competitor bioremediation products

[2] Calculated from the reaction of substrate and water to bicarbonate, hydrogen ion and hydrogen gas

[3] Calculated from % composition (by weight)

"Footrace of Hydrogen"

- Native microbes will deplete most easily reduced electron acceptors first
- Added substrate must be sufficient to overcome background demand before sulfate-reducing conditions occur and reductive dechlorination

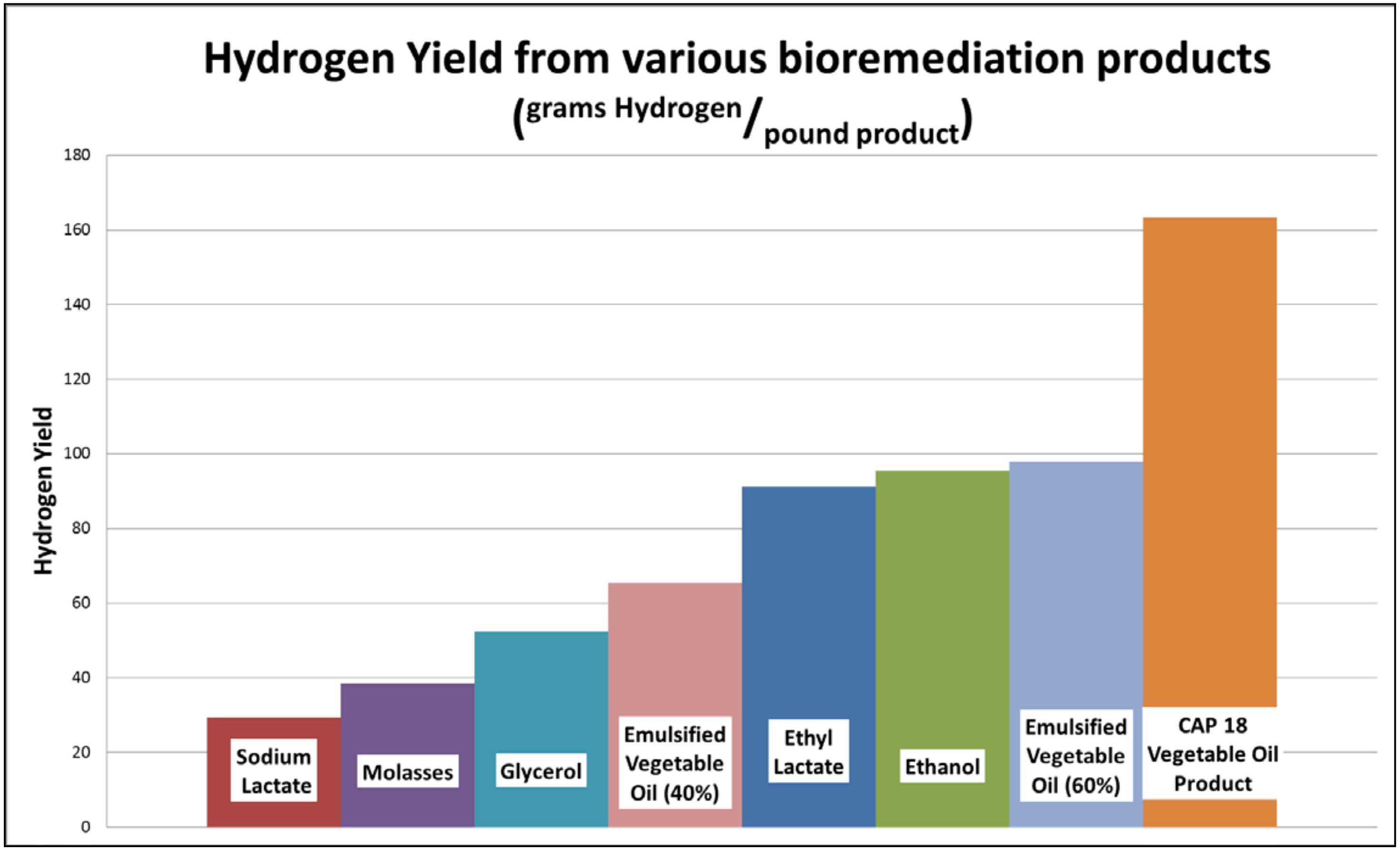


Significant Cost Savings

More hydrogen = longer lasting activity

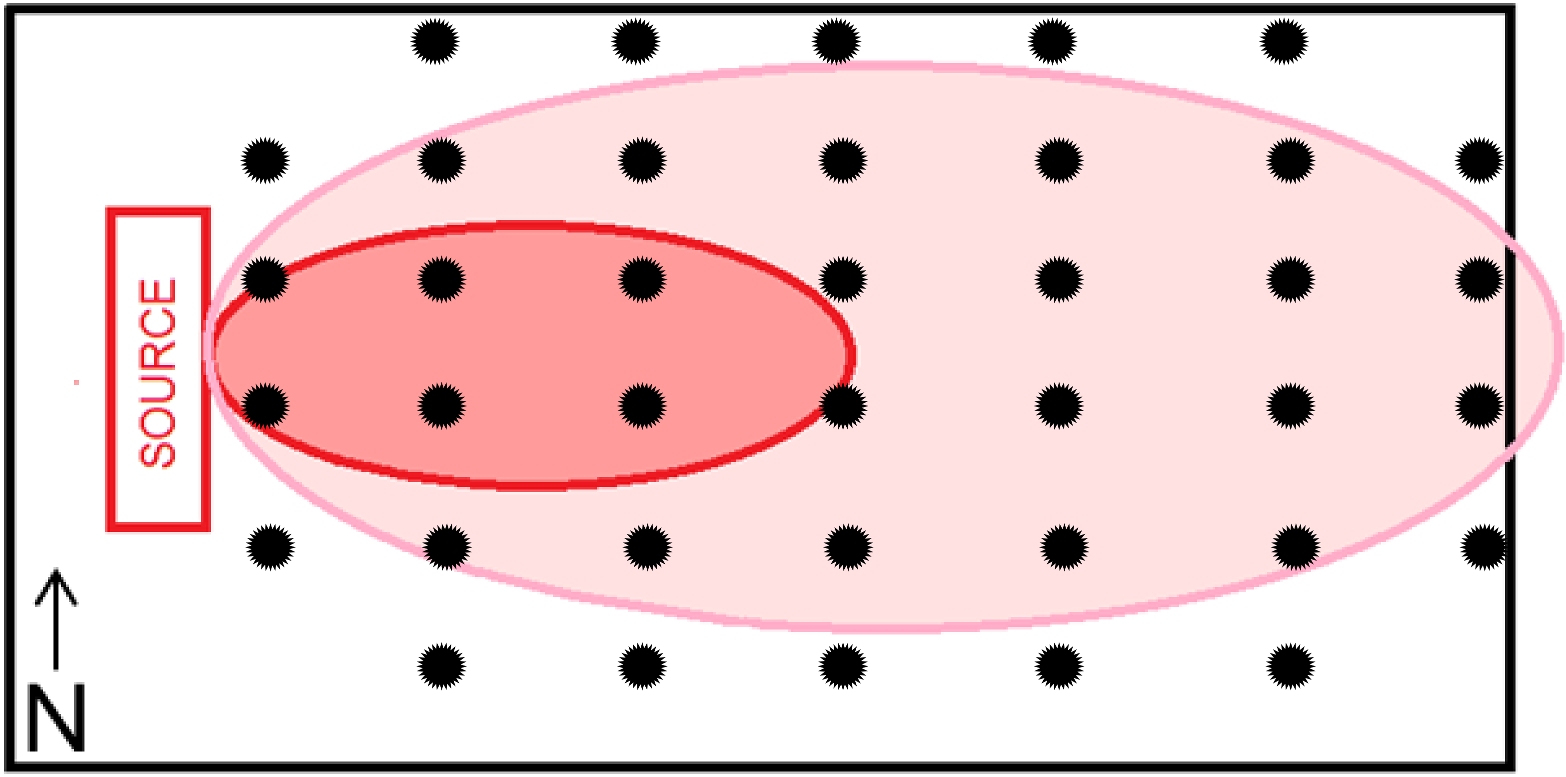
The result is more cost savings

$$



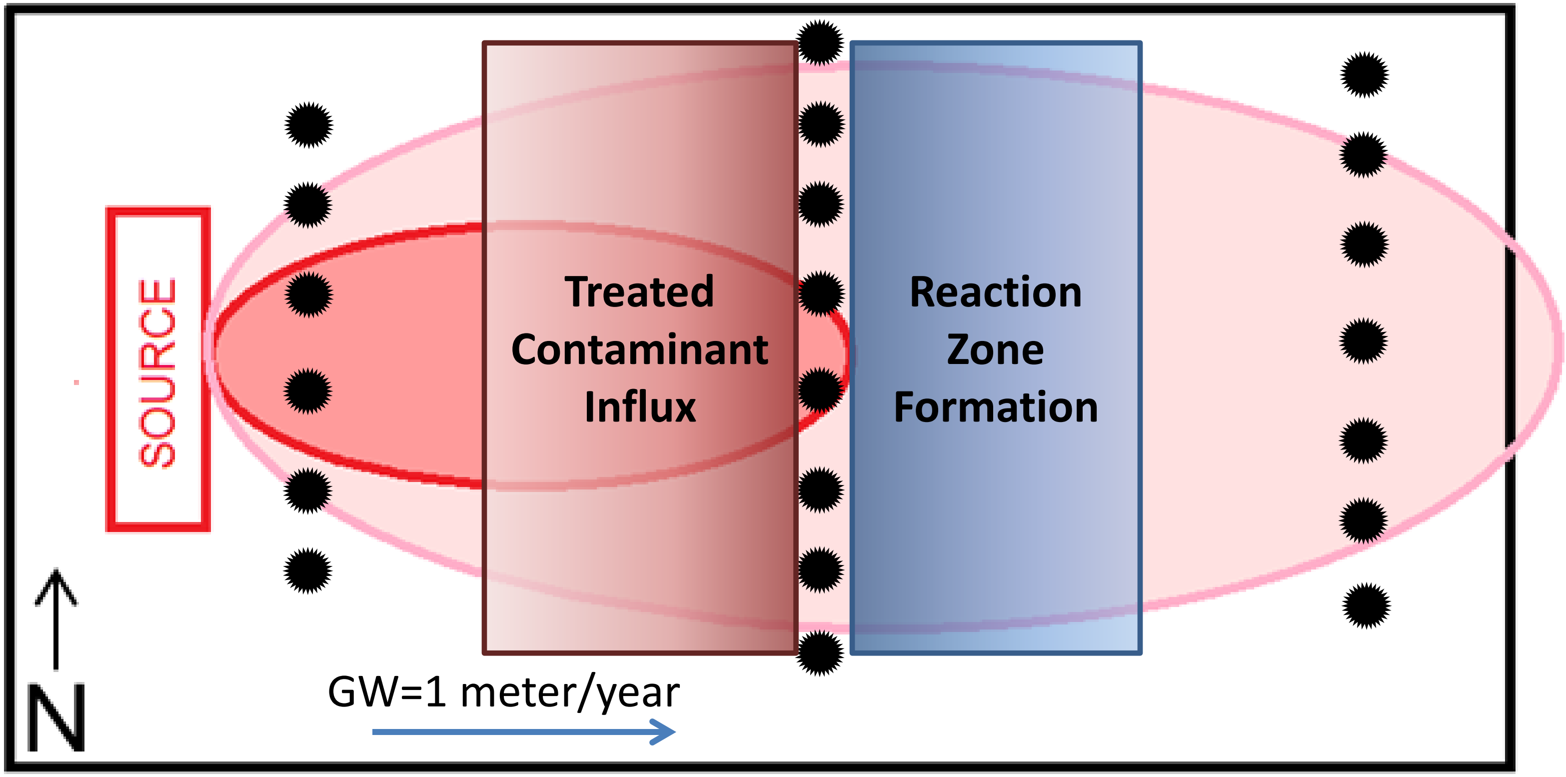
CAP18 results in better hydrogen utilization efficiency and additional cost savings

Design Example 1: Cascade (Grid Reactive Zone)



Accounts for contaminant mass in aqueous phase, but also contaminant mass that is sorbed to soil

Design Example 2: Curtain (Repeating Barriers)



- **Accounts for contaminant mass in the aqueous phase**
- **Curtains designed to have an estimated lifetime of 3-5 years**

CAP 18 and CAP 18 ME Design Calculator

- Site Conditions
  - Contaminated Area
  - Depth
  - Porosity
  - Hydraulic Gradient/Conductivity
- Contaminant Properties
  - Types
  - Concentration
- Background Demand
  - Oxygen
  - Nitrate
  - Reduced Metals (Fe, Mn)
  - Anions (SO4, NO3)
  - Water Hardness

Carus Remediation Technologies
ISCO (In Situ Chemical Oxidation) BIO (In Situ Bioremediation)

CAP 18® and CAP 18 ME® Anaerobic Bioremediation Products Estimation Spreadsheet
Input data into boxes with blue font.

Enable macros prior to entering site parameters into the spreadsheet

SITE NAME: Holiday Dry Cleaners
PREPARED BY: Input Your Name and Company Here **DATE PREPARED:** 4/23/12

Reset Sheet

1. Site Model / Treatment Area Volume
1.1. Treatment Area Volume

Curtain Length (perpendicular to predominant groundwater flow direction)	130	Ft
Thickness of Treatment Zone	20	Ft
Well Spacing	10	Ft

1.2. Treatment Area Characteristics
Soil Characteristics

Nominal Soil Type (enter clay, silt, silty sand, sand, or gravel)	Silt	

Hydraulic Characteristics

Total Porosity (accept default or enter n)	0.43	(decimal)
Effective Porosity (accept default or n_e)	0.19	(decimal)
Hydraulic Conductivity (accept default or enter K)	10	Ft/day
Hydraulic Conductivity Units Conversion =	3.5E-03	cm/sec
Hydraulic Gradient (accept default or enter i)	0.004	Ft/Ft
CAP18® or CAP18 ME® Lifespan (accept default or enter T_w)	4	yr

Recommended lifetimes: typically 3-5 years for the first curtain, 1 year for subsequent curtains (see instructions for more detail)

1.3. Calculations

Seepage Velocity (V_x)	0.2105	Ft/day	=	76.84	Ft/yr
Water Volume Passing in Time T_w (V_w)	151,840	cu. Ft	=	1,135,842	gallons

2. Hydrogen Demand
2.1. Dissolved Contaminant Demand

	Concentration (mg/L)	Mass (lbs)	Stoichiometric Demand (wt/wt H_2)	Hydrogen Demand (lbs)
Tetrachloroethene (PCE)	1.8	17.1	20.6	0.8
Trichloroethene (TCE)	0.065	0.6	21.7	0.0
cis-1,2-Dichloroethene (DCE)	0.0265	0.3	24.0	0.0
Vinyl Chloride	0	0.0	31.0	0.0
Carbon Tetrachloride	0	0.0	25.4	0.0
1,1,1-Trichloroethane (TCA)	0	0.0	33.1	0.0
1,1-Dichloroethane (DCA)	0	0.0	49.1	0.0
Perchlorate	0	0.0	12.3	0.0
User-Supplied Electron Acceptor	0	0.0	0	0
User-Supplied Electron Acceptor	0	0.0	0	0

2.2. Background Demand

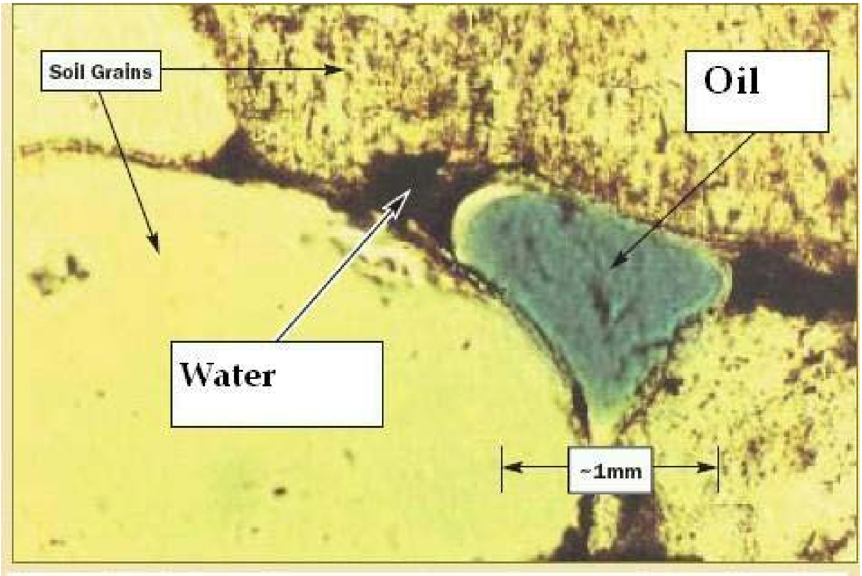
	Concentration (mg/L)	Mass (lbs)	Stoichiometric Demand (wt/wt H_2)	Hydrogen Demand (lbs)
Oxygen	1.2	11.4	7.9	1.4
Nitrate	0.02	0.2	12.3	0.0
Manganese	0	0.0	27.3	0.0
Iron	0	0.0	55.4	0.0
Sulfate	10.5	99.5	11.9	8.4
Water Hardness (as $CaCO_3$)	4210	39,904.9	69.6	573.4

3. TOTAL CAP 18 OR CAP 18 ME DEMAND

Dissolved Contaminant Stoichiometric Hydrogen Demand	=	0.9	lbs H_2
Background Stoichiometric Hydrogen Demand	=	583.2	lbs H_2
Total Stoichiometric Hydrogen Demand	=	584.1	lbs H_2
Microbial Degradation Factor (recommend 5x)	=	5	(multiplier)
Design Contingency Factor (recommend 5x)	=	5	(multiplier)
Total Hydrogen Demand	=	6,425	lbs H_2
CAP 18 or CAP 18 ME Requirement	**=**	**62,131**	**lbs CAP 18 or CAP 18 ME**

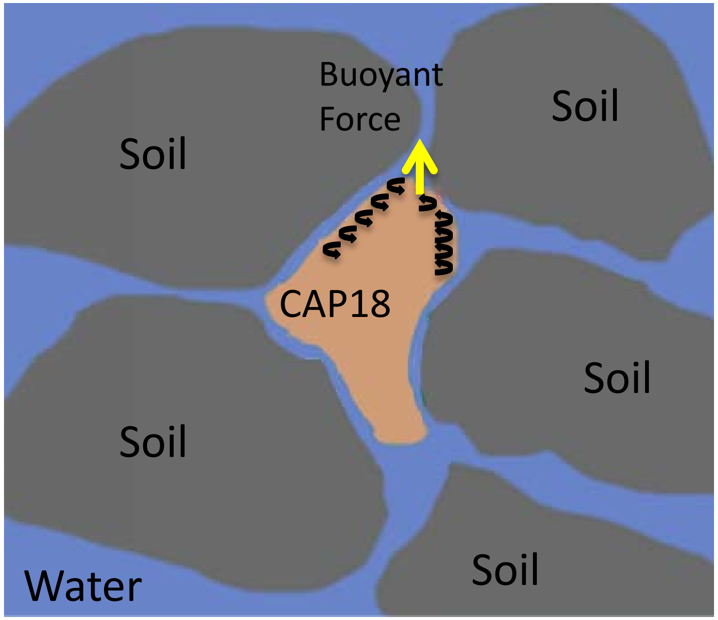
Software Version 2 (beta)

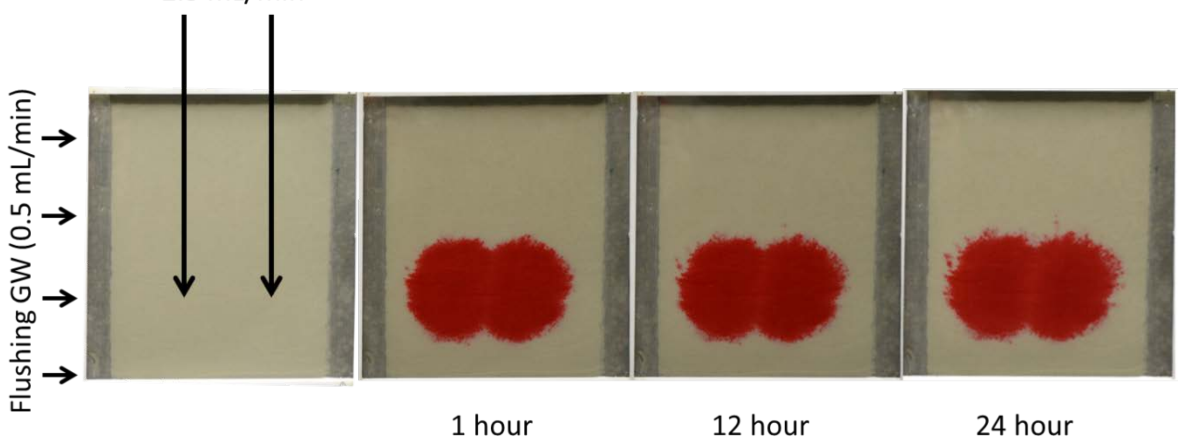
Distribution of CAP 18 and CAP 18 ME in Soil Pores



Microscopic view of entrapped oil in soil

Enbridgecasslake.com

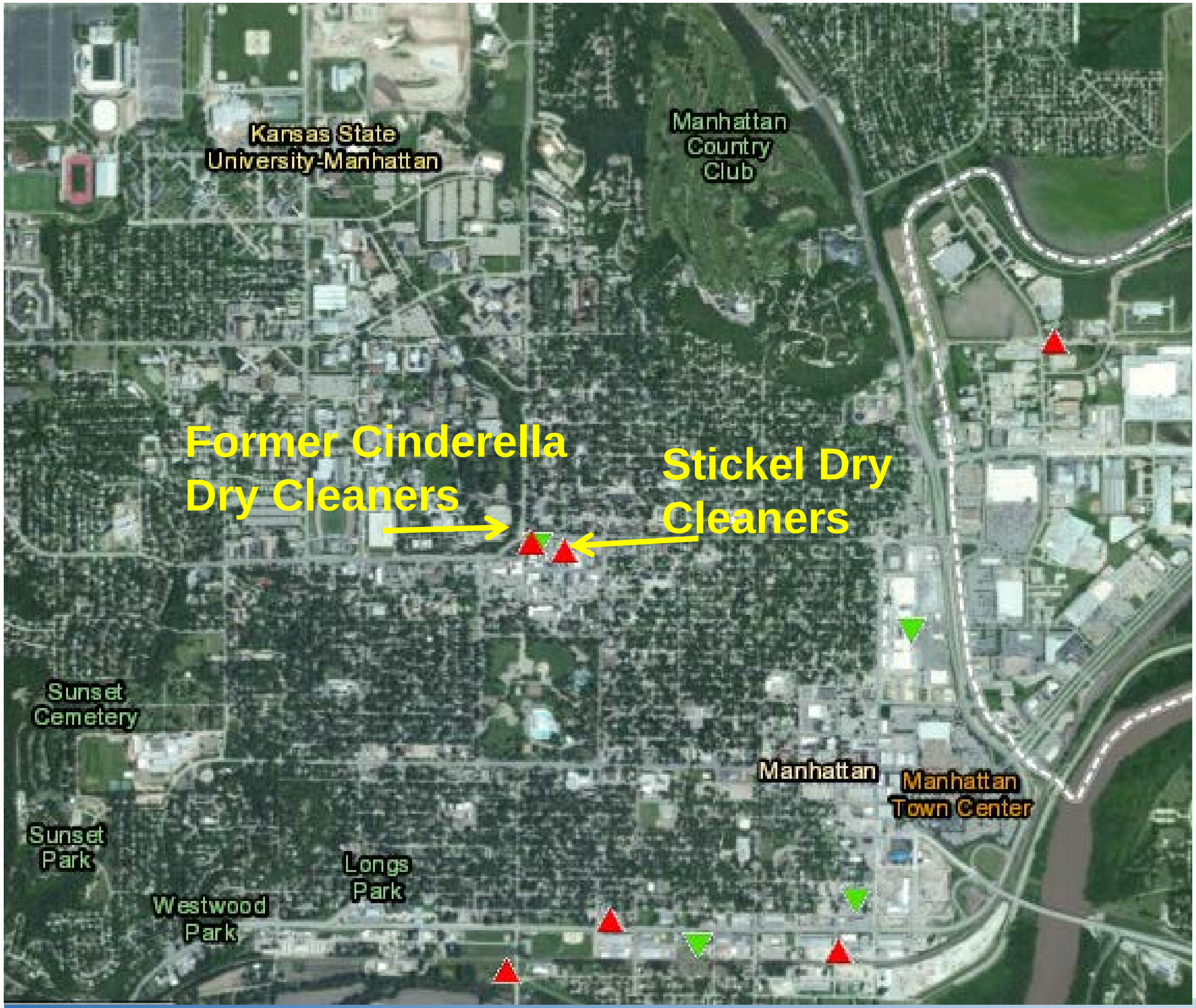




- **The sum of viscous and interfacial tension prevent upward migration of the oil droplets**

CAP 18 Case Study

- Former Cinderella-Stickel Dry Cleaners Manhattan, KS



- Groundwater contamination first discovered in 1986
- Baseline groundwater sampling (July 2009)
  - PCE 11,000 ug/L, TCE 1,770 ug/L, cDCE 700 ug/L, and VC 957 ug/L
  - Comingled plume extends1200 m east-northeast towards the City of Manhattan public wells #12 and #13

CAP18 Site Design
Manhattan, KS

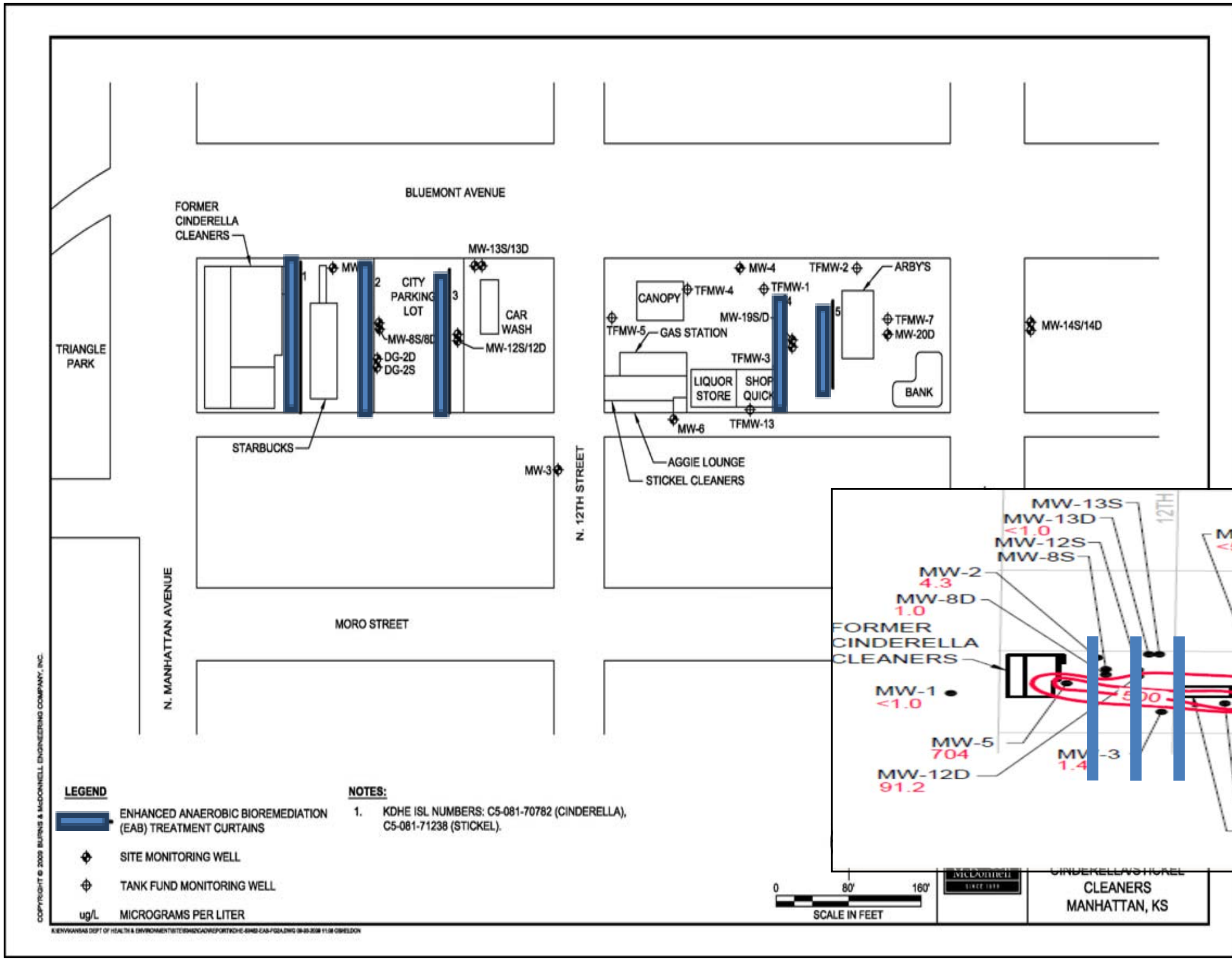
- Burns & McDonnell selected by Kansas Department of Health and Environment to remediate sites with enhanced anaerobic bioremediation

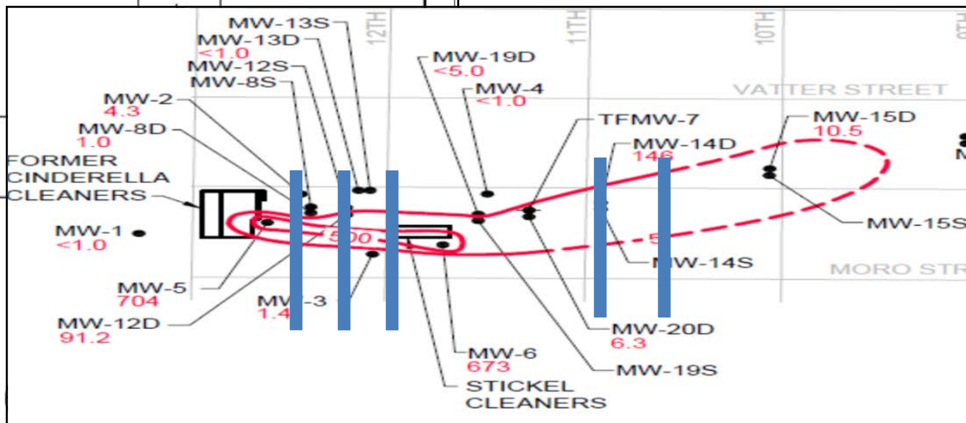
- Seepage velocity used in CAP 18 dosage calculations with estimated velocity ranges for individual aquifer depth intervals:
  - 6-7.6 m bgs: 5.2 m/year (Shallow Unit-Fine-grained Clay)
  - 10.7-13.7 m bgs: 29.6 m/year (Intermediate Unit-Silty Sand)
  - 13.7-18.3 m bgs: 69.2 m/year (Deep Unit-Sandy Alluvium)

- Other design parameters:
  - Average COC concentrations
  - Background demand

CAP18 Site – Manhattan, KS

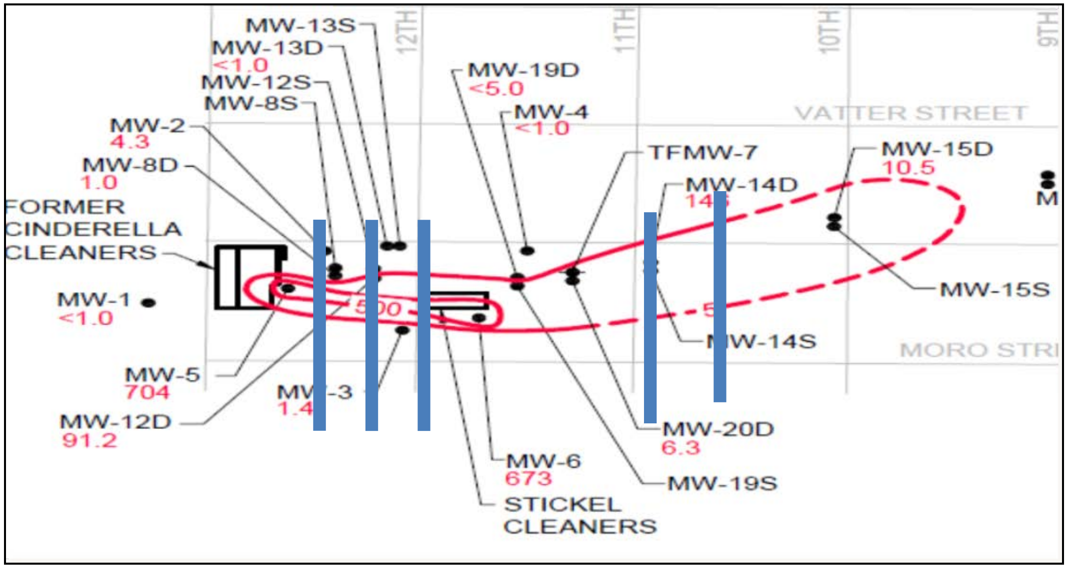
- Target treatment interval
- ~ 6 m below ground surface (bgs)
- Top of bedrock (~ 18 m bgs)

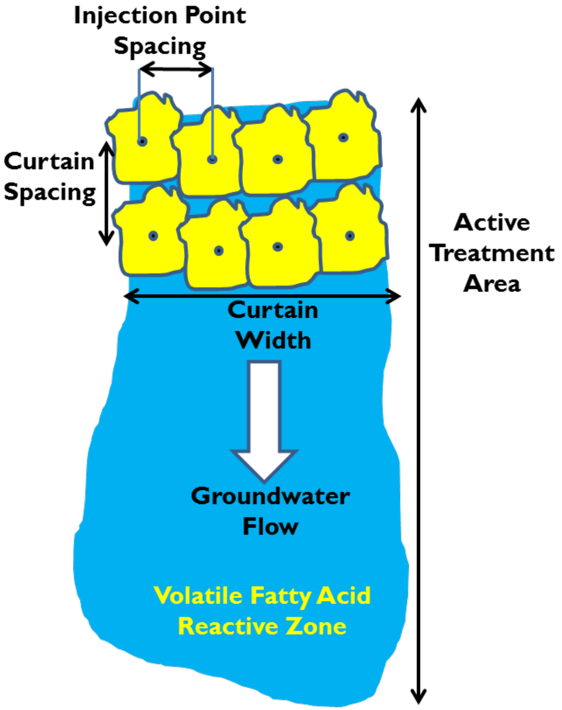




CAP18 Site – Manhattan, KS

- July 2009, five CAP 18 distribution curtains oriented perpendicular to groundwater flow
  - Direct-push injection
  - Each curtain spaced 5 meters apart and spanned width of groundwater plume
  - Total linear footage of 210 meters for 5 injection curtains





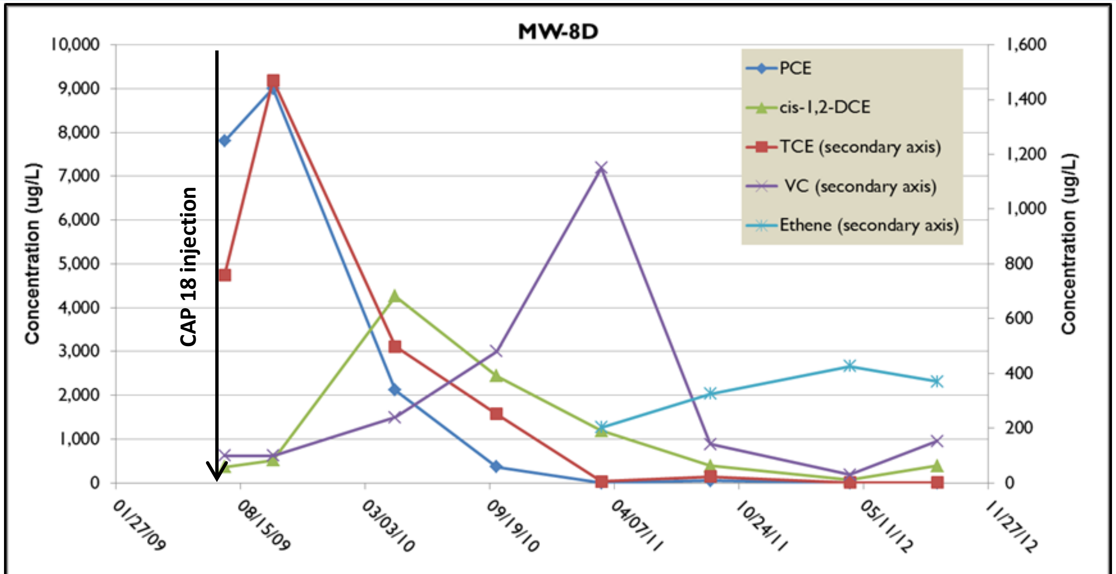
CAP 18 Site – Manhattan, KS

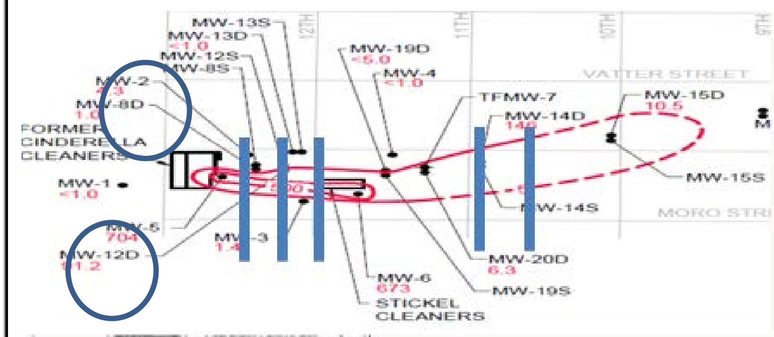
- Each point injected at 1.5 meter intervals with varying CAP 18 injection volumes depending on seepage velocity
- Amounts for each injection interval:
  - 6-11 m bgs: approximately 4 liters per 1-1.5-m interval
  - 11-14 m bgs: approximately 30 liters per 1-1.5-m interval
  - 14-18 m bgs: approximately 132 liters per 1-1.5-m interval
  - 18 m bgs represents top of bedrock in this area
- Approximately **1580 kg (636 liters)** injected per point
- Total of ~ **37,500 liters** of CAP 18 injected during the field implementation

CAP 18 Site – Manhattan, KS

- Post-injection groundwater monitoring conducted on semi-annual basis from 2009 through 2013
- Groundwater sampling conducted at eight monitoring wells to provide performance assessment data
- Performance monitoring sampling included:
  - Temperature
  - pH
  - Specific conductivity
  - Oxidation-reduction potential (ORP)
  - Total organic carbon (TOC)
  - Dissolved oxygen
  - Volatile organic compounds (PCE, TCE, DCE, VC)
  - Methane/ethane/ethene

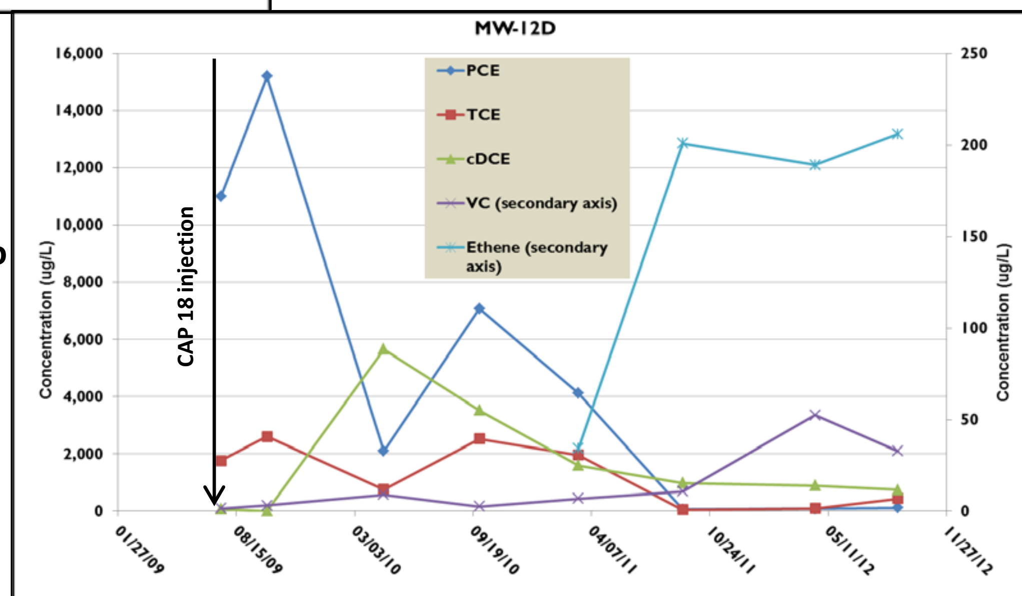
Down-Gradient Monitoring Well VOC Data



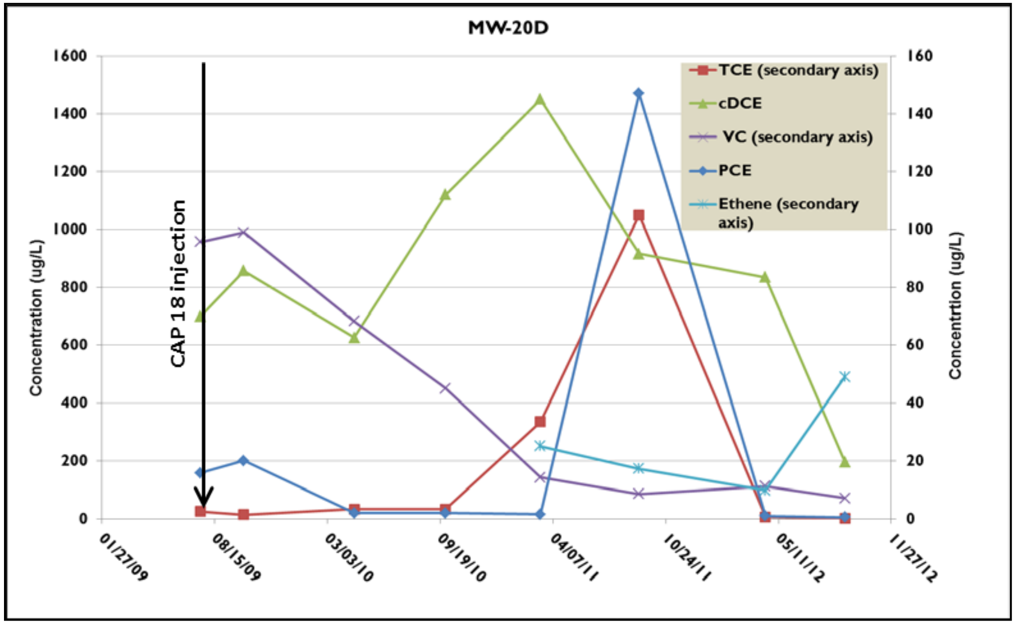


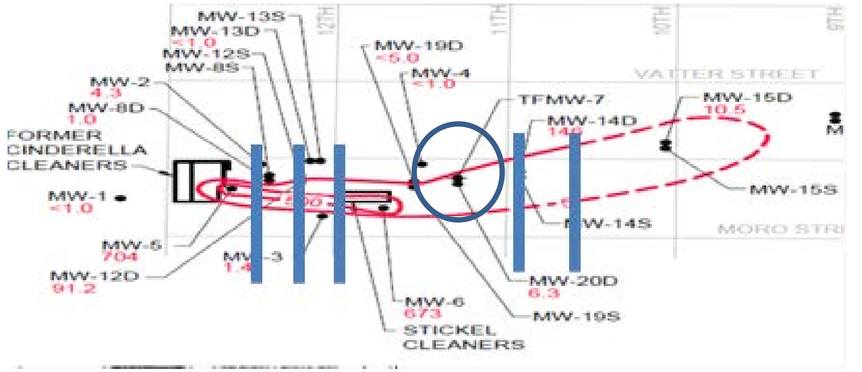
3+ years of biodegradation activity

- **PCE and TCE concentrations increased to 9000 ug/L then decreased rapidly to a low of < 2.0 ug/L (September 2012)**
- **cis-1,2-DCE and VC increases as expected, due to PCE and TCE dechlorination**
- **Ethene analysis began March 2011**
- **MW-8D ethene concentrations increased from March 2011 through April 2012 confirming complete dechlorination of targeted CVOCs**



Down-Gradient Monitoring Well VOC Data



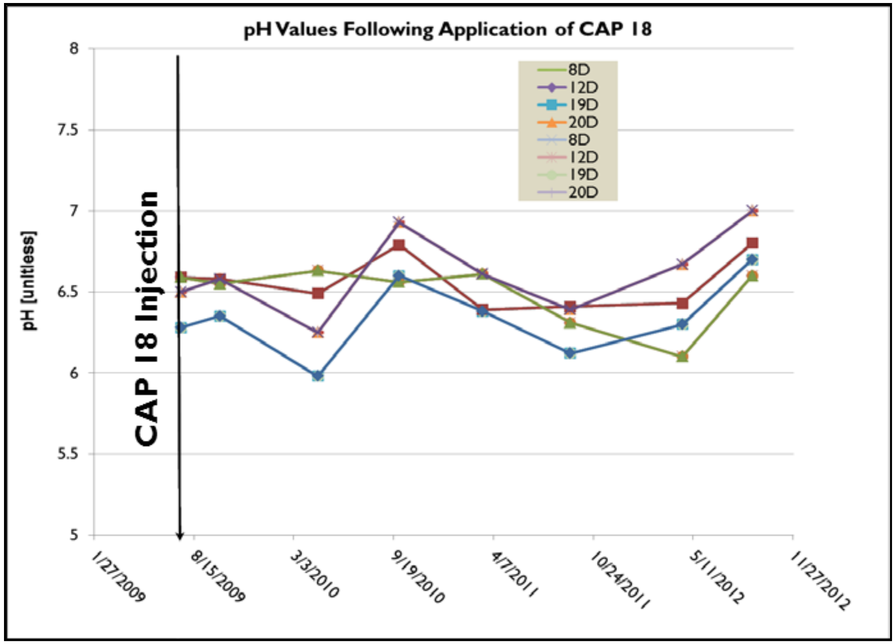


3+ years of biodegradation activity

- PCE and TCE concentrations decreased following CAP 18 injection
- Followed by a spike during October 2011 sampling event
- Declining to consistently low levels

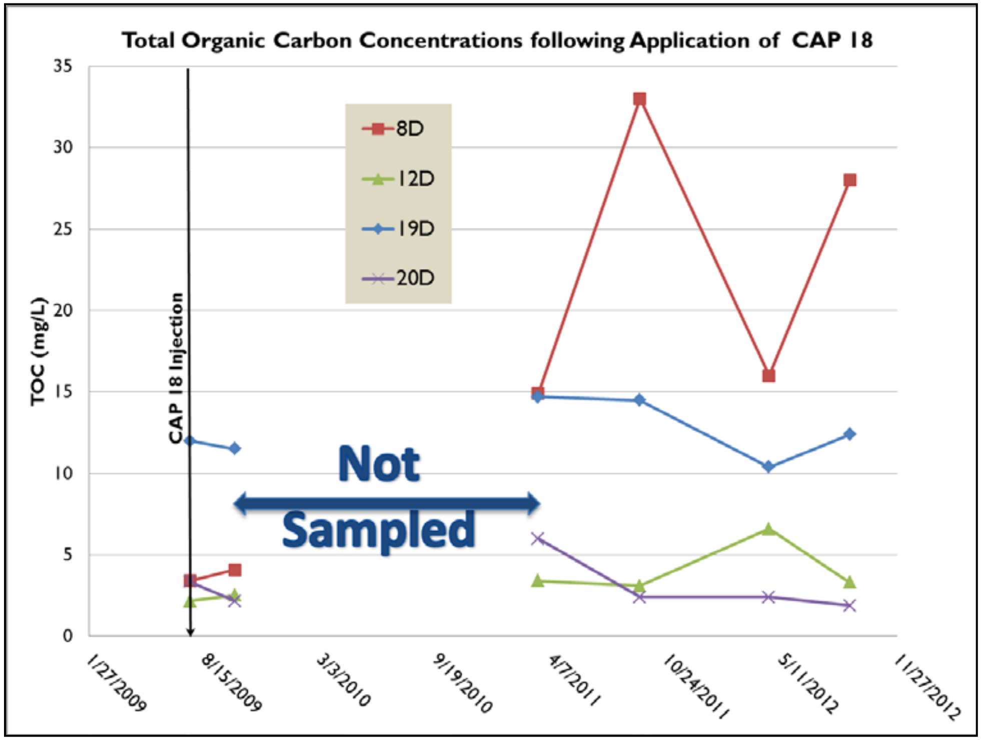
- Cis-1,2-DCE concentrations increased 600 to > 1400 ug/L, followed by a continued and gradual decline
- Ethene detections continue to confirm that complete dechlorination is ongoing

Down-Gradient pH and TOC Data

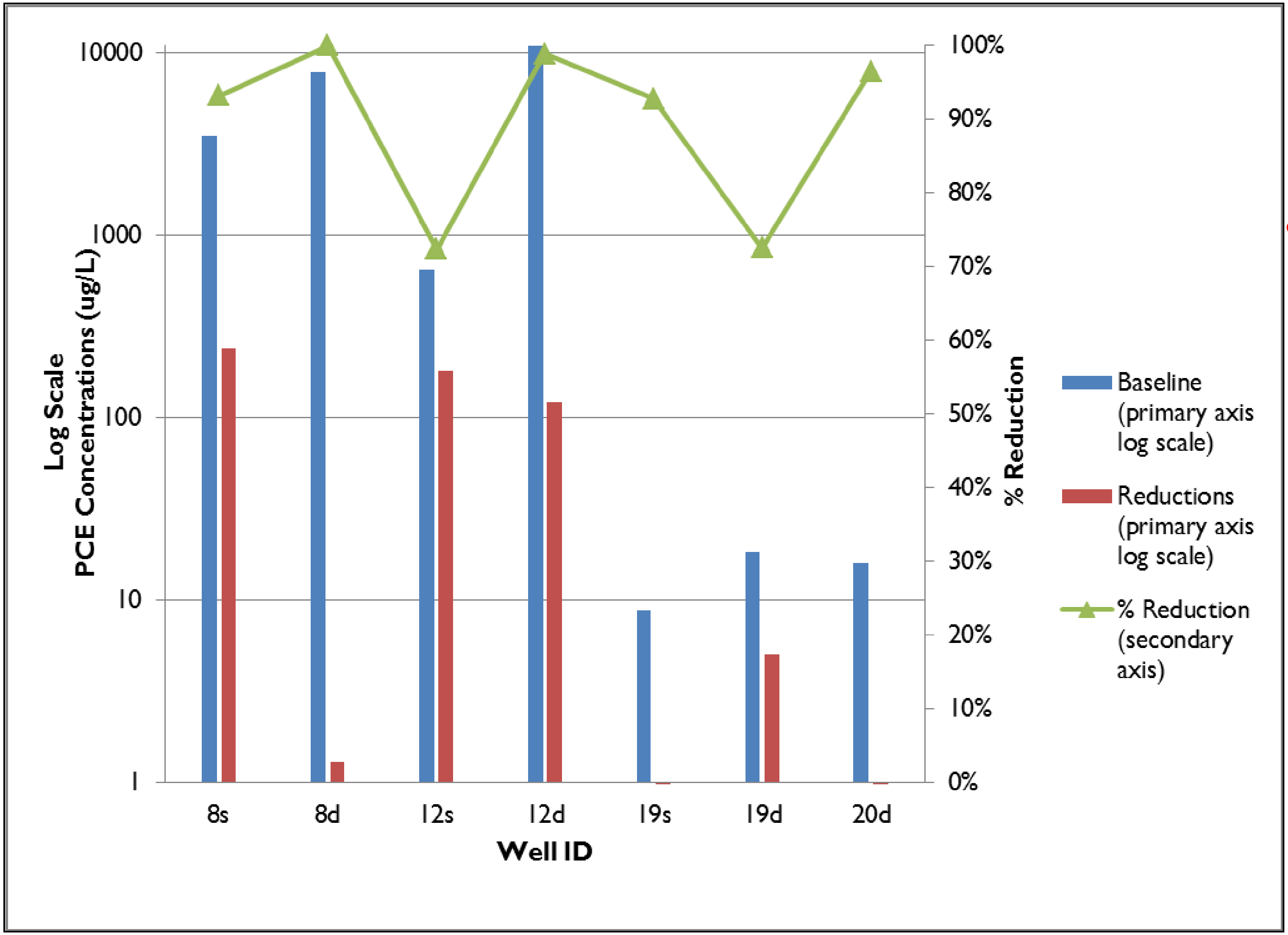


- Following small initial pH decreases near neutral values ranging from 6.6 to 7 (September 2012)
- Promotes sustained microbial activity

- TOC data provides information on organic carbon transport in groundwater downgradient of CAP 18 curtains

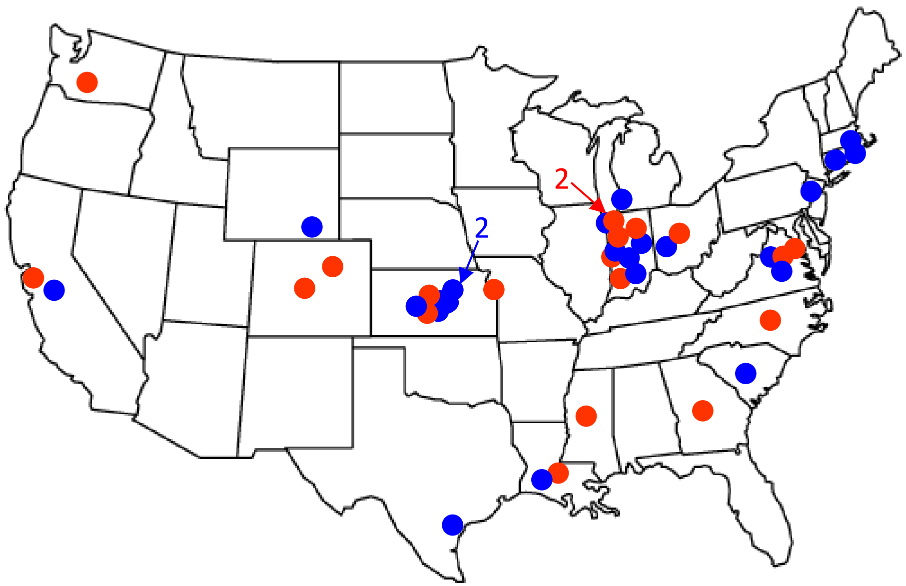


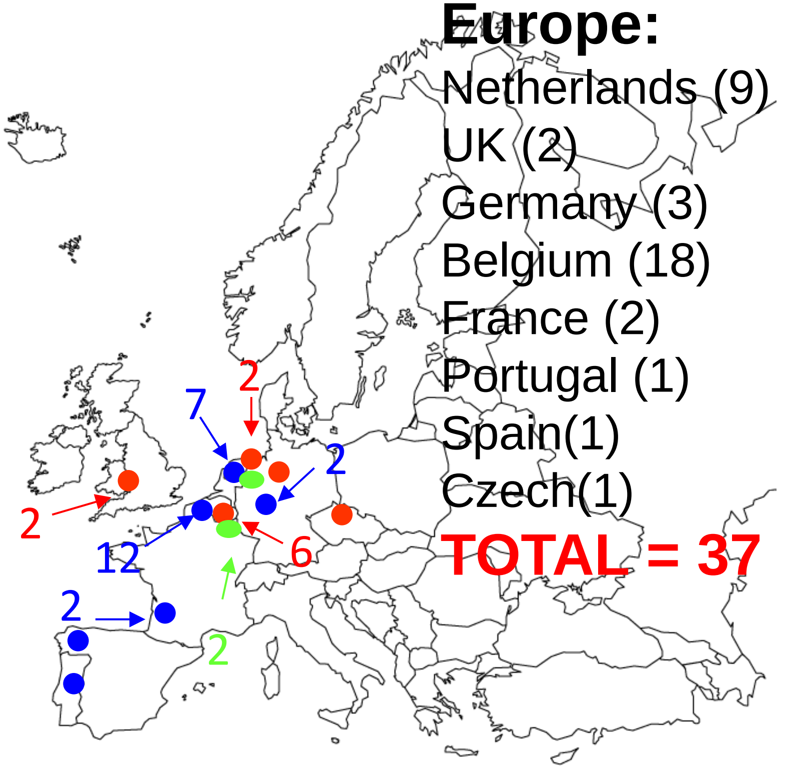
Performance Assessment



- **PCE removal efficiencies ranging from 72% to 100%**

Completed Sites





Europe:
Netherlands (9)
UK (2)
Germany (3)
Belgium (18)
France (2)
Portugal (1)
Spain(1)
Czech(1)
TOTAL = 37

US:
42 sites
(March 2013)

● CAP18 ME
● CAP18

European Remediation Technologies

Conclusions

- Significant VOC reductions ***3+ years*** after single application
- TOC data indicates substrate still releasing
- Increased substrate utilization demonstrates high ***TOC concentrations*** unnecessary to support reductive dechlorination
- Large pH shift was not observed during the barrier lifetime, despite degrading >12,000 ug/L of PCE and ***eliminates co-injection of costly buffers***
- Complete anaerobic reductive dechlorination of PCE to ethene with a single CAP 18 application ***almost 18 m*** from the curtains

Questions?

Friday 9:25-9:55 Shaughnessy
Field Application of Passive Treatment of Chlorinated Solvents using Novel Sustained-Release Oxidant Technologies
Grant Walsom, XCG; Pamela Dugan Carus

Properties of CAP 18 and CAP 18 ME

Compound	Interfacial Tension (dynes/cm)	Specific Gravity
CAP18	**26.6[A]**	**0.93 g/mL**
CAP18 ME	**22.7[A]**	**0.93 g/mL**
BTEX	12.3[A]	0.74 g/mL

[A]Measured using DuNuoy Ring Tensiometer at NAPL-water interface

Compound	Viscosity (cP)
Polylactates	20,000
Sodium Lactate (60%)	100 @ 68F
CAP18	**55.1[B]**
CAP18 ME	**6.63[B]**
BTEX	0.4[C]

[B]Measured using Brookfield Viscometer at 10 s^{-1}

[C]"Remediation Hydraulics", Payne, Quinnan, Potter, 2007